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# Effects of Polymer Modification on Properties and Microstructure of Model Asphalt Systems

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Physical properties and microstructures of computational model asphalts were investigated using molecular dynamics simulations in an all-atom framework. A new model asphalt is proposed that is targeted toward core asphalt AAA-1 of the Strategic Highway Research Program (SHRP) based on elemental composition and speciation. Individual compounds were chosen from the literature to represent asphaltene, polar aromatic, naphthene aromatic, and saturate, with interactions ranked using Hansen solubility parameters. The density and thermal expansion coefficient agreed better with experimental data than had predictions using earlier model asphalts. In addition, one polystyrene molecule with 50 repeat units was added into a ternary model asphalt from earlier work and the new six-component AAA-1 model system to analyze polymer modification effects. The expansion coefficient, isothermal compressibility, and their temperature dependence decreased with one polymer chain present, while density increased. Self-diffusion coefficients of each component in both model asphalts decreased upon including the polymer. To assess microstructure, radial distribution functions  $g(r)$  of asphaltene and simplified resin molecules were calculated at different temperatures. Asphaltene results changed with temperature and upon including one polymer; artifacts of initial configuration were found at lower temperatures. Radial distribution functions for pairs of resin-like molecules (dimethylnaphthalene, benzoquinoline, and ethylbenzothiophene) and for asphaltene–resin pairs retained similar shapes and first peak positions at different temperatures and when including the polymer. Results for unlike molecules indicated a depletion of resin [ $g(r) < 1$ ] immediately surrounding an asphaltene molecule, rather than the enrichment expected from standard “colloid model” descriptions, in which resins solubilize asphaltenes. Intermolecular orientations between closest asphaltene pairs in original and polymer modified systems were strongly peaked toward parallel packing and remained similar at several high temperatures. Orientations between asphaltenes and resins and among resins were weighted toward parallel, compared to random packing, both with and without a polymer and over a range of temperatures.

## Introduction

Asphalt is a black to dark brown material that is sticky, semisolid, and highly viscous at room temperature. It mainly comes from crude oil distillation and is mostly used on road pavement.<sup>1</sup> Asphalt pavement can have rutting problems (flow as a result of stress from traffic loads)<sup>1</sup> in hot summer and fatigue cracking problems (cracks as a result of repeated small loads)<sup>1</sup> in cold winter.

To address rutting and cracking problems, the Strategic Highway Research Program (SHRP)<sup>2,3</sup> identified numerous asphalts for extensive study and led to so-called “performance-graded” asphalts. Those asphalts are rated for roadway applications based on the magnitude and temperature dependence of their mechanical properties, such as complex modulus.<sup>1</sup> Despite

this common basis for initial mechanical performance, recent research has found some indications that comparably graded asphalts that differ in chemistry lead to different performance in roads,<sup>4</sup> and current specification parameters may be inappropriate for polymer-modified asphalts.<sup>5</sup> Understanding the relationships among asphalt chemistry, microstructure, and properties is very important.

Adding a polymer to an asphalt system is a common way to improve asphalt properties and performance.<sup>6</sup> A polymer modifier decreases the temperature dependence of viscosity. This effectively increases high-temperature viscosity, which can help to prevent high-temperature rutting on a road, and decreases low-temperature viscosity, which can prevent low-temperature cracking. Those effects are consistent with field experience results. For example, Nahas et al.<sup>7</sup> analyzed a series of ethylene copolymers as asphalt modifiers for high-performance hot mix pavement binder. They found that those polymer-modified asphalts had their rutting resistance increased with an increasing softening point (temperature at which asphalt flows under a specified load),<sup>1</sup> with little effect on low-temperature properties

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or on fatigue cracking. Kluttz and Dongré<sup>8</sup> found that adding styrene–butadiene–styrene copolymer could improve both low- and high-temperature performance of asphalt binder. More recent studies<sup>9</sup> have compared current specifications (i.e., complex modulus) and other measurements (zero shear viscosity and permanent strain under creep) for a variety of polymer-modified asphalts, finding behaviors that depended upon the polymer modifier and concentration. Numerous papers and studies are now available concerning polymer-modified asphalts, as listed elsewhere.<sup>10</sup>

Asphalt is a mixture composed of millions of compounds.<sup>11</sup> On the basis of its solubility in different solvents, asphalt can be separated into the following parts: asphaltene, resin (including polar aromatic and naphthene aromatic), and saturate (SARA analysis). Choosing one compound to represent each part and keeping the overall composition close to the total C/H ratio reported for the precursor to a real asphalt (i.e., vacuum residue),<sup>12,13</sup> we previously proposed two model asphalts for use in molecular simulations.<sup>14</sup> In that work, we used *n*-C<sub>22</sub> to represent saturate, 1,7-dimethylnaphthalene to represent naphthene aromatic, and two model asphaltene molecules taken from the literature, labeled asphaltene1<sup>15</sup> and asphaltene2,<sup>16</sup> to represent asphaltene. Two model asphalts with these compounds were proposed: ternary asphaltene1 and asphaltene2 systems.<sup>14,17</sup>

There are several weaknesses of those former model asphalt systems. First, in each system, there is no polar aromatic component. The aromaticity and polarity distributions of each system were not very close to real asphalt. Second, the element ratios, such as the C/H ratio, were close to results for a vacuum residue<sup>13</sup> instead of a well-defined highway asphalt, such as those of the SHRP. Because of these speciation differences in model asphalts, the model asphalt densities were always lower than that of SHRP asphalts. We also calculated mechanical properties from simulation (for example, viscosity and modulus) of model asphalt.<sup>18</sup> The viscosity temperature dependences of ternary asphaltene1 and asphaltene2 systems were comparable to those of a PG 64-22 asphalt tested by Zhai and Salomon<sup>19</sup> and of asphalt samples measured by Khong et al.<sup>20</sup> over similar temperature ranges. At room temperature, the estimated viscosity of the ternary asphaltene1 system was too high, while that of the ternary asphaltene2 system was too low, compared to SHRP asphalts.<sup>18</sup> To overcome the above shortcomings of our former model asphalts, in this work we built a new model asphalt targeted toward SHRP asphalt AAA-1.

Solubility parameters provide one method for assessing compounds in a model asphalt. Redelius<sup>21,22</sup> has discussed the importance of considering asphalts as mixtures of many

compounds with a wide range of solubility parameters; he proposed using Hansen solubility parameters to correlate asphalt mixture compatibility. Liquids with similar  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  values can dissolve one another, while disparate values lead to phase separation. Redelius measured the solubility of a Venezuelan bitumen, its components (asphaltene and maltene), and its source (crude oil) in a large number of solvents and determined average Hansen solubility parameters for each component. These provide useful data for comparing individual components when designing or polymer-modifying a model asphalt.

One outcome from simulations of model asphalt systems is estimates of packing among asphaltene and resin compounds. In earlier work,<sup>17</sup> we analyzed the microstructure in model asphalt systems using orientation calculations. We calculated intermolecular orientation between the same and different kinds of aromatic compounds, intramolecular orientation within an aromatic compound, and radial distribution function among the same and different kinds of compounds. We found that average packing between aromatic compounds is influenced by intermolecular distances ( $d_0$ ), molecular structure, and temperature. Because of the poor statistics of asphaltene molecules in those systems (only five asphaltene molecules in each system and short simulation times), the radial distribution function results were sensitive to initial configurations and temperatures. Those results were based on simulation times of 5 ns or less. In this work, we have checked those former findings by running for longer simulation times.

This work had two specific objectives. The first was to devise a model asphalt that contains more subtle gradations in polarity than were present in the model asphalts that we proposed earlier.<sup>14,17</sup> Compounds in the model asphalt proposed here are targeted toward the C, H, N, and S ratios found in the SHRP engineering asphalt AAA-1. The second objective of this work was to quantify how properties and microstructures of ternary asphaltene2 and six-component AAA-1 model asphalt systems changed on the molecular level after adding one polymer chain. In earlier work,<sup>14</sup> we found that adding one polymer could increase the density and modulus at 298 K.<sup>14</sup> Here, we added one polystyrene chain (50 repeat units) into the original ternary asphaltene2 and AAA-1 systems to build polymer-modified systems, and then we analyzed properties and microstructure of the unmodified and modified systems.

## Model Asphalt Composition

A new model asphalt was devised to improve agreement with the chemical constitution of paving asphalts. The elemental composition and speciation of AAA-1 asphalt and the new model are shown in Table 1. Several compounds were chosen from the literature for use in this model system.

