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Tack behaviours of *p*-*t*-octylphenol formaldehyde resin with rubber using a molecular simulation

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Tack behaviours of *p*-*t*-octylphenol formaldehyde resin with rubbers, such as *cis*-1,4-polyisoprene and *cis*-1,4-polybutadiene, were studied using molecular mechanics and dynamics. The structures of *p*-*t*-octylphenol formaldehyde resin were found to be that hydroxyl groups cluster in the centre of the molecule by intramolecular hydrogen bondings and the *t*-octyl groups are extended out. The tack of *p*-*t*-octylphenol formaldehyde resin with rubber is formed by intermolecular non-bond interactions between the *t*-octyl groups of the resin and rubber chains. The interaction energies between one *p*-*t*-octylphenol formaldehyde resin molecule and two rubber molecules were calculated to investigate the effect of the molecular size of the resin on the tack strength. The interaction energies for the dimer and the trimer of *p*-*t*-octylphenol formaldehyde resin are greater than -20 kcal/mol while those for the tetramer–decamer are less than -40 kcal/mol. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: tack; molecular simulation; interaction)

INTRODUCTION

'Tack' is the ability of two materials to resist separation after bringing their surfaces into contact for a short time under a light pressure[1,2]. Compounded rubber stocks used in tyre manufacture must have a certain level of tack and green strength. Tack is important since the components of green tyres must hold together until moulding. Green strength is needed so that the uncured tyres will not creep and hence distort excessively before moulding or tear during the expansion that occurs upon moulding. It is generally believed that tack is determined by three fundamental processes[1]. First, the polymer chains from each surface must come into intimate molecular contact. This requires viscous flow of a material near the interface and displacement of surface impurities. Next, polymer chains must interdiffuse across the interface and become entangled with one another. Finally, the material must have a high cohesive strength so that the bond is able to resist separation.

The tackifier resins used in pressure-sensitive adhesives fall under three main chemical types, namely rosin derivatives, terpene resins (oligomers of α- and β-pinenes), and petroleum resins (oligomers of unsaturated petroleum fractions)[3]. In the early days of manufacturing rubber articles, natural rubber (NR) was primarily used with coumarone–indene resins as processing aids and plasticizers. These types of hydrocarbon resins provided adequate building tack with inherently tacky NR. For synthetic elastomers such as styrene butadiene rubber (SBR), hydrocarbon resins are not adequate tackifiers. Compounds with these elastomers require the addition of *para*-alkylated novolak resins to impart tack. With these phenolic tackifiers, two methods have come into common practice. In the first, the phenolic resin is compounded directly into the stock, while the second employs phenolic resin in ply-splicing cements[4].

Tackification mechanisms have been explored by several groups[4–9], but have not yet been clearly elucidated. One theory states that a tackifier reduces viscosity and thereby facilitates molecular contact, and thus tack. An extension of this theory proposes that the tackifier not only enhances molecular contact through increased flow but also maintains or improves green strength (cohesive strength). Another proposed mechanism is only applicable to polar tackifiers such as phenolic resins. It is hypothesized that polar tackifiers concentrate near the surface to provide strong interfacial interactions such as hydrogen bonding.

In the present work, the tack behaviours of *p*-*t*-octylphenol formaldehyde resin (POP) were studied by molecular mechanics and dynamics. Computer modelling enables us to obtain atomic scale information on the shape and motion of individual chains surrounded by their neighbours[10]. This method can therefore lead us to the evaluation of microscopic properties that cannot be probed by any experimental techniques. Its spatial and temporal resolutions can potentially far exceed the best of any instruments that are currently available. We focussed on the three dimensional structures of the monomer–decamer of POP and the interactions between POP and rubber chains such as *cis*-1,4-polyisoprene (IR) and *cis*-1,4-polybutadiene (BR).

