Influences of Aldehyde Type and *p*-Substituent Type on Structural Characteristics of *p*-Alkylphenol Aldehyde Resins Using a Molecular Simulation

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Received December 29, 1998

Structural characteristics of isotactic *p*-alkylphenol acetaldehyde novolak resins with methyl, *t*-butyl, and *t*-octyl as the *p*-substituent and *p-t*-butylphenol aldehyde novolak resins with methylene, ethylidene, and propylidene as the linkage were calculated using molecular mechanics and molecular dynamics. The five *p*-alkylphenol aldehyde resins were found to have common structural characteristics that hydroxyl groups of the *p*-alkylphenols cluster in the center of the molecule by intramolecular hydrogen bonds of hydroxyl groups of the adjacent *p*-alkylphenols and the alkyl groups are extended out. Distances between oxygen atoms and between *p*-carbon atoms of the adjacent *p*-alkylphenols become longer as the size of the *p*-substituent increases from methyl to *t*-octyl. Bond angles of the linkage built between the adjacent *p*-alkylphenols become wider by increasing the *p*-substituent size and by decreasing the linkage size.

Introduction

Phenolic resins are interesting materials with high thermal stability, excellent resistance to combustion, high dimensional stability, good mechanical properties, and high chemical stability.[1~9] They are produced by the reaction of phenols and aldehydes. Types of phenolic resins are determined by types of used phenols and aldehydes and reaction conditions. Phenolic resins are variously used depending on their types as bonding agents,[10] tackifiers,[9,11] vulcanizing agents,[12] photo resists,[13] and so forth. Alkyl phenol novolak resins are made by reactions of excess alkylphenol with aldehyde in acidic condition. In general, *p-t*-alkylphenol aldehyde novolak resins are used as a tackifier.[11,14]

Structures of phenolic novolak resins were studied using an X-ray crystallography[6,13] and a molecular simulation method[13,15]. Paulus and Böhmer[6] 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 hydroxyl groups of adjacent phenolic units. Templeton and coworkers[13] studied intramolecular hydrogen bonded phenol formaldehyde resin dimer-tetramer by molecular mechanics energy minimization techniques, which was consisted well with X-ray crystallography data. In the previous work,[15] we studied the effect of tacticity (isotactic, syndiotactic, and atactic) on structures of *p-t*-butylphenol acetaldehyde resins and found that the resins with isotactic sequence was be more stable than those with syndiotactic and atactic sequences.

Alkylphenol-aldehyde condensations, performed in different reaction conditions, generally result in the formation of a very complex mixture of oligomeric products. Thus, it is hard to investigate structures of the alkylphenol aldehyde resins experimentally. One can consider that alkylphenol type and aldehyde type of the alkylphenol aldehyde novolak resins affect their structures and properties. In this work, *p*-alkylphenol aldehyde resins with various *p*-substituents and linkage types were studied by molecular mechanics and molecular dynamics. Their structural stabilities depending on types of the *p*-substituent and linkage were studied by conformational search and molecular dynamics were also performed at 303, 373, 473, and 573 K.

Modeling and Calculations

General formulae of *p-t*-butylphenol acetaldehyde resin (BA resin), *p-t*-butylphenol formaldehyde resin (BF resin), *p-t*-butylphenol propionaldehyde resin (BP resin), *p*-methylphenol acetaldehyde resin (MA resin), and *p-t*-octylphenol acetaldehyde resin (OA resin) are shown in Figure 1. All the *p*-alkylphenol aldehyde resins except the BF resin have a tacticity since a carbon atom in the linkage built between *p*-alkylphenols is a chiral center. In this study, only the *p*-alkylphenol aldehyde resins with isotactic sequence were compared.