On the basis of Redelius's work, one way for assessing compounds for use in model asphalts is to compare their Hansen solubility parameters with established ranges<sup>22</sup> for asphalts. Through comparing solubility parameters of compounds, we can judge if they can form a homogeneous system, which is necessary for good performance of unmodified asphalt on road pavement.<sup>6</sup>

Hansen solubility parameters were estimated for possible components in asphalt using correlations from the literature.<sup>23,24</sup> The correlations account for different contributions from each segment of a molecule. Parameters for the sulfur atom in

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**Table 1. Distribution of Atom and Molecule Types in the Model Original and Modified AAA-1 Systems, Compared to SHRP Asphalt AAA-1<sup>33</sup>**

mass ratio	C	H	N	O	S	percent asphaltene	percent polar aromatic	percent naphthene aromatic	percent saturate
original	84.2	9.4	1.2	0	5.1	18	38	33	11
modified	85	9.3	1.1	0	4.7	16	34	29	20
experiment <sup>33</sup>	84.2	10.5	1.2	0.6	5.3	18	38	33	11
experiment <sup>a</sup>	82.6	10.3	1.2	0.6	5.2				

<sup>a</sup> Recalculated using the "average" molecule structure C<sub>55</sub>H<sub>82</sub>N<sub>0.7</sub>O<sub>0.3</sub>S<sub>1.3</sub>,<sup>33</sup> to ensure proper normalization.

**Table 2. Hansen Solubility Parameters<sup>a</sup>**

system	$\delta_d$	$\delta_p$ (J/cm <sup>3</sup> ) <sup>1/2</sup>	$\delta_h$	V (cm <sup>3</sup> /mol)
crude oil	17.7	4.0	0.6	
asphalt	18.4	3.9	3.6	
asphaltenes	19.6	3.4	4.4	
maltenes	17.7	5.8	2.5	
polystyrene	18.5	4.5	2.9	
<i>n</i> -C <sub>22</sub>	15.85	0.0	0.0	393.6
1,7-dimethylnaphthalene	18.8	0.0	0.0	143.7
asphaltene1	23.6	0.56	4.5	476.9
asphaltene2	17.8	0.2	2.36	865.5
ethylbenzothiophene	21.1	1.6	6.0	135.7
3-pentylthiophene	18.9	1.25	2.6	151.4
7,8-benzoquinoline	19.5	3.7	5.7	153.8
ethyltetralin	20.4	0.49	0.0	158.5

<sup>a</sup> Parameters shown for a Venezuelan asphalt,<sup>22</sup> its components, and its original crude oil; for polystyrene;<sup>27</sup> and for compounds in model asphalts based on correlations.<sup>23</sup>

thiophene were not available in the correlation. Literature values for the Hansen solubility parameters of thiophene<sup>25</sup> were used to estimate sulfur contributions to  $\delta_p$  and  $\delta_h$ , leading to  $F_{p-s} = 189.6 \text{ J}^{1/2} \text{ cm}^{3/2} \text{ mol}^{-1}$  and  $U_{h-s} = 4806 \text{ J}^{1/2} \text{ cm}^{3/2} \text{ mol}^{-1}$ .<sup>26</sup> In the absence of parameters for highly substituted aromatic rings, the appropriate number of parameters for  $=\text{CH}-$  or  $=\text{C}<$  were used instead.

The estimated Hansen solubility parameters for compounds used in model asphalts are shown in Table 2. The asphaltene1 molecule dipole contribution  $\delta_d$  is higher than the experimental value for asphaltenes, while the hydrogen-bonding component  $\delta_h$  is similar. The  $\delta_d$  and  $\delta_h$  parameters for the asphaltene2 molecule are both lower than experimental values. The predicted polar contribution  $\delta_p$  is much lower than experimental values for both asphaltenes. This potentially indicates a poor ability of the new thiophene sulfur parameter in the  $\delta_p$  correlation to extrapolate. Another possible cause is the choice regarding aromatic ring parameters: the correlation suggests polar contributions of  $F_p = 110 \text{ J}^{1/2} \text{ cm}^2 \text{ mol}^{-1}$  for each aromatic ring, while the contribution is  $F_p = 0$  for these individual C or CH units. Including a  $F_p$  contribution when calculating the polar solubility parameter would increase its magnitude, which would bring the calculated asphaltene results closer to those estimated by Redelius from solubility measurements. The *n*-C<sub>22</sub> has a slightly lower dipole contribution compared to typical maltenes, and its  $\delta_p$  and  $\delta_h$  values are much lower. Dimethylnaphthalene has  $\delta_p$  and  $\delta_h$  values of zero, and its dipole contribution is between that of asphaltenes and maltenes. When its Hansen solubility parameters are compared to components in model asphalt, its  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  values are smaller than those of asphaltene1, close to those of asphaltene2, while higher than those of maltene. These intermediate values indicate the ability for 1,7-dimethylnaphthalene to function as a resin from a

polarity perspective. For polystyrene, recommended values of solubility parameters  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  are available from a manual written by Hansen.<sup>27</sup>

For a new model asphalt system of AAA-1, we represent the asphaltene part using a molecule suggested by Groenzin and Mullins<sup>16</sup> based on fluorescence measurements, referred to here as asphaltene2. It has long aliphatic chains surrounding a core of fused aromatic rings. We chose *n*-C<sub>22</sub> to represent the saturate. The prevalence of this size (among alkanes) was suggested by Kowalewski et al.<sup>28</sup>

One polar aromatic component (7,8-benzoquinoline) was taken from work by Masson and Lacasse.<sup>29</sup> The structure of a second (ethylbenzothiophene) was suggested from degradation studies on bitumen.<sup>30</sup> Two additional components (3-pentylthiophene and 1-ethyltetralin) were chosen to match the aromaticity and C, H, S, and N ratios of resins in real AAA-1 asphalt. 7,8-Benzoquinoline supplies a nitrogen heteroatom, while ethylbenzothiophene and 3-pentylthiophene supply sulfur heteroatoms into the model system. Together, these compounds approximate the polar aromatic component. Ethyltetralin resembles many compounds identified by mass spectrometry of heavy crude extracts<sup>31</sup> and has a molecular structure closer to naphthene aromatics. Its rings balance the ratio of total aromatic and aliphatic carbon in the system. The molecular weights of these model compounds (150–180 g/mol) are lower than those implied for resins via rotational relaxation time (300–500 g/mol).<sup>32</sup> While the impact of this size difference on intermolecular packing is not known, hypotheses about differences between two- and three-ring compounds are raised in the Discussion based on results presented in this work.

The new resin compounds provide a more broad polarity range than found in earlier model asphalts that we proposed.<sup>14</sup> Ethylbenzothiophene, 3-pentylthiophene, and 7,8-benzoquinoline have higher polarity and hydrogen-bonding contributions than those of dimethylnaphthalene, on the basis of Hansen solubility parameters, while ethyltetralin has parameters closer to those of dimethylnaphthalene. Dispersion contributions for ethylbenzothiophene and ethyltetralin are slightly higher than those of asphaltenes. Dispersion contributions for benzoquinoline and 3-pentylthiophene are between those of asphaltenes and maltenes. The  $\delta_d$  parameters for these four compounds are higher than that of *n*-C<sub>22</sub>, lower than that of asphaltene1, and close to that of asphaltene2. Thus, they have the capability to dissolve asphaltene and saturate together, making the whole system stable. On an absolute scale, ethylbenzothiophene, 3-pentyl-

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Table 3. Overall Composition of Original and Modified AAA-1 Systems

system		component						
		asphaltene	ethyltetralin	3-pentylthiophene	benzoquinoline	ethylbenzothiophene	n-C <sub>22</sub>	polystyrene
original	number of molecules	9	100	50	43	20	18	0
AAA-1	mass fraction (%)	18.2	32.5	15.7	15.7	6.6	11.4	0
modified	number of molecules	9	100	50	43	20	18	1
AAA-1	mass fraction (%)	16.5	29.4	14.2	14.1	6.0	10.3	9.6

thiophene, and ethyltetralin have low  $\delta_p$  values. This finding parallels asphaltene molecules and most likely indicates a non-optimal aromatic sulfur parameter and the need for an aromatic ring contribution to  $\delta_p$ . The benzoquinoline  $\delta_p$  parameter, calculated using only terms existing in the correlation, is larger than  $\delta_p$  for other resins, although it is still smaller than that of maltenes assessed by Redelius. This suggests that actual polar aromatic resins are more polar than the compounds employed here.

The numbers of each molecule type and corresponding mass fractions for the AAA-1 model system are listed in Table 3. The number of asphaltene molecules (9) was increased compared to our earlier work<sup>14,17,18</sup> in order to increase the signal-to-noise ratio when tabulating asphaltene–asphaltene correlations. No oxygen-containing compounds have been included in the model asphalt, because of the low oxygen concentration in AAA-1. The mass fractions of different atom types are close to those of SHRP AAA-1 asphalt, as shown in Table 1. The balance among asphaltene, polar aromatic, naphthene aromatic, and saturate are similar in the model and real asphalt as well.

To analyze polymer modification effects, we added one polystyrene chain into each model asphalt system. Polystyrene was chosen because it is part of the common SBS triblock copolymer asphalt modifier. This also parallels earlier polymer modification of the original ternary asphaltene2 system.<sup>14</sup> The polymer mass fraction reaches 9.6% in the AAA-1 system and 18% in the ternary asphaltene2 system. Using more than one polymer molecule would be desirable for improved statistics. Computational system size limitations prevented this, however. Indeed, longer polymer chain lengths and smaller mass fractions in asphalt are used in pavement applications.<sup>6</sup>

### Simulation Methods

In the simulations, we used the OPLS all-atom interaction force field.<sup>34,35</sup> An all-atom approach was chosen because the use of united atoms has been shown<sup>36</sup> to alter detailed molecular packing, which is a subject of this study.