MODELLING AND CALCULATIONS

The classical force field calculation was used in order to obtain the molecular structures. The potential energy

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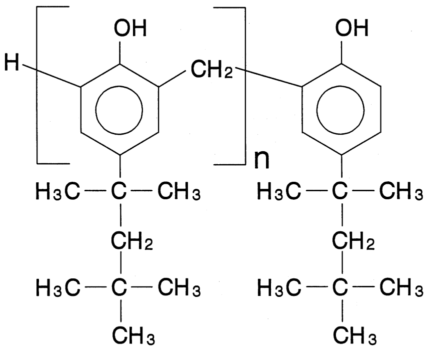

Figure 1 General formula of *p*-*t*-octylphenol formaldehyde resin

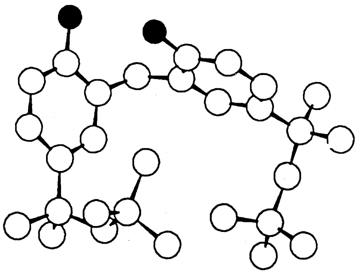

Figure 2 Energy-minimized skeletal structure of *p*-*t*-octylphenol formaldehyde resin dimer. Closed circles represent oxygen atoms

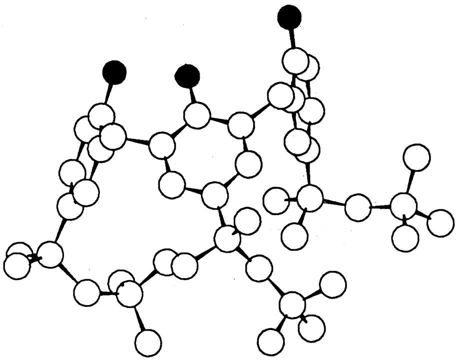

Figure 3 Energy-minimized skeletal structure of *p*-*t*-octylphenol formaldehyde resin trimer. Closed circles represent oxygen atoms

function adopted in the simulations can be divided into several specific energetic contributions which are stretching, bending, torsion, inversion, Coulombic, and van der Waals energy as in the following equation:

$$E = E_{\mathrm{s}} + E_{\mathrm{b}} + E_{\mathrm{t}} + E_{\mathrm{i}} + E_{\mathrm{c}} + E_{\mathrm{v}}. \tag{1}$$

Each energy term has been well parameterized so that the calculated energy and frequencies can agree with the experiments. We used one of the parameter sets, the CFF91 force field[11,12]. The CFF91 force field employs a quartic polynomial for bond stretching and angle bending and a three-term Fourier expansion for torsions. The out-of-plane coordinate is defined according to Wilson *et al.*[13]. All the cross terms up to the third order that have been found to be important are also included. The electrostatic interaction is given by the Coulombic interaction term. The van der Waals interactions use an inverse 9th-power term for the repulsive part rather than the more customary 12th-power term. 10.0 Å of potential cutoff distance and distance dependent dielectric constants are employed.

POP used in tyre manufacturing is a mixture containing monomer, oligomer and polymer. Our calculational targets of POP were monomer to decamer. The initial structures of those molecules were generated by the *Insight II* package. 2-methyl-4-*t*-octylphenol was used as the repeat unit. The input molecules of POP were constructed by linking the repeat unit by a head-to-tail orientation. The general formula of POP is shown in *Figure 1*. $n = 0, 1, ..., 9$ in *Figure 1* indicates monomer, dimer, ..., decamer, respectively. Interaction energies between one POP molecule and two rubber chains were calculated as the tack strength. The rubbers employed in these calculations were IR and BR. The rubber chains of IR and BR were composed of 50 repeat units. IR and BR were constructed by linking the repeat unit by a head-to-tail orientation and an all-*cis* configuration was employed.