The initial structures of input molecules were generated by the *Insight II* package of MSI. *o*-Ethyl-*p-t*-butylphenol, *o*-methyl-*p-t*-butylphenol, *o*-propyl-*p-t*-butylphenol, *o*-ethyl-*p*-methylphenol, and *o*-ethyl-*p-t*-octylphenol were used as repeat units for the BA resin, BF resin, BP resin, MA resin, and OA resin, respectively. The input molecules were constructed by linking the repeat unit with head-to-tail orientation. Dimer-decamer of the resins were calculated. Calculations were carried out by molecular mechanics and molecular dynamics with CFF91 force field.[16] 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*.[17] All the cross terms up to the third order that have been found to be important are also included. Coulombic interactions between atomic charges and van der Waals interactions using an inverse 9th-power term for the repulsive part rather than the more customary 12th-power term are
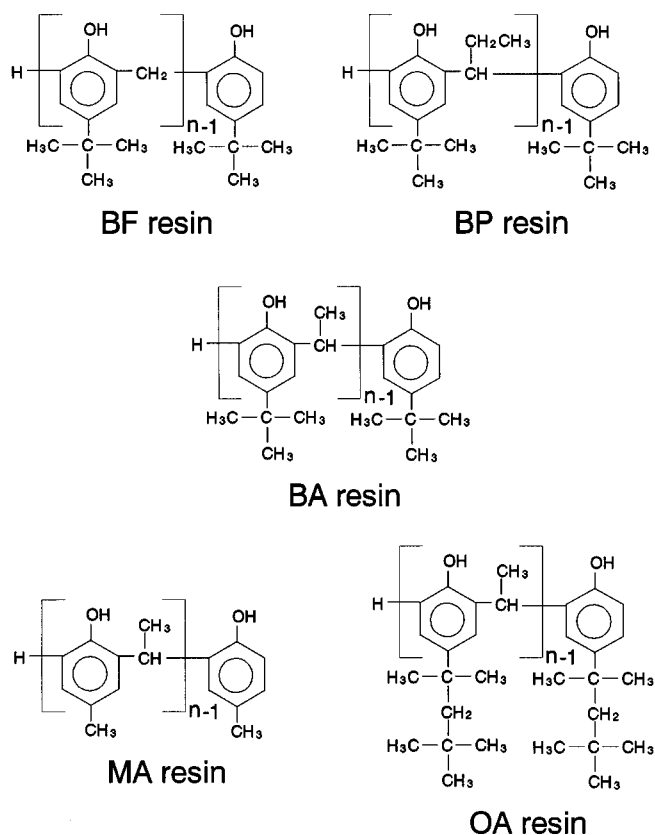
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Figure 1. General formulae of *p*-alkylphenol aldehyde resins.

Figure 2. Skeletal structure of energy-minimized *p-t*-butylphenol acetaldehyde resin (BA resin) hexamer. Closed and open circles stand for oxygen and carbon atoms, respectively.

Figure 3. Skeletal structure of energy-minimized *p-t*-butylphenol formaldehyde resin (BF resin) hexamer. Closed and open circles stand for oxygen and carbon atoms, respectively.

Figure 4. Skeletal structure of energy-minimized *p-t*-butylphenol propionaldehyde resin (BP resin) hexamer. Closed and open circles stand for oxygen and carbon atoms, respectively.

employed. Potential cutoff distance of 10.0 Å and distance dependent dielectric constants were employed.

The energy-minimized structures of the resins were obtained by conformational search. The conformational search was done by the annealing technique consisting of 200 ps molecular dynamics at 900 K and 200 times sampling for further minimizations. With the lowest energetic conformation among 200 conformers, molecular dynamic simulations were performed at 303, 373, 473, and 573 K for 300 ps to investigate stability of the resins. At each temperature, average total energy of the each resin was obtained by averaging the 300 ps dynamic fluctuation.