To analyze the temperature dependence of the model asphalt systems, four temperatures were chosen for the original ternary asphaltene2 system: 298.15, 358.15, 400, and 443.15 K. A fifth temperature of 458.15 K was added for the polymer-modified asphaltene2 system. The temperatures 298.15, 333.15, 400, and 443.15 K were chosen in the AAA-1 systems, with 358.15, 458.15, and 473.15 K also studied in the polymer-modified AAA-1 system.

To initiate the simulations, we placed molecules on a cubic lattice and then used Monte Carlo (Towhee program)<sup>37,38</sup> to move molecules away from unlikely positions in this initial configuration. We used molecular dynamics (LAMMPS2001 program)<sup>39,40</sup> to equilibrate and sample each system, as we did earlier.<sup>14,17,18</sup> Constant volume and temperature (NVT) using the velocity rescaling method were used for the first 100 ps to dissipate high forces and energies present in early configurations. The isothermal–isobaric (NPT) ensemble using the Nosé–Hoover thermostat and barostat<sup>41</sup> was used next for at least 2 ns, with a time step of 0.5 fs. This was sufficient to equilibrate mechanical forces: beyond 2 ns, the volume fluctuated about a well-defined average. Next, we continued with NVT simulation (Nosé–Hoover) at the average volume with a time step of 1 fs and ran for 8 ns or longer. We used atom positions and total stress components stored every 12 fs to perform viscosity, diffusion coefficient, and orientation calculations.

To figure out if changes in initial configuration would lead to differences in asphalt property simulation results, we reran the polymer-modified ternary asphaltene2 system at 400 and 443.15 K using different random seeds to initiate the Monte Carlo simulation. The density, diffusion coefficient, and orientation results from different initial configurations are compared below. We also reran the original ternary asphaltene2 system at 443.15 K from a different configuration. The simulation time attained was long enough to lead to converged density results but not orientation results.

We calculated the diffusion coefficient by calculating the displacement of the center of mass, as we did earlier<sup>18</sup> for ternary model asphalts without a polymer present. Results were averaged over all molecules of the same type in all directions. Simultaneously, we calculated the viscosity using the Green–Kubo method (integrating the stress time correlation function) and Einstein method (mean-squared “displacement” of stress) for the original and polymer-modified asphaltene2 and AAA-1 systems at 443.15 K. Diagonal and off-diagonal elements of the molecular virial-based stress tensor were averaged to improve convergence.<sup>42–44</sup> Viscosity was not calculated at lower temperatures because of slow stress relaxations.

The microstructure of model asphalt systems was analyzed to infer additional polymer modification effects. Microstructure includes distances and packing angles between aromatic compounds and folding angles between fused aromatic rings. These properties were calculated for components in original and polymer-modified model asphalt systems.

For original asphalt systems and those with one polystyrene molecule present, we calculated the molecule–molecule radial

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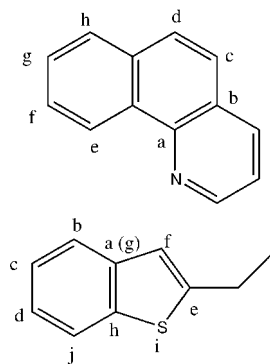
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**Figure 1.** Benzoquinoline and ethylbenzothiophene molecular structures, with letters indicating atom tags for orientation calculations.

distribution functions  $g(r)$  for components in model asphalt systems. We labeled the first peak position as  $d_0$  in each  $g(r)$  function. Then we calculated the intermolecular orientations<sup>17</sup> between molecules separated by distances up to  $d_0$ . We also calculated angles between different sections of a molecule (intramolecular orientations) for asphaltene2 and small aromatic molecules. In the AAA-1 system, we calculated intra- and intermolecular orientation for multi-ring aromatic compounds benzoquinoline and ethylbenzothiophene. The atom index used to calculate molecular orientation for benzoquinoline and ethylbenzothiophene are shown in Figure 1, with the same definition of normal vectors used as was shown for asphaltene2 molecules in our earlier work.<sup>17</sup>

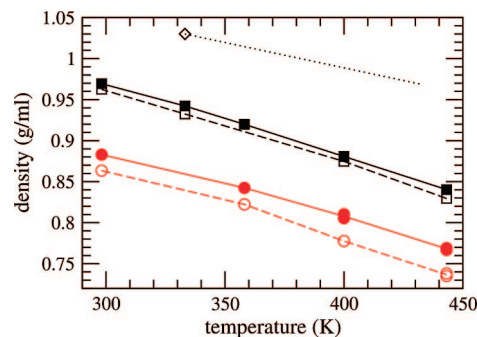
### Simulation Results

**Density, Isothermal Compressibility, and Expansion Coefficient.** To find out how a polymer modifies model asphalt properties, we analyzed the temperature dependence of density, isothermal compressibility, and expansion coefficient in the original and polymer-modified systems. Results are shown in Figures 2–4.

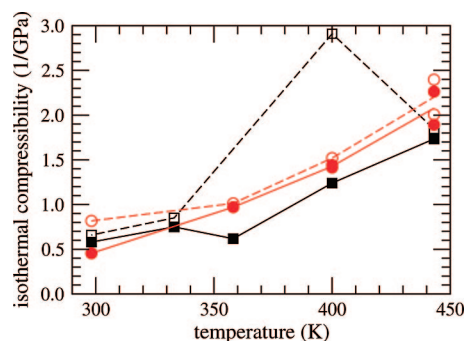
Figure 2 shows that both ternary asphaltene2 and six-component AAA-1 systems have a lower density than SHRP AAA-1 asphalt at 333.15 K.<sup>45</sup> The experimental density at higher temperatures (dotted line) was estimated on the basis of the thermal expansion coefficient of SHRP AAA-1 asphalt.<sup>46</sup> After one polymer chain was added, the density at each temperature increased, while the temperature dependence remained essentially unchanged and close to the experimental temperature dependence. Rerunning simulations from different initial configurations led to very similar density results, as shown by multiple symbols for the original ternary asphaltene2 system at 443.15 K and the modified asphaltene2 system at 400 and 443.15 K. From differential scanning calorimetry, the glass transition temperature for AAA-1 spans a range from  $-8.75$  to  $-40.45$  °C,<sup>45</sup> which is lower than the lowest temperature simulated here. Fitting a line over 358–443 K and extrapolating to 298 K shows only a small deviation from the predicted density at 298 K; thus, we do not observe a dilatometry-based  $T_g$  in this work.

(45) Robertson, R. E.; Branthaver, J. F.; Harnsberger, P. M.; Petersen, J. C.; Dorrence, S. M.; McKay, J. F.; Turner, T. F.; Pauli, A. T.; Huang, S.-C.; Huh, J.-D.; Tauer, J. E.; Thomas, K. P.; Netzel, D. A.; Miknis, F. P.; Williams, T.; Duvall, J. J.; Barbour, F. A.; Wright, C. Fundamental properties of asphalts and modified asphalts volume I: Interpretive report. Technical Report FHWA-RD-99-212, Federal Highway Administration, 2001.

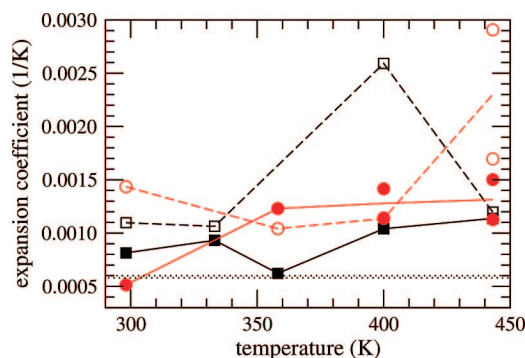
(46) Anderson, D. A.; Christensen, D. W.; Bahia, H. U.; Dongre, R.; Sharma, M. G.; Antle, C. E. Binder characterization and evaluation, volume 3. Technical Report SHRP-A-369, Strategic Highway Research Program, 1994.



**Figure 2.** Density comparison among original and polymer-modified (○) ternary asphaltene2<sup>14</sup> and (□) model AAA-1 systems and the experimental value<sup>45</sup> (◇) for SHRP AAA-1 asphalt. Open symbols and dashed lines indicate original systems, while filled symbols and solid lines indicate polymer-modified systems in all figures, except where noted otherwise. The dotted line indicates the slope dictated by the experimental thermal expansion coefficient. Other lines are guides for the eye.



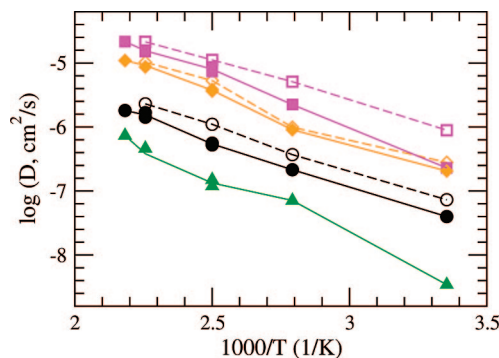
**Figure 3.** Isothermal compressibility of original and polymer-modified (○) ternary asphaltene2 and (□) AAA-1 systems.