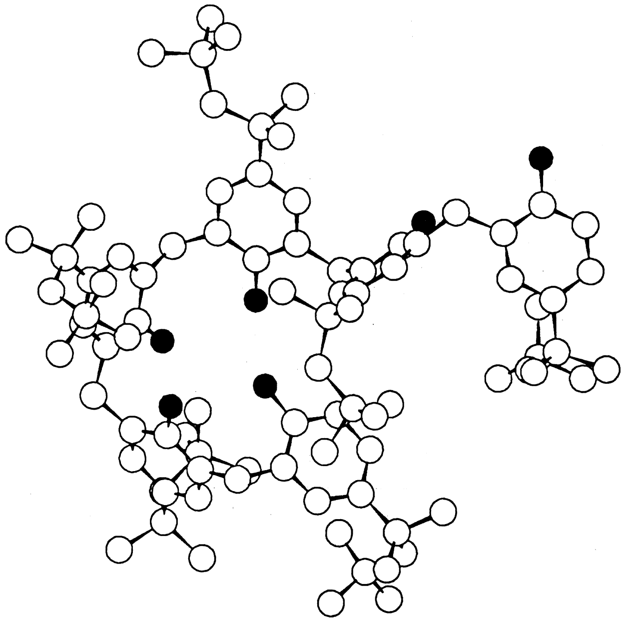

Figure 4 Energy-minimized skeletal structure of *p*-*t*-octylphenol formaldehyde resin hexamer. Closed circles represent oxygen atoms

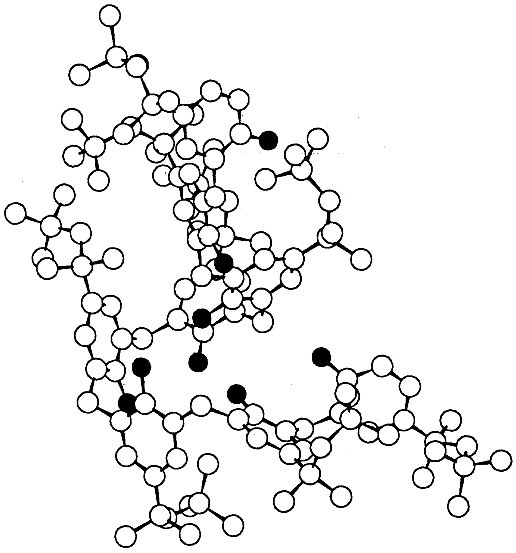

Figure 5 Energy-minimized skeletal structure of *p*-*t*-octylphenol formaldehyde resin octamer. Closed circles represent oxygen atoms

The energy-minimized structures of the monomer–decamer of POP were the lowest energetic conformations obtained by a conformational search. The conformational

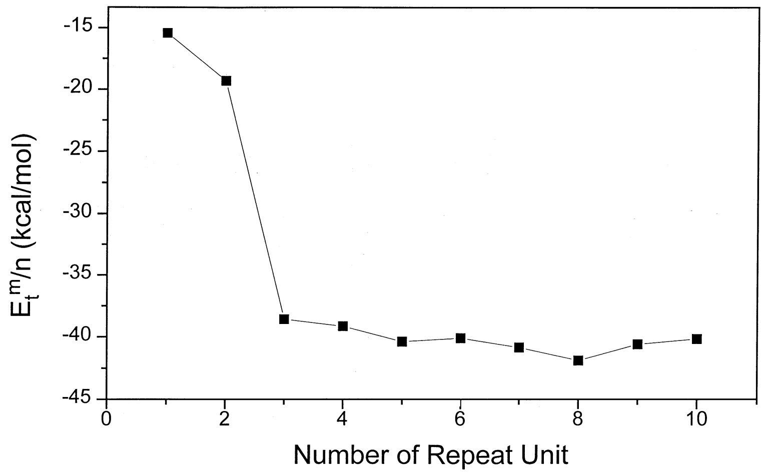

Figure 6 Variation of total energies per repeat unit of energy-minimized structures of *p*-*t*-octylphenol formaldehyde resin, E_t^m/n, depending on POP size