Results and Discussion

The energy-minimized structures of the *p*-alkylphenol aldehyde resins were obtained from the conformational search. The hexamers were displayed representatively in Figures 2 - 6. Figures 2, 3, 4, 5, and 6 give the skeletal structures of the hexamers of the BA resin, BF resin, BP resin, MA resin, and OA resin, respectively. The molecular structures were displayed with only oxygen and carbon atoms, where closed and open circles stand for oxygen and carbon atoms, respectively. The *p*-alkylphenol aldehyde resins, irrespective of types of the *p*-substituent and linkage, have common structural characteristics that hydroxyl groups cluster in the center of the molecule by intramolecular hydrogen bondings between hydroxyl groups of the adjacent *p*-alkylphenol
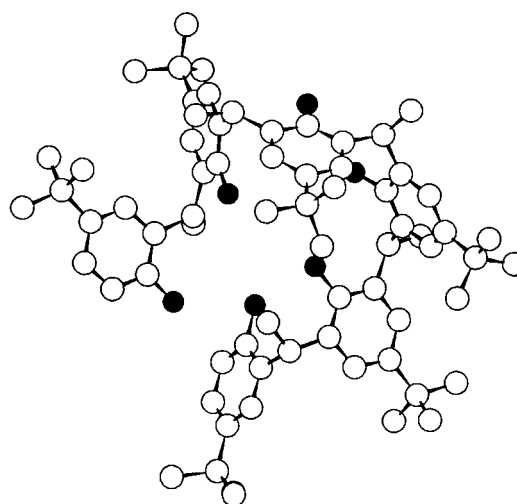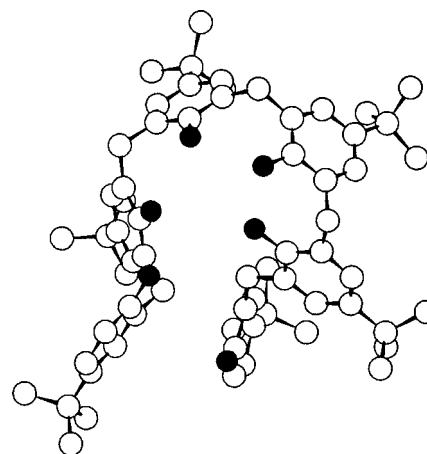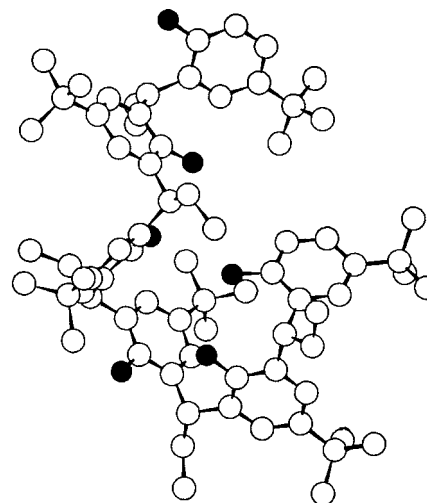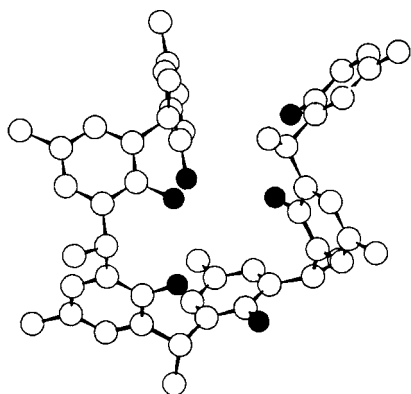
Figure 5. Skeletal structure of energy-minimized *p*-methylphenol acetaldehyde resin (MA resin) hexamer. Closed and open circles stand for oxygen and carbon atoms, respectively.
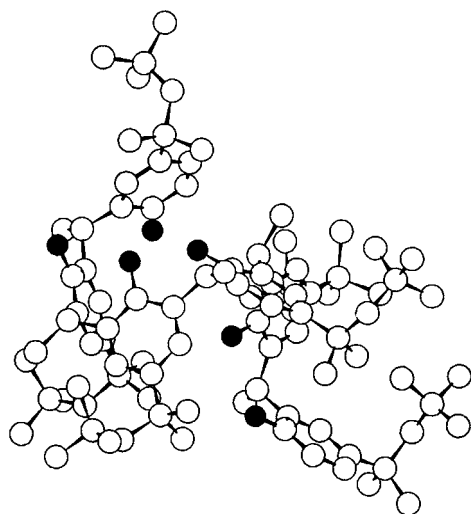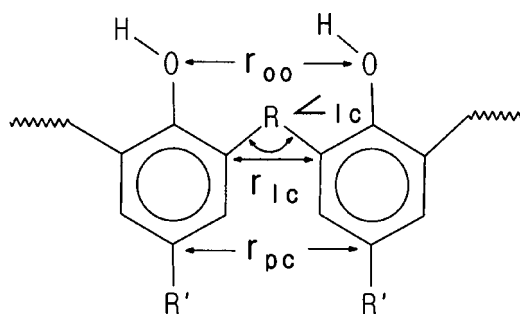

Figure 6. Skeletal structure of energy-minimized *p-t*-octylphenol acetaldehyde resin (OA resin) hexamer. Closed and open circles stand for oxygen and carbon atoms, respectively.

Scheme 1

and the alkyl groups are extended out. The intramolecular hydrogen bonds between hydroxyl groups of the adjacent *p*-alkylphenols of the *p*-alkylphenol aldehyde novolak resins are typical.