**Figure 4.** Thermal expansion coefficient of original and polymer-modified (○) asphaltene2 and (□) AAA-1 systems. Symbols are the same as in Figure 2. Lower and upper dotted lines indicate reference data<sup>46</sup> of AAA-1 below and above  $T_g$ .

The higher density of model AAA-1 compared to ternary asphaltene2 shows an effect of speciation. Achieving better elemental analysis agreement leads to a model system density closer to that of a real asphalt.

On the basis of Figure 3, we find that, after adding one polymer chain into the system, the isothermal compressibility decreased at each temperature for both kinds of model asphalts. Rerunning simulations from different initial configurations led to similar isothermal compressibilities. Bulk modulus is the inverse of isothermal compressibility. Therefore, after the polymer was added, the modulus of all systems increased, while their temperature dependences remained nearly constant. Including a polymer increased the stress required to change the volume. For a constant Poisson ratio, this suggests a tendency for the model asphalt to exhibit smaller strain when under shear



**Figure 5.** Diffusion coefficients of components in original and polymer-modified ternary asphaltene2 systems. Diffusivity decreases as  $\square$ , dimethylnaphthalene molecules;  $\diamond$ ,  $n$ -C<sub>22</sub> molecules;  $\circ$ , asphaltene2 molecules; and  $\Delta$ , polystyrene.

stress, as found in practice for the shear modulus in polymer-modified asphalts.<sup>47</sup>

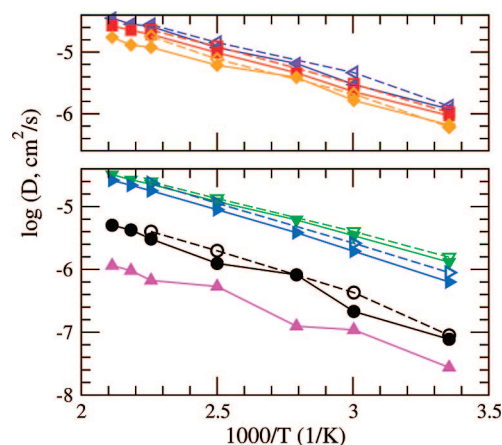
Figure 4 shows that thermal expansion coefficients of four model asphalts are of the same order of magnitude but slightly higher than measured values<sup>46</sup> for SHRP AAA-1. Adding one polymer chain decreased the expansion coefficient for the model AAA-1 system, leading to values closer to SHRP AAA-1 data. Differences in expansion coefficient from different initial configurations are comparable to the range spanned by different temperatures. In the ternary asphaltene2 system, the expansion coefficient decreased at 298 and 443 K upon adding a polymer, while it remained similar at 358 and 400 K. We think those differences could reflect simulation noise more than underlying physics, because different results from independent runs span almost the same magnitude.

After one polymer molecule was added into the original model asphalt systems, their densities increased, expansion coefficients became less sensitive to temperature change, and modulus increased. Those are good signs for asphalt performance, because ideal asphalt binders<sup>6</sup> are supposed to have a nearly consistent modulus under a very wide temperature range. With a polymer present, AAA-1 and ternary asphaltene2-based system densities increased, bringing them closer to experimental values for SHRP asphalts.<sup>45</sup>

**Diffusion Coefficients.** Figures 5 and 6 show the self-diffusion coefficient of each compound in the model asphalts. The diffusion coefficient was calculated via mean-squared displacement of the center of mass, and no attempt was made to account for mixture effects.

Figure 5 shows that the polymer chain has the smallest diffusion coefficient among the four kinds of molecules in the polymer-modified ternary asphaltene2 system. Asphaltene molecules diffused slower than dimethylnaphthalene and  $n$ -C<sub>22</sub> molecules, and dimethylnaphthalene molecules diffused the fastest. These results are consistent with the molecule sizes. The long chains and aromatic rings of polystyrene could easily be blocked by the surrounding big and small molecules; therefore, its center of mass could not diffuse easily. After a polymer was added into the ternary asphaltene2 system, the diffusion rates of all components decreased because of an obstacle effect of the polymer. The polymer chain moves very little; therefore, other molecules must diffuse around it. The bigger the molecule size, the smaller the influence from the polymer.

As the temperature decreased, the diffusion coefficient of all four components decreased. Asphaltene and small-molecule



**Figure 6.** Diffusion coefficients of components in original and polymer-modified AAA-1 systems. Diffusivity decreases as left-facing triangle, ethylbenzothiophene;  $\nabla$ , 3-pentylthiophene;  $\square$ , ethyltetralin; right-facing triangle, 7,8-benzoquinoline;  $\diamond$ ,  $n$ -C<sub>22</sub>;  $\circ$ , asphaltene;  $\Delta$ , polystyrene.

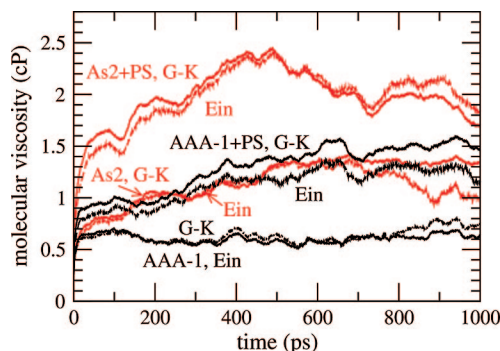
diffusion coefficients have relatively similar temperature dependences when comparing original and polymer-modified systems. That indicates that adding one polymer chain into the system did not change the diffusion activation energy. The diffusion coefficient temperature dependence was not consistent for polymer molecules. From 443.15 to 358 K, its activation energy was 6.82 kcal/mol, while at 298.15 K, its diffusion coefficient was smaller than would be extrapolated from higher temperatures. The change in temperature dependence between 358 and 298 K reflects a slowing of dynamics as  $T_g$  is approached. Decreased accuracy may also play a role, because the mean-squared displacement was only 0.88 Å<sup>2</sup> in 4 ns at 298 K, which is much less than the box size squared (2058 Å<sup>2</sup>).

Repeated 443.15 and 400 K simulations for polymer-modified ternary asphaltene2 systems led to diffusion coefficient results that showed little scatter, as shown in Figure 5 for each component. Differences in the diffusion coefficient are smaller for asphaltene than for polystyrene. This is likely due to improved statistics (5 molecules versus 1 molecule). The results provide support that both simulations for each case are similarly equilibrated.

Diffusion coefficients for each component in the AAA-1 system are shown in Figure 6. Polystyrene again has the slowest diffusion rate, although its diffusion rate at 443.15 K is almost doubled in the AAA-1 system compared to its rate in the ternary asphaltene2 system. The lower the temperature, the faster its relative speed in the AAA-1 system. Asphaltene2 molecules diffused the second slowest, and their diffusion rate is consistently doubled in AAA-1 systems compared to ternary asphaltene2 systems. The  $n$ -C<sub>22</sub> molecules diffused the third slowest in both systems, and their diffusion rate in AAA-1 systems is faster by at least 30% (at 443.15 K) than in ternary asphaltene2 systems. Benzoquinoline molecules diffused faster within the system than  $n$ -C<sub>22</sub> molecules but slower than other resins, while ethylbenzothiophene, pentylthiophene, and ethyltetralin molecules diffused at almost the same rates. Those results indicate as in our earlier work<sup>18</sup> that diffusion coefficients are related to the molecule size and surrounding environment. Asphaltene2 has a lower mass ratio in the AAA-1 system (18%) than in the ternary asphaltene2 system (21.1%), leading to a higher concentration of smaller molecules. Thus, component diffusion coefficients in AAA-1 are correspondingly larger compared to those in the ternary asphaltene2 system. These higher component

(47) Chen, J.-S.; Liao, M.-C.; Shiah, M.-S. *J. Mater. Civ. Eng.* **2002**, *14*, 224–229.





**Figure 7.** Viscosity results as a function of integration time at 443.15 K for original and polymer-modified ternary asphaltene2 and AAA-1 systems. Solid and dashed lines show Green–Kubo and Einstein method results.

diffusion coefficients in the AAA-1 system persist after adding polystyrene. After one polymer was added into AAA-1 systems, every component diffused slightly slower, in part because they are in a more dense environment. Because the polymer chain has a smaller mass fraction in the AAA-1 system (9.6%) than in the ternary asphaltene2 system (18%), its obstacle effect on diffusion is smaller and component diffusion rates decreased less in the AAA-1 system than in the ternary asphaltene2 system.

**Viscosity.** The viscosity was calculated at 443.15 K for original and polymer-modified asphaltene2 and AAA-1 systems using the Green–Kubo and Einstein methods. Results are shown in Figure 7. The viscosity estimate corresponds to the plateau value reached after a sufficiently long time but before poor statistics lead to noise dominating the results. A viscosity estimate of 1.35 cP for the ternary asphaltene2 system at 443.15 K was reported previously.<sup>18</sup> Here, we estimate 0.65 cP for the original AAA-1 system at 443.15 K. The relaxation times are longer in the polymer-modified systems, and no plateau was attained before noise dominated. Qualitatively, the viscosity almost doubled in the ternary asphaltene2 system and increased by approximately 33% in the AAA-1 system after adding one polymer chain. These estimates are based on the ranges spanned in Figure 7. The bigger polymer mass ratio in the ternary asphaltene2 system (18%) than in the AAA-1 system (9.6%) contributes to the different viscosity increase. The increase differs from that expected from intrinsic viscosity (fractional increase proportional to concentration) because neither system is a dilute polymer solution.