Table 1 Total energies of *p*-*t*-octylphenol formaldehyde resin with energy-minimized structures, E_t^m, obtained from conformational search

Size of molecule	Total energy (kcal/mol)
monomer	−15.44
dimer	−38.64
trimer	−115.74
tetramer	−156.64
pentamer	−201.93
hexamer	−240.62
heptamer	−285.94
octamer	−335.11
nonamer	−365.18
decamer	−401.62

search was carried out by the annealing technique consisting of 50 ps molecular dynamics at 900 K and 100 times sampling for further minimizations. In order that the energy at the start of the minimization is sufficiently higher than that of the potential energy surface, the initial molecular dynamics for the minimization was performed at 900 K. With the lowest energetic conformation among the 100 conformers, 100 ps of molecular dynamic simulations were performed at 273, 303, and 353 K to investigate thermal stabilities of POP. At each temperature, the average total energy of each POP was obtained by averaging the 100 ps dynamic fluctuations.

In order to calculate the tack strength, we generated the assembly of POP and two rubber chains for each POP molecule and used restraint dynamics. The constraint condition was an artificial bonding potential possessing 1000 N/cm of force constant and 5 Å of equilibrium distance between the two methyl groups of POP and any carbons of the two rubber chains. Under the constraint, the molecular dynamics was carried out on the assemblies at 900 K during 150 ps. The intermediate structure at every 5 ps was put into the minimization to obtain the 30 conformers of the assembly system. Similarly to the single POP molecule, the lowest energetic conformation among the 30 conformers was chosen to carry out further simulations. The molecular dynamics simulation was repeated with the lowest energetic conformation at 900 K after removing the constraint condition during 10 ps. 10 conformers were sampled at every 1 ps and minimized to obtain the most energetically favourable structure. The non-bond interactions such as the van der Waals and electrostatic interactions between one POP molecule and two rubber chains in the most stable conformation were calculated. The interaction energies obtained by the above process on each assembly were used as the tack strength.

RESULTS AND DISCUSSION

Structural characteristics of POP

Three dimensional structures of the POP monomer–decamer were calculated by molecular mechanics to elucidate its role as a tackifier. The energy-minimized structures of the dimer, trimer, hexamer, and octamer of POP obtained from conformational analysis are shown in *Figures 2*, *3*, *4* and *5*, respectively. The structures are displayed with carbon and oxygen atoms only for clarity. Closed circles represent oxygen atoms. The structural characteristic of POP is that hydroxyl groups cluster in the centre of the molecule by intramolecular hydrogen bondings between the hydroxyl groups of adjacent phenolic units and the *t*-octyl groups are extended out. Intramolecular hydrogen bonds of phenol novolak resins have been studied by several groups[14–18]. Structures of phenol novolak oligomers, in which intramolecular hydrogen bonds were formed between all hydroxyl groups of adjacent phenolic units, have been determined by X-ray crystallography[14,15] and molecular mechanics calculations[16,18]. Paulus and Böhmer[15] studied crystal structures of *p*-alkylphenol formaldehyde resin tetramer with hydrogen, methyl, and *t*-butyl as the *p*-substituent by single crystal X-ray analysis and found intramolecular hydrogen bonds between all hydroxyl groups of adjacent phenolic units. Templeton *et al.*[16] studied intramolecular hydrogen bonded phenol formaldehyde resin dimer–tetramer by molecular mechanics energy minimization techniques and compared them with X-ray crystallography data. They found that the calculated results agree well with X-ray crystallography data. From the calculated results of *p*-*t*-butylphenol formaldehyde novolak resin, the hydroxyl groups of *p*-*t*-butylphenols cluster in the centre of the molecule by intramolecular hydrogen bonds of adjacent hydroxyl groups[18].