In order to investigate the structural difference of the *p*-alkylphenol aldehyde novolak resins depending on types of the linkage and the *p*-substituent, geometries such as bond distances and bond angles in their energy-minimized structures were measured and compared. Since the intramolecular hydrogen bonds between hydroxyl groups of the adjacent *p*-alkylphenols of the resins are typical, the distances between oxygen atoms of the adjacent *p*-alkylphenols, r_{oo}, were measured. When the linkage built between the adjacent *p*-alkylphenols is changed, the angle and length of the linkage ($\angle_{lc}$ and r_{lc}, respectively) will be also changed. There are two important intramolecular interactions in the resins. The one is the intramolecular hydrogen bonds of the hydroxyl groups. The other one is the van der Waals interactions of the *p*-alkyl groups. It can be considered that the van der Waals interactions of the *p*-alkyl groups relate to the distances between *p*-carbon atoms of the adjacent *p*-alkylphenols, r_{pc}. The r_{oo}, r_{pc}, r_{lc}, and $\angle_{lc}$ in the energy-minimized structures of the resins were measured. The definitions of the r_{oo}, r_{pc}, r_{lc}, and $\angle_{lc}$ were demonstrated in Scheme 1. The

Table 1. Distances between oxygen atoms of the adjacent *p*-alkylphenols (r_{oo}) of the energy-minimized *p*-alkylphenol aldehyde resins. Units are Å

Size of Molecule	BA resin	BF resin	BP resin	MA resin	OA resin
dimer	3.94	2.79	2.97	3.00	3.45
trimer	3.06-4.14	2.75-3.14	2.92-3.03	2.96-3.06	3.33-3.04
tetramer	3.65-3.41-2.89	2.76-2.83-2.73	3.13-3.61-3.36	2.86-2.87-2.89	2.87-4.78-3.62
pentamer	3.37-3.68-3.62-3.02	2.61-2.78-2.77-4.13	2.94-3.78-2.87-4.98	2.91-2.96-2.96-3.10	2.98-3.21-3.94-4.03
hexamer	4.70-4.07-3.19-3.43 -2.93	2.78-2.84-2.70-2.89 -4.91	2.88-3.08-4.71-2.90 -4.86	3.02-2.90-3.26-4.43 -2.87	2.92-3.87-2.84-2.96 -5.70
heptamer	3.07-3.74-3.11-3.94 -5.76-3.07	2.80-2.70-2.65-2.68 -2.67-4.89	2.85-2.98-2.85-4.42 -4.35-4.15	3.11-2.86-3.24-2.81 -5.40-3.32	2.84-4.03-5.81-4.37 -2.93-3.57
octamer	3.13-3.85-3.21-3.16 -3.87-4.10-3.18	2.87-2.97-2.69-4.79 -3.45-2.65-3.40	2.92-5.89-2.90-3.19 -3.14-3.54-3.51	3.21-3.43-3.74-3.13 -3.16-2.87-3.11	3.28-4.26-3.27-3.11 -4.38-2.96-4.49
nonamer	3.86-2.86-2.77-2.90 -4.17-4.03-4.20-3.13	2.70-5.72-3.58-3.01 -2.93-4.96-4.24-2.83	3.03-2.91-3.60-3.05 -2.96-4.57-3.10-2.98	2.96-4.28-3.08-3.00 -4.06-3.04-4.38-3.43	4.22-2.91-2.91-5.52 -3.91-4.00-4.41-5.65
decamer	2.94-3.22-4.19-4.23 -4.50-3.23-3.22-3.44 -2.98	2.81-5.78-2.83-5.00 -3.12-2.72-4.10-5.15 -3.19	3.25-3.57-3.69-4.22 -2.82-3.20-2.81-5.63 -4.30	3.38-2.84-2.89-2.90 -3.37-3.73-3.22-3.45 -3.02	2.91-3.91-3.98-3.02 -3.84-5.46-3.05-3.06 -4.01

Table 2. Distances between *para*-carbon atoms of the adjacent *p*-alkylphenols (r_{pc}) of the energy-minimized *p*-alkylphenol aldehyde resins. Units are Å