**Radial Distribution Function, Same Kind of Molecules.** The radial distribution function  $g(r)$  reflects the relative concentration of molecules as a function of distance  $r$  from a given molecule. At longer distances, the concentration reaches its average value and  $g(r)$  tends to unity. We calculated  $g(r)$  for asphaltene–asphaltene, asphaltene–resin, and resin–resin pairs in both original systems and compared their results with polymer-modified systems. Intermolecular distances were based on center of mass positions.

Results are shown in Figure 8 and Figure S1 (in the Supporting Information) for asphaltene–asphaltene pairs. On the basis of these  $g(r)$  results, we determined the first peak distance values  $d_0$ , listed in Table 4. In this work, we used atom position data from NVT simulation-based results collected over a much longer simulation time (8 ns or longer) than NPT simulation results shown in our former publication (5 ns or less).<sup>17</sup> The  $g(r)$  peaks from the longer simulations move among the  $g(r)$  peaks seen earlier for different starting conditions. The first peak positions decreased, as shown in Table 4.

Figure 8 and Table 4 show that in the polymer-modified model AAA-1 system, the closest distance between molecule

centers decreased by several angstroms at 443 and 400 K, compared to the original systems. At two lower temperatures, the asphaltene2 first peak positions differed slightly between the original and polymer-modified cases, while the shapes of the  $g(r)$  peaks were similar. The separations at all four temperatures over the time simulated are larger than the 3.5 Å that defines asphaltene aggregation in Yen's model.<sup>48</sup> Detailed results for the asphaltene2 systems are described in the Supporting Information.

Comparing  $g(r)$  results in ternary asphaltene2 and AAA-1 systems shows that the first peak position and shape vary slightly less with temperature in the AAA-1 system than in the ternary asphaltene2 system. The first peak distance ranges in the original systems are very close, however, spanning from 6.6 to 8.5 Å. Including one polymer changed the asphaltene mass fraction and the distance ranges between asphaltene2 molecules in both systems. At 298.15 K in the modified ternary asphaltene2 system, the first peak position is larger than any other  $d_0$ . That difference at the lowest temperature could result from poor sampling (asphaltene molecules kinetically unable to attain closer packings) or from a mixture  $T_g$  effect. The many possible orientations of nearby asphaltene molecules<sup>17</sup> also complicate the results at all temperatures by distributing the center-of-mass positions over different distances for parallel versus offset  $\pi$ -stacked arrangements.

In asphaltene2 systems, we calculated  $g(r)$  for dimethylnaphthalene molecule pairs and compared these results in the original ternary system and the polymer-modified system. Results in Figure 9 show that dimethylnaphthalene packing distances have similar distributions and a consistent first peak position under all conditions; after including one polymer in each system, the first peak position remained unchanged. Lower temperatures indicate increased local concentrations at small separations. We read the first peak position as 6.6 Å at all temperatures for analyzing intermolecular orientation.

In original and polymer-modified AAA-1 systems, we also calculated  $g(r)$  for benzoquinoline and ethylbenzothiophene pairs (curves are shown in the Supporting Information). For benzoquinoline, the  $g(r)$  results are similar to those of dimethylnaphthalene pairs. As the temperature decreased, the first peak height of  $g(r)$  increased (always higher than 1.8), while its position changed little. With the presence of one polymer,  $g(r)$  results remained similar at each temperature. Results were similar for ethylbenzothiophene molecule pairs, except that the first  $g(r)$  peak heights were in the range of 1.2–1.4. The first  $g(r)$  peak was highest (1.4) at 298 K in the polymer-modified AAA-1 system. We used common first peak positions for benzoquinoline and ethylbenzothiophene pairs of 7.0 and 6.7 Å in the intermolecular orientation calculations.

Comparing the  $g(r)$  results for pairs of small aromatic molecules shows that nearest neighbors concentrated more at the first peak position as the temperature decreased. Including a polymer in the model asphalt systems left the first peak position almost unchanged for these resin molecules. Packing distances among resins were not affected by the presence of a polymer chain, even at a concentration of 18% by mass.

**Radial Distribution Function, Different Kinds of Molecules.** In the ternary asphaltene2 system, we analyzed the radial distribution function for asphaltene2 and dimethylnaphthalene molecule pairs at four temperatures and compared results between the original and polymer-modified systems. Results are shown in Figure 10, except for 298.15 K, where poor sampling

(48) Yen, T. F.; Erdman, J. G.; Pollack, S. S. *Anal. Chem.* **1961**, *33*, 1587–1594.



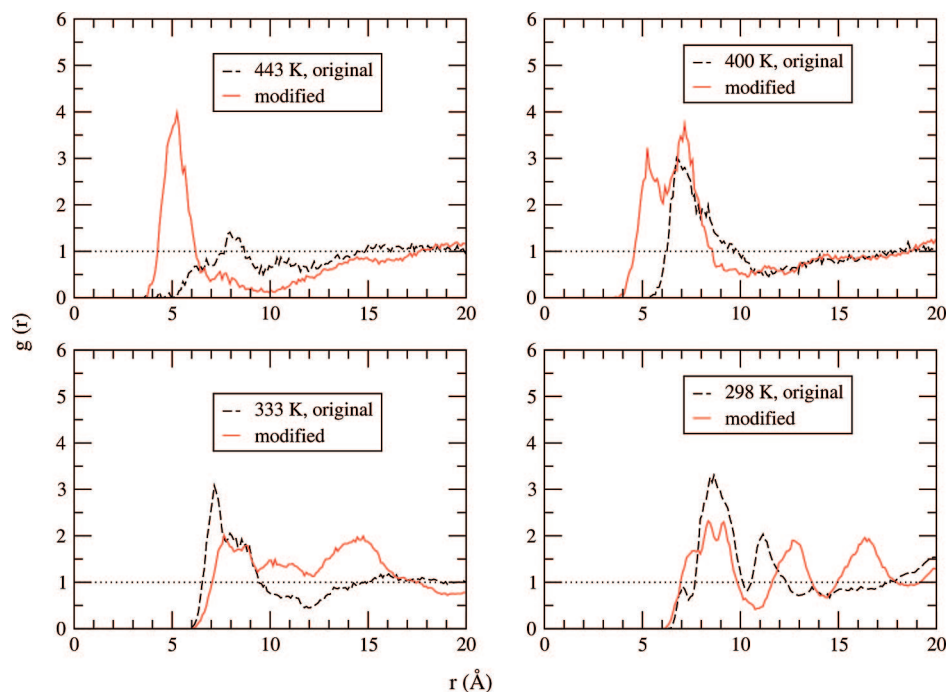


Figure 8. Asphaltene–asphaltene  $g(r)$  in original and polymer-modified AAA-1 systems.

Table 4. First Peak Distance  $d_0$  for Asphaltene2 Molecule Pairs in Original and Polymer-Modified Ternary Asphaltene2 and AAA-1 Systems

temperature (K)	ternary asphaltene2 systems			AAA-1 systems	
	prior NPT $d_0^{17}$ (Å)	original $d_0$ (Å)	modified $d_0$ (Å)	original $d_0$ (Å)	modified $d_0$ (Å)
443.15	9.3	6.6	3.9	8.0	5.3
400		8.6	8.1	6.8	5.3
358.15	8.6	7.2	5.6		8.8
333.15				7.2	7.7
298.15	8.6	8.2	11.8	8.5	7.5

was exhibited. The  $g(r)$  results in most cases did not display a peak before reaching the average  $g(r) = 1$  plateau, i.e., the average concentrations of each molecule. These results suggest that dimethylnaphthalene molecules prefer not to surround asphaltene molecules at high temperatures, because the number of neighboring molecules at small to moderate separations is smaller than the average. No first peak position is clear under most conditions. As a compromise, we chose a common distance of  $d_0 = 6.02$  Å for analyzing intermolecular orientation. The  $g(r)$  function at 358 K differed from the high-temperature results. At 358.15 K with the polymer,  $g(r)$  rose above 1 and fell below the average value at distances less than half the box edge. This

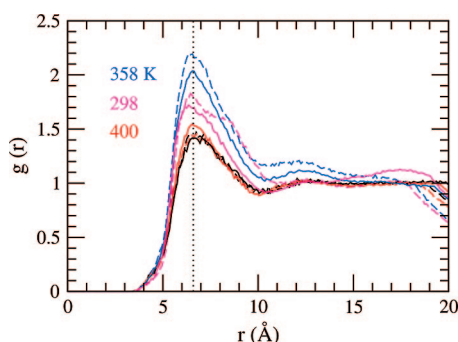


Figure 9. Dimethylnaphthalene–dimethylnaphthalene  $g(r)$  in original and polymer-modified ternary asphaltene2 systems. The dotted line indicates a common  $d_0$  value.