By increasing the molecular size of POP, the total energy of the energy-minimized structure, E_t^m, decreases as listed in *Table 1*. Particularly, when the POP size is equal to or larger than the trimer, the total energy decreases remarkably. E_t^m of the monomer and the dimer are −15.44 and −38.64 kcal/mol, respectively, while that of the trimer

Table 2 Average total energies of *p*-*t*-octylphenolformaldehyde resin, $\langle E_t \rangle$, at 273, 303, and 353 Kobtained from molecular dynamic fluctuations. Units are kcal/mol

Temperature	273 K	303 K	353 K
dimer	22.26	29.34	40.86
trimer	−31.06	−18.28	−1.99
tetramer	−43.02	−25.48	−2.48
pentamer	−61.97	−40.32	−5.13
hexamer	−74.53	−52.95	−17.26
heptamer	−91.62	−62.77	−22.56
octamer	−106.78	−78.87	−37.98
nonamer	−120.44	−92.08	−43.53
decamer	−124.80	−87.63	−33.95

Table 3 Average total energy of *p*-*t*-octylphenolformaldehyde resin per unit temperature attemperature ranges of 273–303 K and 303–353 K, $\langle E_t \rangle / T$. Units are kcal/mol·K

Temperature range	273–303 K	303–353 K
dimer	0.24	0.23
trimer	0.43	0.33
tetramer	0.58	0.45
pentamer	0.72	0.70
hexamer	0.72	0.71
heptamer	0.96	0.80
octamer	0.93	0.82
nonamer	0.95	0.97
decamer	1.24	1.07

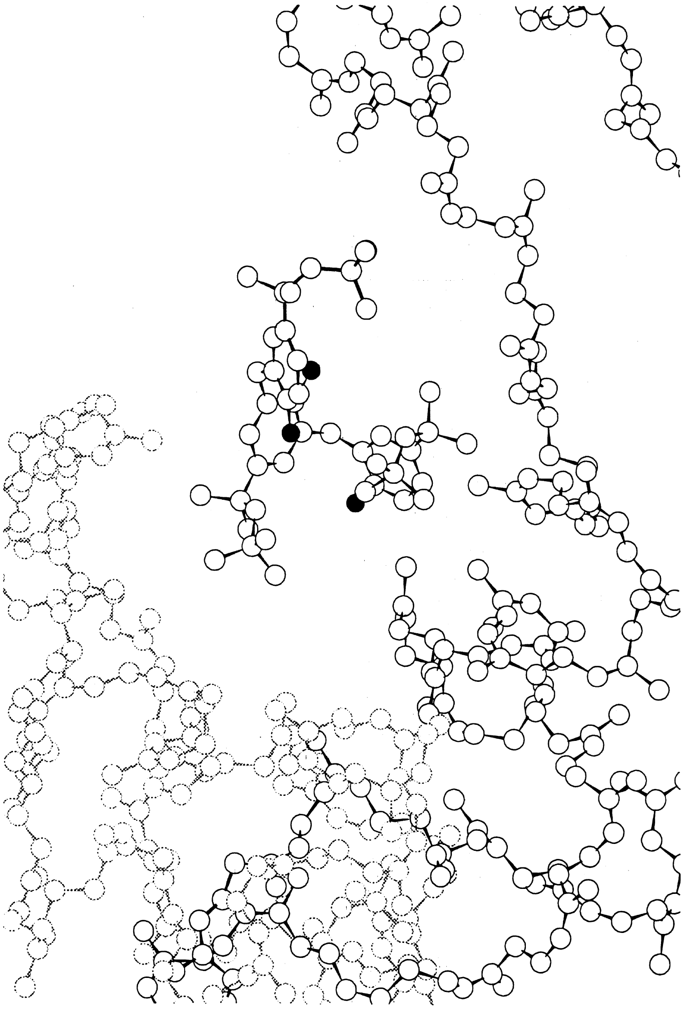

Figure 7 Interactive structure of one POP trimer with two *cis*-1,4-polyisoprene chains. Closed circles represent oxygen of *p*-*t*-octylphenol formaldehyde resin