Size of Molecule	BA resin	BF resin	BP resin	MA resin	OA resin
dimer	7.27	5.95	5.74	5.91	6.05
trimer	5.84-7.20	6.10-6.18	5.68-5.72	5.87-5.91	5.76-6.11
tetramer	6.79-6.17-7.30	6.10-6.15-6.15	5.65-5.75-5.59	5.81-5.77-5.78	6.26-7.06-5.86
pentamer	5.69-5.55-5.83-5.92	6.46-6.30-6.04-6.98	5.74-5.61-5.77-6.75	5.78-5.85-5.82-5.83	5.92-6.03-5.88-5.88
hexamer	6.92-6.30-5.64-5.85 -5.74	6.19-5.53-6.04-5.73 -5.89	5.65-6.02-6.88-5.67 -6.90	6.00-5.78-5.83-7.10 -5.82	5.81-6.22-5.91-5.83 -6.45
heptamer	5.83-7.04-5.74-5.52 -5.59-7.40	5.92-5.62-6.11-6.23 -6.73-6.94	5.95-5.68-5.82-5.70 -5.72-7.22	5.89-5.76-5.84-6.05 -6.44-5.96	6.32-7.15-5.82-7.13 -5.81-5.66
octamer	6.03-7.11-7.14-6.18 -5.91-6.95-6.21	6.05-5.71-5.87-5.48 -5.61-6.19-6.58	5.79-5.54-5.65-5.71 -5.54-6.02-5.82	6.07-5.76-7.22-6.03 -5.94-5.89-5.99	6.11-5.56-7.36-6.00 -5.96-5.96-5.61
nonamer	5.65-5.59-5.58-5.98 -5.58-5.75-5.81-6.67	5.96-6.01-6.05-5.71 -5.85-5.53-7.08-6.02	5.85-5.65-5.70-5.52 -5.67-7.11-5.93-5.75	6.12-5.87-5.76-5.97 -7.16-5.77-5.72-7.30	7.10-5.74-6.36-6.54 -7.29-5.92-7.11-6.25
decamer	5.36-5.82-7.35-5.98 -6.09-7.31-5.54-5.73 -5.78	5.56-5.87-5.73-5.94 -5.70-6.19-6.13-5.76 -6.13	5.61-5.87-7.31-5.77 -6.15-5.45-5.71-6.12 -7.05	5.70-5.74-6.06-5.78 -5.77-7.29-5.61-7.33 -6.05	6.20-7.21-7.21-5.87 -5.85-6.67-5.59-5.81 -5.73

Table 3. Distances between *ortho*-carbon atoms bridged by the linkage (r_{lc}) of the energy-minimized *p*-alkylphenol aldehyde resins. Units are Å

Size of Molecule	BA resin	BF resin	BP resin	MA resin	OA resin
dimer	2.57	2.50	2.49	2.51	2.53
trimer	2.51-2.56	2.52-2.52	2.50-2.49	2.51-2.51	2.51-2.54
tetramer	2.63-2.56-2.62	2.53-2.51-2.53	2.49-2.52-2.49	2.52-2.51-2.51	2.57-2.58-2.55
pentamer	2.52-2.53-2.53-2.50	2.61-2.55-2.52-2.65	2.51-2.51-2.50-2.51	2.51-2.51-2.51-2.51	2.51-2.54-2.56-2.55
hexamer	2.66-2.61-2.57-2.58 -2.56	2.56-2.47-2.55-2.46 -2.58	2.48-2.51-2.53-2.47 -2.53	2.53-2.52-2.53-2.57 -2.52	2.51-2.58-2.53-2.49 -2.54
heptamer	2.49-2.57-2.52-2.54 -2.57-2.51	2.50-2.46-2.53-2.56 -2.62-2.54	2.51-2.47-2.52-2.56 -2.55-2.58	2.51-2.51-2.52-2.53 -2.51-2.52	2.56-2.56-2.55-2.60 -2.52-2.51
octamer	2.55-2.61-2.54-2.56 -2.62-2.56-2.54	2.55-2.49-2.50-2.54 -2.48-2.56-2.56	2.51-2.53-2.49-2.51 -2.49-2.54-2.53	2.52-2.52-2.57-2.52 -2.52-2.52-2.52	2.53-2.54-2.65-2.53 -2.58-2.54-2.60
nonamer	2.53-2.51-2.57-2.52 -2.54-2.56-2.59-2.50	2.51-2.52-2.51-2.50 -2.52-2.54-2.54-2.52	2.51-2.49-2.51-2.49 -2.49-2.59-2.52-2.49	2.54-2.58-2.51-2.53 -2.56-2.51-2.58-2.63	2.55-2.48-2.57-2.55 -2.61-2.57-2.58-2.50
decamer	2.48-2.54-2.53-2.53 -2.58-2.56-2.56-2.51 -2.48	2.44-2.59-2.50-2.63 -2.46-2.55-2.59-2.60 -2.55	2.50-2.52-2.59-2.56 -2.54-2.49-2.48-2.60 -2.52	2.52-2.50-2.53-2.52 -2.55-2.60-2.53-2.62 -2.53	2.55-2.59-2.57-2.55 -2.58-2.55-2.46-2.52 -2.61

results of the measured r_{oo}, r_{pc}, r_{lc}, and $\angle_{lc}$ were summarized in Tables 1, 2, 3, and 4, respectively.