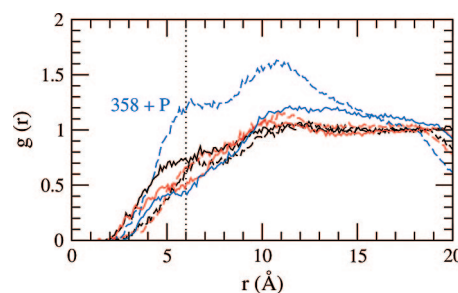
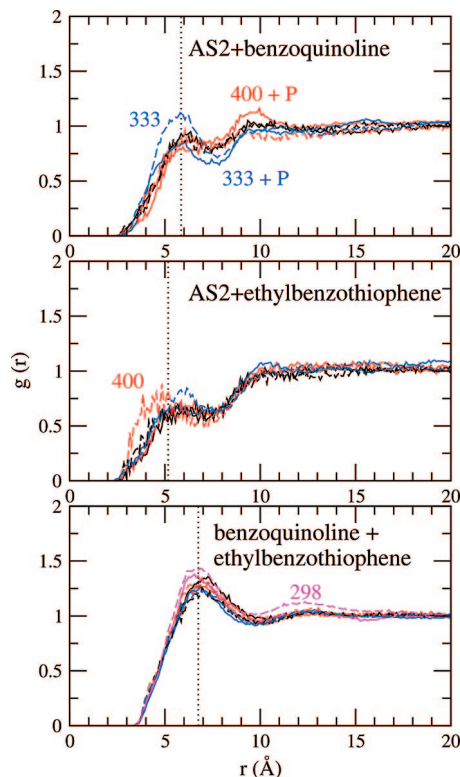


Figure 10. Asphaltene2–dimethylnaphthalene  $g(r)$  in original and polymer-modified ternary asphaltene2 systems. Results are shown for three temperatures.

suggests domains of likely and unlikely asphaltene–resin interaction distances for this system.

$g(r)$  results for different kinds of molecule pairs in AAA-1 systems are shown in Figure 11. Results for 298 K are not shown for pairs involving asphaltenes because they also exhibited poor sampling. Asphaltene2 and benzoquinoline pairs at different temperatures have almost the same initial rise to a subunity  $g(r)$ , other than the labeled exceptions. Asphaltene2 and ethylbenzothiophene pairs have a near-common initial rise to a still lower  $g(r)$ , while benzoquinoline and ethylbenzothiophene pairs have a very consistent first peak at a  $g(r)$  above 1. The first peak height of asphaltene2 and ethylbenzothiophene pairs is always lower than 1. This indicates that asphaltene2 and ethylbenzothiophene avoid packing in close proximity, compared to random packing. In addition, visualization revealed that ethylbenzothiophene molecules were not able to diffuse throughout the regions unoccupied by asphaltene and polymer. The ultimate rises to  $g(r) = 1$  indicate common distances of 10 Å from an asphaltene, beyond which small-molecule packing is random. The first peak heights of benzoquinoline and ethylbenzothiophene pairs are higher than 1; these molecules show a slight preference to associate.

**Intramolecular Orientation.** We compared intramolecular orientation in original and polymer-modified asphaltene2 and AAA-1 systems to see if folding angles between adjacent fused aromatic rings in one molecule changed after adding one



**Figure 11.** Asphaltene2–benzoquinoline, asphaltene2–ethylbenzothiophene, and benzoquinoline–ethylbenzothiophene  $g(r)$  in original and polymer-modified AAA-1 systems. Results are not shown for asphaltene–model resin pairs at 298.15 K.

polymer. After one polymer was added, intramolecular orientations for all cases in both model asphalt systems remained the same. Plots for all cases are shown in the Supporting Information. With increasing temperature, the distribution of folding angles between aromatic rings became slightly broader for all five kinds of compounds. The consistent trends result from using the same force field for each of these molecule types. Ethylbenzothiophene has the broadest intramolecular orientation

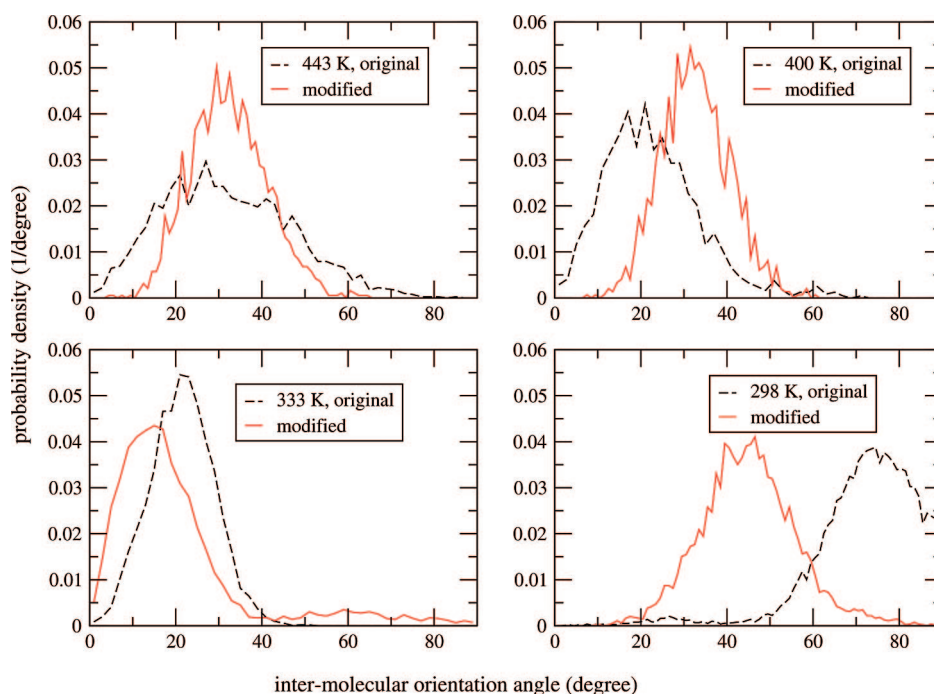
distribution ( $0-30^\circ$ ), which relates to the presence of S in the ring. That result is consistent with the broader distribution that we found earlier<sup>14</sup> for sulfur-containing rings in a different asphaltene molecule than used here.

**Intermolecular Orientation, Same Molecule Type.** Next, we calculated distributions of angles between molecule pairs (intermolecular orientation) for asphaltene2, dimethylnaphthalene, benzoquinoline, and ethylbenzothiophene. Only molecules with pair separations up to  $g(r)$  first peak positions  $d_0$  were used in the calculation. Such a restriction is necessary to limit orientation to nearest neighbors.<sup>17</sup>

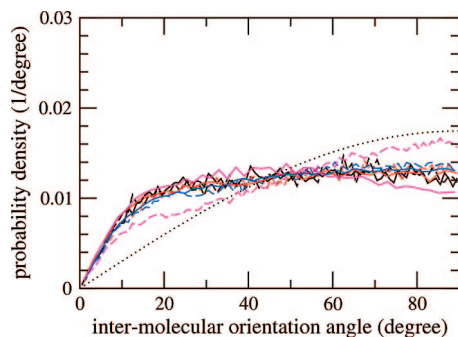
**Asphaltene Molecules.** Orientations in the ternary asphaltene2 and AAA-1 systems were averaged over the 5 and 9 asphaltene molecules found in each system. The small number of pairs separated by distances less than  $d_0$  limited statistical accuracy. Detailed results that compare original and polymer-modified AAA-1 systems are shown in Figure 12; results for ternary asphaltene2 systems are shown in the Supporting Information.

In the original ternary asphaltene2 system, consistent orientation results from different initial configurations indicate converged simulation results at 443 K (see Figure S6 and further discussion in the Supporting Information). The general trend observed in AAA-1 systems was for neighboring asphaltenes to pack at angles distributed between 20 and  $60^\circ$ , with a more broad distribution at higher temperatures. Differences in the presence of a polymer and at lower temperatures are potentially an effect of statistical noise, rather than well-converged results. Comparing changes in intermolecular orientation after polymer modification, we found smaller changes in AAA-1 systems compared to ternary asphaltene2 systems. In both systems, the angles between closest packed asphaltene2 molecules remained similar, except for the 298.15 K cases and one of the ternary asphaltene2 results at 400 K.

**Smaller Molecules.** We calculated intermolecular orientation probability density for dimethylnaphthalene molecule pairs at four different temperatures and compared results from original and polymer-modified systems, using a common  $d_0$  value. Results are shown in Figure 13. A dotted line indicates random packing,  $\pi(\sin \theta)/180$ . Dimethylnaphthalene molecules within



**Figure 12.** Intermolecular orientation probability density of asphaltene2 in original and polymer-modified AAA-1 systems.



**Figure 13.** Intermolecular orientation probability density between dimethylnaphthalene molecules in original and polymer-modified ternary asphaltene2 systems, using a common first peak position. The dotted line indicates random packing.

the common first peak distance prefer to pack more parallel than random packing at all temperatures, both with or without one polymer chain in the system. Angles below  $40^\circ$  are more common than random packing. The results for the original ternary asphaltene2 system at 298 K deviated from the other cases and were closer to random packing.