is −115.74 kcal/mol. The total energies per repeat unit of the POP monomer–decamer of the energy-minimized structure were calculated to investigate the stabilities of POP upon its size in detail. The total energies per repeat unit of the energy-minimized structure, E_t^m/n, were obtained by dividing E_t^m of POP by n, the number of repeat units. Variation of E_t^m/n with POP size is demonstrated in *Figure 6*. E_t^m/n strikingly decrease from −19.32 to −38.58 kcal/mol as the POP size increases from dimer to trimer, while they slightly decrease from −38.58 to −41.89 kcal/mol by increasing the POP size from trimer to octamer. However, with an increase of the POP size from octamer to decamer, E_t^m/n slightly increase from −41.89 to −40.16 kcal/mol. The jump of E_t^m/n between dimer and trimer can be considered to be due to the increases of intramolecular non-bond interactions, hydrogen bonds between the hydroxyl groups and van der Waals interactions between the *t*-octyl groups of adjacent phenolic units. There are three hydroxyl groups (A, B, and C) and three *t*-octyl groups in the trimer, while there are two hydroxyl groups (A and B) and two *t*-octyl groups in the dimer. The number of possible hydrogen bonds in the POP dimer is one (A–B), while that in the POP trimer is three (A–B, B–C, and C–A). Thus, the intramolecular non-bond interactions of the trimer may be stronger than those of the dimer by at least twice. The van der Waals interactions between *t*-octyl

Table 4 Interaction energies between one *p*-*t*-octylphenol formaldehyde-resin molecule and two rubber chains. Units are kcal/mol

Rubber	*cis*-1,4-polyisoprene	*cis*-1,4-polybutadiene
dimer	−18.41	−16.68
trimer	−19.90	−18.05
tetramer	−45.62	−43.43
pentamer	−41.85	−55.47
hexamer	−42.50	−55.59
heptamer	−48.01	−56.06
octamer	−55.60	−42.44
nonamer	−43.07	−40.32
decamer	−54.82	−52.63

groups may be notably increased since the distance between *para*-carbons of adjacent phenolic units, r_{cc}, of the trimer is shorter than that of the dimer by 0.20 Å. r_{cc} of the dimer is 6.19 Å (*Figure 2*), while the average r_{cc} of the trimer is 5.99 Å (*Figure 3*). Regarding the increase of POP size beyond the trimer, E_t^m decreases by about 40 kcal/mol per single repeat unit. As the POP size increases from trimer to octamer, E_t^m/n slightly decreases. This can be considered to be due to the increase of the intramolecular non-bond interactions. But, on the other hand, E_t^m/n is slightly increased by the increase of POP size from octamer to decamer. This may be because of the repulsions between the *t*-octyl groups by a steric complication.

Thermal stabilities

Average total energies obtained by averaging the 100 ps dynamic fluctuation, $\langle E_t \rangle$, were calculated at 273, 303, and 353 K to investigate thermal stabilities of POP. The average total energies are summarized in *Table 2*. $\langle E_t \rangle$ at 273, 303, and 353 K decrease with increasing size of the POP molecule. But $\langle E_t \rangle$ of the decamer were higher than those of the nonamer at 303 and 353 K. $\langle E_t \rangle$ also strikingly decrease with an increase in the POP size from dimer to trimer similarly to E_t^m. The average total energies per repeat unit, $\langle E_t \rangle/n$, were calculated from *Table 2* to investigate thermal stabilities of POP depending on POP size and temperature in detail. By increasing the POP size, $\langle E_t \rangle/n$ decrease, except for the decamer, at temperatures of 273, 303, and 353 K. $\langle E_t \rangle/n$ of the nonamer were −13.38, −10.23, and −4.84 kcal/mol at 273, 303, and 353 K, respectively, while those of the decamer were −12.48, −8.76, and −3.40 kcal/mol, respectively. $\langle E_t \rangle/n$ decrease from −10.35 to −13.38, from −6.09 to −10.23, and from −0.63 to −4.84 kcal/mol at 273, 303, and 353 K, respectively, by increasing the POP size from trimer to nonamer. Absolute values of $\langle E_t \rangle/n$ at low temperatures are higher than those at high temperatures.