Effect of the linkage type on the resin structure. The BF resin, BA resin, and BP resin have different linkages of methylene, ethylidene, and propylidene, respectively. The linkage size has an order, methylene (-CH$_2$-) < ethylidene (-CH(CH$_3$)-) < propylidene (-CH(CH$_2$CH$_3$)-). The r_{oo} and r_{pc} of the BA resin and BP resin are longer than those of the BF resin. The average r_{oo} from dimer to decamer for the BF resin, BA resin, and BP resin are 3.36, 3.55, and 3.50 Å, respectively. This means that the intramolecular hydrogen bonds between hydroxyl groups of the adjacent *p*-alkylphenols of the BF resin are more favorable than those of the BA resin and BP resin. It may be because the ethylidene and propylidene linkages prevent the intramolecular hydrogen bonds between hydroxyl groups of the adjacent *p-t*-

butylphenols by the steric hindrance. The average r_{pc} from dimer to decamer for the BF resin, BA resin, and BP resin are 5.94, 6.15, and 6.05 Å, respectively. This means that the intramolecular van der Waals interactions between *p-t*-butyl groups of the adjacent *p*-alkylphenols of the BF resin are more favorable than those of the BA resin and BP resin. This may be due to the steric hindrance of the methyl (BA resin) and ethyl groups (BP resin) of the linkage. The r_{oo} and r_{pc} of the BA resin are slightly longer than those of the BP resin although the size of the linkage of the BA resin (ethylidene) is smaller than that of the BP resin (propylidene).

Variation of the r_{lc} of the *p*-alkylphenol aldehyde resin depending on the linkage type do not show a clear trend. The r_{lc} of the BA resin is slightly longer than those of the BF resin and BP resin, while the r_{lc} of the BP resin is slightly shorter than that of the BF resin. The average r_{lc} from dimer

Table 4. Bond angles of the linkages built between the adjacent *p*-alkylphenols ($\angle_{lc}$) of the energy-minimized *p*-alkylphenol aldehyde resins. Units are degree

Size of Molecule	BA resin	BF resin	BP resin	MA resin	OA resin
dimer	113.75	111.35	109.28	110.53	111.10
trimer	110.11-113.24	112.09-111.93	109.42-109.04	110.10-110.10	110.18-112.01
tetramer	116.93-112.79-116.46	112.69-111.04-112.97	108.75-110.47-109.14	110.67-110.02-110.49	114.02-114.16-112.68
pentamer	110.64-111.53-110.90 -109.59	116.89-113.50-111.57 -20.11	110.25-109.74-109.30 109.91	110.59-110.19-110.15 -110.22	109.89-111.93-112.78 -112.15
hexamer	115.28-113.64-111.09 -111.37-110.52	115.03-109.00-113.56 -108.08-115.71	108.23-109.73-110.71 -107.51-111.48	111.39-110.73-111.29 -113.74-110.79	110.51-114.71-111.46 -108.50-111.62
heptamer	109.04-113.59-110.52 -112.08-113.82-110.06	110.41-107.85-112.39 -114.48-117.53-112.77	110.27-107.38-110.75 -112.56-111.42-113.82	110.45-110.60-110.75 -111.06-109.70-110.45	113.22-112.58-112.55 -115.64-111.26-110.20
octamer	112.09-115.56-111.47 -113.01-116.88-112.78 -111.70	114.12-110.47-111.06 -112.80-109.32-114.33 -114.37	110.04-110.63-108.99 -110.23-108.76-111.02 -111.36	110.68-110.91-113.63 -110.46-110.31-110.75 -110.74	111.15-111.53-117.90 -110.72-114.35-112.24 -115.85
nonamer	111.18-110.22-113.47 -110.98-111.57-112.84 114.54-109.76	111.51-111.75-111.12 -111.50-112.42-112.83 -112.75-112.26	110.21-109.25-109.63 -108.63-108.54-115.00 -111.03-109.41	111.90-114.11-110.07 -111.26-113.10-110.14 -114.12-117.05	112.08-108.47-113.43 -112.30-115.94-113.64 -114.48-109.30
decamer	108.27-111.48-111.66 -111.88-114.35-112.73 -113.75-109.66-108.67	106.87-115.82-110.73 -118.49-108.60-113.36 -116.08-116.09-113.82	109.44-110.51-114.50 -112.12-111.83-108.63 -108.07-114.79-110.60	111.15-110.03-110.96 -110.89-112.52-115.26 -111.54-115.90-111.74	112.39-114.46-113.74 -112.77-114.69-112.96 -107.32-111.20-116.45