Intermolecular orientation density for benzoquinoline and ethylbenzothiophene at five different temperatures were also compared for original and polymer-modified AAA-1 systems (curves shown in the Supporting Information). As the temperature decreased from 443.15 to 298 K, the benzoquinoline molecules consistently packed almost parallel, similar to the dimethylnaphthalene results, while ethylbenzothiophene molecules consistently packed closer to randomly, with a slightly higher than random extent of packing at angles below  $40^\circ$ . The packing between benzoquinoline molecules and between ethylbenzothiophene molecules did not change after adding one polymer into the AAA-1 system.

**Intermolecular Orientation, Different Molecule Types.** For different kinds of aromatic ring compounds, we analyzed intermolecular orientation in the distance range  $d_0$ , choosing a common  $d_0$  value for all temperatures. In the AAA-1 system, we calculated intermolecular orientations for three multi-ring aromatic compound pairs: (a) asphaltene2 and benzoquinoline ( $d_0 = 5.9$  Å), (b) asphaltene2 and ethylbenzothiophene ( $d_0 = 5.2$  Å), and (c) benzoquinoline and ethylbenzothiophene ( $d_0 = 6.7$  Å). In the ternary asphaltene2 system, we analyzed orientations between asphaltene2 and dimethylnaphthalene ( $d_0 = 6.0$  Å). Comparing different  $d_0$  values between asphaltene2 and dimethylnaphthalene molecules led to intermolecular orientation results that showed an increased tendency toward random packing as neighbors further away are considered, as shown in Figure 14 of our earlier work.<sup>17</sup>

Asphaltene2 and benzoquinoline pairs packed toward parallel at different temperatures compared to a random distribution, as shown in Figure 14. After one polymer was added into the AAA-1 system, the orientation angle distribution typically remained similar. An exception was at 298 K, where some molecules packed near  $90^\circ$  in the presence of one polymer. Asphaltene2 and ethylbenzothiophene molecule pairs have a tendency to pack over a wider range of angles than asphaltene2–benzoquinoline (curves shown in the Supporting Information). The most probable orientations occurred from 10 to  $40^\circ$ , except at 298 K, where molecules packed with a more flat distribution that extended to almost perpendicular. In the presence of a polymer, the most probable orientations remained similar at each temperature.

For benzoquinoline and ethylbenzothiophene molecule pairs (curves shown in the Supporting Information), packing was close

to random at different temperatures in original and polymer-modified systems, with slightly more molecules packed parallel than would occur randomly. Adding one polymer did not change the intermolecular orientation between benzoquinoline and ethylbenzothiophene molecule pairs. The results closely resembled those for dimethylnaphthalene pairs (Figure 13).

Results for asphaltene2 and dimethylnaphthalene in the ternary asphaltene2 system were qualitatively similar to those for asphaltene2 and benzoquinoline in the AAA-1 system. Detailed plots in the Supporting Information compare results from original and polymer-modified systems.

In summary, asphaltene2–benzoquinoline, asphaltene2–ethylbenzothiophene, and asphaltene2–dimethylnaphthalene molecule pairs pack closer to parallel than to perpendicular at different temperatures. In the presence of a polymer, the packing between those two kinds of molecules did not change in the AAA-1 system; in the ternary asphaltene2 system, it was not clear if changes were statistically significant. Benzoquinoline–ethylbenzothiophene molecule pairs packed close to random, with few molecules packed close to parallel. The packing between benzoquinoline and ethylbenzothiophene molecules did not change as the temperature changed or as the composition changed by adding a polymer into the system.

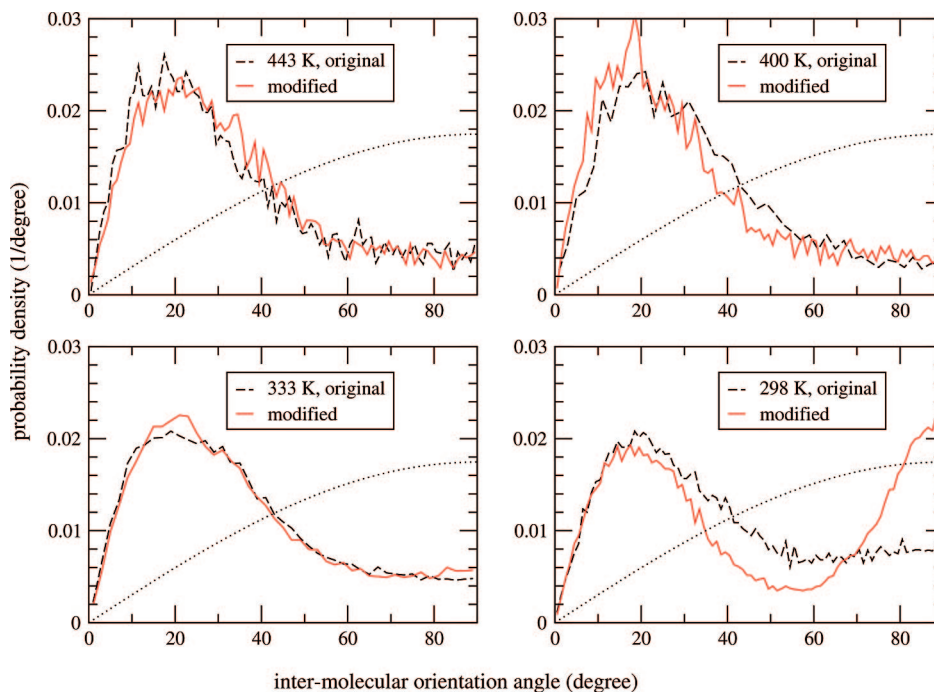
## Discussion

A key utility of studying asphalts by simulating simplified model systems is to infer aspects of molecular behaviors that are difficult or impossible to measure directly. The rich composition of asphalts (millions of types of compounds, many of which contain similar carbon chemistries) complicate or even prohibit *in situ* experiments that report properties of individual molecules or molecule types in the model system.

Several results from this work connote implications for real asphalts. Here, we relate this work to the packing among resin-like and asphaltene molecules, the effects of a polymer on this packing, and polymer effects on single-molecule dynamics. We also comment on aspects of simulating model asphalts, including overall density and convergence of simulation results.

The radial distribution function results directly report which molecules neighbor each other in model asphalts. They indirectly provide guidance about how molecules may pack in real asphalts. To the extent that the molecules chosen here accurately depict the molecules found in each SARA solubility class, our results are counter to the popular view<sup>2</sup> that resin molecules closely surround asphaltene molecules to enhance their solubility. Such a picture would be supported by an enhanced concentration of resin-like molecules around each asphaltene. Instead, we found that the first layer of benzoquinoline molecules around asphaltene2 reached only the average concentration; no enhancement was found. The concentration of ethylbenzothiophene molecules surrounding asphaltene2 molecules was lower than average, showing a first “peak” height of just over half the average concentration before reaching the average value at a separation of 10 Å. These effects were consistent at different temperatures. Dimethylnaphthalene, a model naphthene aromatic, showed behavior similar to ethylbenzothiophene; its concentration was depleted adjacent to asphaltene2 molecules. Resin is supposed to function as a medium that surrounds asphaltene molecules and helps them to dissolve in saturate molecules. Instead, the resin-like molecules employed here either locate away from asphaltene molecules or pack at their average concentration. In both systems, with and without polymer, the environment immediately around an asphaltene molecule has a lower-than-





**Figure 14.** Comparison of intermolecular orientation between asphaltene2 and benzoquinoline molecules in original and polymer-modified AAA-1 systems.

average concentration of resin. We note that concentrations of both two-ring molecules (dimethylnaphthalene and ethylbenzothiophene) were depleted surrounding asphaltene molecules to the same extent. The three-ring molecule (benzoquinoline) concentration was depleted as well but to a lesser extent. This suggests that differences in ring size between asphaltenes and resins are important when considering local packing.

Radial distribution function results for resin–resin packing indicate that the resins chosen here do surround themselves with other resins. The self–self and mixed pair  $g(r)$  results both showed initial peaks of 1.2–2.3 times the average concentration. Benzoquinoline prefers other benzoquinoline [ $g(r)$  peak up to 2.3]; ethylbenzothiophene shows a weaker self-preference [ $g(r)$  peak up to 1.4]; and dimethylnaphthalene is in between [ $g(r)$  peak between 1.5 and 2]. These indicate that preferential packing can occur in the simulations.

The implication for asphalts is that further investigations are needed to explain the chemical environment that surrounds each asphaltene molecule. One possibility is that other molecules are better representations of resins for use in model asphalts; considering larger ring sizes in model resins could provide an important comparison. Another is that the in-plane size of an asphaltene molecule excludes resins from many locations near the center of mass, making the average concentration in a small spherical shell a less effective measure of the local environment. Understanding the molecule ordering within the system could be a useful prerequisite for effectively altering the contributions of asphaltene molecules to mechanical properties, such as viscosity and complex modulus.

Adding a polystyrene chain to the system had little effect on resin packing. The radial distribution function peak positions for small-molecule pairs, such as dimethylnaphthalene, benzoquinoline, and ethylbenzothiophene, remained similar after adding one polymer. Lower temperatures tended to display higher peaks. Intermolecular orientation between those molecules essentially did not change after adding one polymer. In total, polystyrene did not induce changes in ordering among resin compounds. Single-molecule dynamics slowed, as shown by lower diffusion coefficients.