The average total energies per unit temperature of POP at temperature ranges of 273–303 and 303–353 K, $\langle E_t \rangle/T$, were calculated from *Table 2* to investigate increments of $\langle E_t \rangle$ depending on temperature. $\langle E_t \rangle/T$ were obtained by dividing the $\langle E_t \rangle$ difference between two temperatures by the temperature difference. $\langle E_t \rangle/T$ are summarized in *Table 3*. The overall trends for $\langle E_t \rangle/T$ are that the values of $\langle E_t \rangle/T$ increase with increasing POP size and $\langle E_t \rangle/T$ at the low temperature range of 273–303 K are higher than those at the high temperature range of 303–353 K. These trends may appear because of the increase of degrees of freedom with an increase of the POP size. $\langle E_t \rangle/T$ of the decamer at 303 and 353 K are higher than the nonamer while at 273 K they are lower than the nonamer.

Interactions between POP and rubbers

We constructed the assembly system with two rubber chains and one POP molecule to calculate tack behaviour and strength. The intermolecular interaction structures with one POP molecule and two rubber chains are so complicated that the structures with the POP trimer and the hexamer representatively are displayed. *Figure 7* shows the interactive structure of the assembly of one POP trimer and two IR chains. One can see the intermolecular van der Waals interactions between the *t*-octyl groups of the POP trimer and the IR chains from *Figure 7*. *Figure 8* shows the interactive structure of the assembly of one POP hexamer and two IR chains. The assembly structures of one POP molecule and two rubber chains of IR and BR have common characteristics in which the hydroxyl groups of POP are located far from the rubber chains and cluster in the centre of POP while the *t*-octyl groups of POP are located near the rubber chains and interact with them. Thus, this leads to a conclusion that the tack is formed mainly by intermolecular van der Waals interactions between the *t*-octyl groups of POP and the rubber chains.

Specific differences of tack behaviour and strength between IR and BR were not found. In both IR and BR, the tack is formed by intermolecular interactions between POP and rubber chains, and the values of the interaction energies are similar when the POP size is the same. The absolute values of interaction energies for the dimer and the trimer were less than 20 kcal/mol in both IR and BR, while those for POP equal to or beyond the tetramer were greater than 40 kcal/mol as shown in *Table 4*. The interaction energies decrease remarkably by increasing the POP size from trimer to tetramer. This can be explained because the size of the POP tetramer is large enough to cover two sides composed by two rubber chains but that of the POP trimer is not enough to cover the two sides. Since the tack is a phenomenon occurring between two surfaces, the tackifier, POP, should have a size large enough to interact with two surfaces. Thus, one can expect that the interaction energies decrease by increasing the POP size. But the interaction energies for the tetramer–decamer obtained from calculations do not show the specific trends with the increase of POP size as listed in *Table 4*. This is because only two rubber chains are considered in the calculation. In this study, we constructed the system composed of two rubber chains as two rubber surfaces. Thus, the larger the POP size is, the more the parts not interacting with rubber chains there are. Assemblies with many rubber chains or periodic boundary conditions are so complicated and time-consuming that we used the assembly with one POP molecule and two rubber chains.