to decamer for the BF resin, BA resin, and BP resin are 2.53, 2.55, and 2.52 Å, respectively. These results can not be explained by only the linkage size. However, variation of the $\angle_{lc}$ of the *p*-alkylphenol aldehyde resin depending on the linkage type show a specific trend. The $\angle_{lc}$ of the resin with a big linkage is narrower than that of the resin with a small one. The average $\angle_{lc}$ from dimer to decamer for the BF resin, BA resin, and BP resin are 112.56, 112.20, and 110.28°, respectively. This is due to the steric effect of the linkage. When the linkage is bulky, it should have large space. Thus, the $\angle_{lc}$ of the resin becomes narrower by increasing the linkage size from methylene to propylidene.

Effect of the *p*-substituent type on the resin structure. The MA resin, BA resin, and OA resin have different *p*-substituents of methyl, *t*-butyl, and *t*-octyl, respectively. Variation of The r_{oo} and r_{pc} of the resins depending on the *p*-substituent type show a specific trend. The r_{oo} and r_{pc} of the resins become longer by increasing the *p*-substituent size from methyl to *t*-octyl. The average r_{oo} from dimer to decamer for the MA resin, BA resin, and OA resin are 3.19, 3.55, and 3.77 Å, respectively. The average r_{pc} from dimer to decamer for the MA resin, BA resin, and OA resin are 6.06, 6.15, and 6.22 Å, respectively. This can be explained by the steric effect of the *p*-substituent. When the *p*-substituent is bulky, direction of the adjacent *p*-alkylphenols becomes reverse each other to prevent the steric hindrance. The average r_{oo} and r_{pc} become longer by increasing the reverse direction of the *p*-substituent of the adjacent *p*-alkylphenols.

Variation of the $\angle_{lc}$ of the resins depending on the *p*-substituent also show a specific trend. The $\angle_{lc}$ of the resin with a big *p*-substituent is wider than that of the resin with a small one. The average $\angle_{lc}$ from dimer to decamer of the MA

resin, BA resin, and OA resin are 111.41, 112.20, 112.37°, respectively. This can be also explained by the steric hindrance of the *p*-substituent. The long distance between the *p*-substituents to prevent the steric hindrance by the bulky alkyl groups, as discussed above, may make the $\angle_{lc}$ wide. However, the *p*-substituent type hardly affect the r_{lc}. The r_{lc} of the MA resin, BA resin, and OA resin are nearly same. The average of r_{lc} from dimer to decamer of the MA resin, BA resin, and OA resin are 2.53, 2.55, and 2.55 Å, respectively.

Effect of the linkage type on energetic stability. The total energies of the energy-minimized structures, E_t^m, were obtained by the conformational search. Figure 7 shows variation of the total energies of the energy-minimized structures per repeat unit, E_t^m/n, as a function of the molecular size. The E_t^m/n were obtained by dividing the E_t^m by the number of repeat unit, n. Absolute values of the E_t^m/n of the BA resin, BF resin, BP resin, MA resin, and OA resin are 19.91-22.27, 12.52-14.78, 18.80-21.69, 6.22-9.39, and 36.86-39.42 kcal/mol, respectively. In general, the total energy of the energy-minimized structure of a molecule with a high molecular weight is lower than that of a molecule with a low molecular weight when they have a similar chemical structure. However, the variation of the E_t^m/n of the *p*-*t*-butylphenol aldehyde resins (BF resin, BA resin, and BP resin) depending on the linkage type is different to some extent from the general trend. The E_t^m/n of the BF resin having the methylene linkage are higher than those of the BA resin and BP resin having the ethylidene and propylidene linkages, respectively. But, the E_t^m/n of the BA resin are slightly lower than those of the BP resin although the ethylidene is smaller than the propylidene. This can not be explained by only the
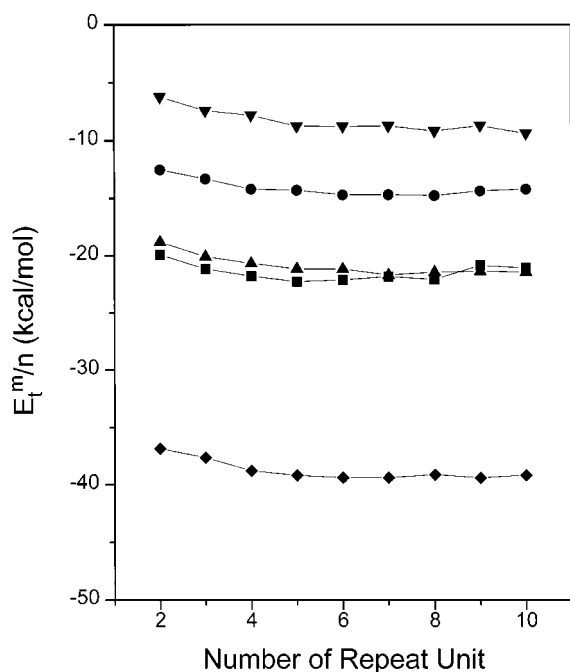
Figure 7. Variation of minimum total energies per repeat unit, E_t^m/n, of the *p*-alkylphenol aldehyde resins depending on the number of repeat unit. Rectangles, circles, up-triangles, down-triangles, and diamonds indicate BA resin, BF resin, BP resin, MA resin, and OA resin, respectively.