The asphaltene–asphaltene  $g(r)$  and orientation results indicate that different chemistries and polarities in the resin and maltene can affect the ways that asphaltenes pack in model asphalts. In the more polar environment of the model AAA-1 system, neighboring asphaltenes packed over a more narrow range of angles (Figure 12) than in the less polar ternary asphaltene2 system (Figure S6 in the Supporting Information). Distances between asphaltene centers of mass (Figure 8 and Figure S1 in the Supporting Information) also differed between the two systems. The implication is that resin and maltene may implicitly affect the properties of asphalt systems under stress. A difference in molecule separation and orientation can modify the extent to which shear and normal forces are transmitted from one asphaltene molecule to another. For a given macro-scale displacement, different thicknesses of resin and maltene between asphaltene molecules correspond to different shear forces, due to force transmission across a lower viscosity medium. Real asphalts with the same total asphaltene content may potentially behave differently because of different contributions from the resin and maltene fractions.

The density results here provide guidance toward the design of new model asphalts. The higher predicted densities of the original and polymer-modified AAA-1 systems are closer to experimental values for SHRP core asphalts<sup>45</sup> than those for original and polymer-modified ternary asphaltene2 systems in the same temperature range. Initially, the asphaltene2-based system was designed on the basis of a detailed analysis of vacuum residue,<sup>12,13</sup> while the AAA-1 system was targeted toward SHRP AAA-1 asphalt. The elemental composition and mass ratio of components for vacuum residue and SHRP AAA-1 core asphalt are different. The vacuum residue contained 70+% of oils,<sup>12</sup> while SHRP core asphalts typically contain less;<sup>33</sup> this likely leads to a lower density for vacuum residue. Using a more asphalt-specific speciation in the molecular simulation increased the density but not enough. Additional heteroatoms and higher resin molecular weights are required to reach a density even closer to that of real asphalts. Heteroatoms provide more mass per volume, while higher molecular-weight resin decreases the number of chain ends and their accompanying free volume.

Despite the better speciation of the AAA-1 model asphalt, its high-temperature viscosity is low and relaxation time results<sup>49</sup> suggest that it models room-temperature viscosity of asphalt poorly. We conclude that a reasonable bulk modulus value does not indicate that all mechanical properties will take on values comparable to those of real asphalts. While bulk modulus is predicted to change little with temperature, the viscosity can be expected to change dramatically, on the basis of single-molecule rotational relaxation time.<sup>18</sup>

Precision of the results here can be interpreted in terms of asphaltene rotational relaxation time. At the highest temperature (443.15 K), the relaxation time for asphaltene2 molecules in the ternary asphaltene2 system is 1.2 ns.<sup>18</sup> 5 ns is potentially long enough to obtain a well-sampled average asphaltene2 intermolecular orientation. This is consistent with the finding that different initial configurations, different sampling methods, and different asphalt systems do not change the packing angle between closest asphaltene2 pairs at 443.15 K. In addition, density and diffusion coefficient results obtained from different initial configurations were self-consistent, while expansion coefficient and isothermal compressibility results were similar. We have found that asphaltene2 molecules in AAA-1 systems relax faster than 1 ns at 333 K and above.<sup>49</sup> Thus, we expect better sampling of average orientation results in AAA-1 than in ternary asphaltene2. Decreased noise in the intermolecular orientation (Figure 12 and Figure S6 in the Supporting Information) is consistent with this expectation. In the polymer-modified ternary asphaltene2 system at 443 K, packing distributions of asphaltene2 molecules depended upon initial configuration, because of poor statistics. In the polymer-modified AAA-1 system, the packing between asphaltene molecules remained similar. At 400 K, the asphaltene relaxation time in ternary asphaltene2 can reach 4 ns.<sup>18</sup> Observing its orientation over 5 ns samples only an intermediate extent of overall relaxation, and its orientation results changed after a longer simulation time, compared to our earlier work. At lower temperatures, the simulation time did not reach the asphaltene2 molecule rotational relaxation time. Those orientation results are more susceptible to effects of initial molecule positions and orientations. The increased number of asphaltene molecules in AAA-1 systems (9) compared to ternary asphaltene2 systems (5) improved the statistics [by  $((9 \times 8/2)/(5 \times 4/2))^{1/2} \approx 1.9$ ] but not enough to eliminate some uncertainties.

An open question concerns the structure and orientation results that would be obtained for asphaltene molecules in model asphalts, with and without polymer, in the thermodynamic limit. We hypothesize that the structural similarities between resin molecules and asphaltene molecules enable the consistent intermolecular orientation and radial distribution function results of resin molecules to provide guidance on asphaltene2 molecules. Following this logic, we anticipate that the intermolecular orientation of asphaltene2 molecules would also retain similar packing angles as the temperature decreases, if the simulation time could be long enough (for example, several multiples of relaxation time). The radial distribution functions at low temperatures would also then be likely to keep almost the same first peak position, with a higher peak.

## Conclusions

A new model asphalt has been proposed to improve agreement between the physical and mechanical properties of model

and real asphalts. The six-component AAA-1 system has an elemental composition very close to that of SHRP AAA-1 asphalt. Estimated solubility parameters indicate a better match to those of real asphalts<sup>21</sup> compared to those in our prior work.<sup>14</sup> The ability of molecular simulation to describe polymer modification was tested by adding one polystyrene chain into the ternary asphaltene2 and AAA-1 systems. After one polymer was added, the density of systems increased, while bulk modulus, isothermal compressibility, and expansion coefficient had less temperature dependence than without a polymer. Those property changes showed a tendency toward more desirable asphalt behavior. Self-diffusion coefficients decreased with molecule size and decreasing temperature. Diffusion slowed in the presence of a polymer chain, with larger molecules slowing more than smaller molecules. Viscosity increased in the presence of a polymer but could not be quantified.

To analyze molecule packing and orientation, we calculated the radial distribution function  $g(r)$  for pairs of the same and different molecules. Asphaltene2  $g(r)$  results indicate that nearest neighbor (first peak) positions changed with temperature and also with adding one polymer in both the ternary asphaltene2 and AAA-1 systems. For small molecules, radial distribution functions kept almost the same shape at different temperatures and in the presence of one polymer. The first peak positions remained similar. Radial distribution function between pairs of different kinds of molecules also kept similar shapes, and their first peak positions were very close, at different temperatures and with or without a polymer. A surprising finding was a depletion of resin-like molecules in the region near the center of an asphaltene, compared to their average concentration.

Intramolecular orientation was analyzed for each multi-ring aromatic component in model asphalt systems. The higher the temperature, the wider the distribution of folding angles between aromatic rings in one molecule. The distribution remained essentially the same after adding one polymer.

Using first peak positions from radial distribution functions, orientations between molecule pairs were analyzed. We found that asphaltene2 molecules prefer to pack toward parallel at 443.15 K in the ternary asphaltene2 system. Packing was consistent among different ensembles and initial conditions, although angles moved away from parallel after adding one polymer. At lower temperatures, because of the much shorter simulation time compared to that required to surpass the rotational relaxation time of asphaltene, the intermolecular orientation changed by various extents after longer simulation times and also after adding one polymer. In the AAA-1 system, packing between asphaltene2 molecules tended toward parallel. After one polymer was added, intermolecular orientation changed by different amounts at different temperatures. For dimethylnaphthalene, benzoquinoline, and ethylbenzothiophene molecules, intermolecular orientation changed little at different temperatures, even after adding one polymer. Benzoquinoline molecule pairs packed close to a random distribution, with a larger than random number of molecules packed near parallel in the range of the first peak position. Dimethylnaphthalene and ethylbenzothiophene molecules packed even closer to a random distribution in the range of the first peak position. Asphaltene2 and benzoquinoline pairs preferred to pack toward parallel at different temperatures, even after adding one polymer. Asphaltene2 and ethylbenzothiophene molecules also preferred to pack toward parallel at four different temperatures in original and polymer-modified systems. Pairs of benzoquinoline and ethylbenzothiophene molecules packed in a distribution similar to benzoquinoline pairs: close to random in the first peak position

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distance range, with a small amount of molecules packed parallel, in original and polymer-modified systems.

In total, adding polymer did not change the radial distribution function  $g(r)$  or the packing (intermolecular orientation) of small molecules dimethylnaphthalene, benzoquinoline, and ethylbenzothiophene. It did not change the intramolecular orientation of molecules, which is primarily determined by the force field. It did not change the packing and radial distribution between different kinds of molecule pairs. The presence of a polymer chain did change the distribution of asphaltene<sub>2</sub> molecules and intermolecular orientation at low temperatures in both kinds of systems. It increased the density of the system, decreased the temperature dependence of modulus and isothermal compressibility, and decreased the diffusion coefficients of all components. The increase in modulus and slowdown in single-molecule

dynamics are consistent with the behavior of real polymer-modified asphalt systems.

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**Supporting Information Available:** Discussions and plots of  $g(r)$  and intra- and intermolecular orientations for asphaltene–asphaltene, asphaltene–(model resin), and (model resin)–(model resin) pairs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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