Effects of kinds of *p*-alkylphenol formaldehyde novolak resin and its molecular weights on tack have been studied by several groups[4,9,19], but the reasons for the effects were not explained. The reasons can be stated from the present study. Magnus and Hamed[4] studied the difference of tack strength between *p*-*t*-octylphenol monomer and *p*-*t*-octylphenol resin. They reported that cohesive strengths of IR compounds containing 5 phr of *p*-*t*-octylphenol monomer and *p*-*t*-octylphenol resin, Dyphene 8318, were 2.45 and 3.40 kN/m, respectively. Dyphene 8318 is a mixture containing monomer to polymer of POP. Since the tack of POP becomes strong when the POP size is equal to or larger than the tetramer, the tack strength of an IR compound containing *p*-*t*-octylphenol monomer is weaker than that containing *p*-*t*-octylphenol resin. Wolny and Lamb[19]

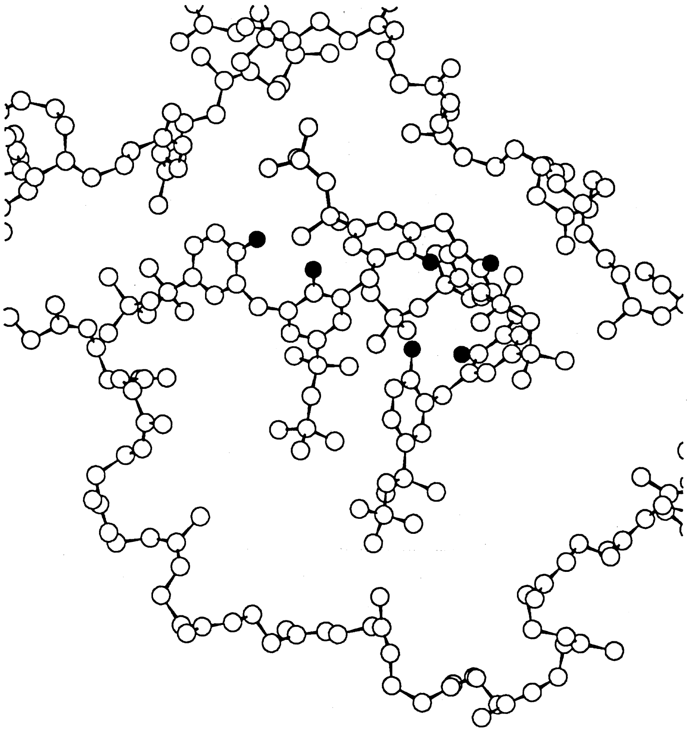

Figure 8 Interactive structure of one POP hexamer with two *cis*-1,4-polyisoprene chains. Closed circles represent oxygen of *p*-*t*-octylphenol formaldehyde resin

studied the effect of a molecular weight distribution of a tackifier on tack. They reported that the tack strength of *p*-*t*-butylphenol novolaks with molecular weight range of 480–635, corresponding to the tetramer, is stronger than that of 430–515, corresponding to the trimer, by about five times. As discussed above, the tack strength (interaction energy) of the POP notably increases by increasing the POP size from trimer to tetramer.

CONCLUSIONS

The structures of POP show that the hydroxyl groups cluster in the centre of the molecule by intramolecular hydrogen bonds between the hydroxyl groups of adjacent *p*-*t*-octylphenols and the *t*-octyl groups are extended out. When the size of POP is equal to or larger than the trimer, the total energy of the energy-minimized structure, E_t^m, decreases remarkably. This is because of the increase of intramolecular non-bond interactions such as hydrogen bonds and van der Waals interactions between adjacent phenolic units. The average total energies obtained by averaging 100 ps dynamic fluctuations, $\langle E_t \rangle$, at 273, 303, and 353 K decrease by increasing the size of POP. But $\langle E_t \rangle$ of the decamer were higher than the nonamer at 303 and 353 K. It was found that the tack between one POP molecule and two rubber chains is formed mainly by van der Waals interactions between *t*-octyl groups of the POP and the rubber chains. The interaction energies between one POP molecule and two rubber chains strikingly decrease when the POP size is equal to or larger than the tetramer. The interaction energies of the dimer and the trimer are less than -20 kcal/mol, while those for POP equal to or larger than the tetramer are greater than -40 kcal/mol.

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