r_{oo} and r_{pc} since the r_{oo} and r_{pc} of the BA resin are longer than those of the BP resin as discussed previously. It can be considered that the BA resin has more packed structure. The BA resin has a pseudo-helical structure. For the BA resin hexamer (Figure 2), distances between the 1-carbon atoms of the phenyl rings of the first *p*-*t*-butylphenol and the others (r_{1m}, *m* is the number of the counter alkylphenol sequence) are 4.54, 7.86, 8.59, 6.55, and 4.38Å for the r_{12}, r_{13}, r_{14}, r_{15}, r_{16}, respectively. The r_{1m} of the BA resin hexamer become long (from r_{12} to r_{14}) and then become short (from r_{14} to r_{16}) by increasing the sequence number. This means that the BA resin hexamer has a pseudo-helical structure and is well packed.

In general, average total energies of a molecule at temperatures, which molecular motions of rotation and vibration are activated enough, have positive values. If molecules have the similar chemical structure and the molecular motions are activated enough, the average total energies of a molecule with a high molecular weight are higher than those with a low molecular weight in the same temperature. Variations of the average total energies per repeat unit, $\langle E_t \rangle/n$, at 303, 373, 473, and 573 K as a function of the molecular size of the BA resin, BF resin, BP resin, MA resin, and OA resin are given in Figs. 8, 9, 10, 11, and 12, respectively. The average total energies of the each resin, $\langle E_t \rangle$, were obtained by averaging the 300 ps dynamic fluctuation. The $\langle E_t \rangle/n$ were obtained by dividing the $\langle E_t \rangle$ by the number of repeat unit, *n*. The $\langle E_t \rangle/n$ of the BA resin at 303-573 K are lower than those of the BF resin and BP resin. The $\langle E_t \rangle/n$ of the BA resin at 303, 373, 473, and 573 K are
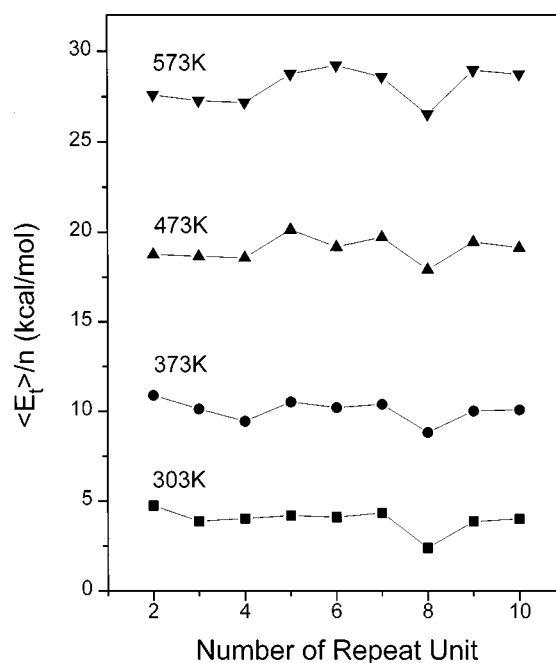

Figure 8. Variation of average total energies for 300 ps per repeat unit, $\langle E_t \rangle/n$, of the *p*-*t*-butylphenol acetaldehyde resin (BA resin) depending on the number of repeat unit.
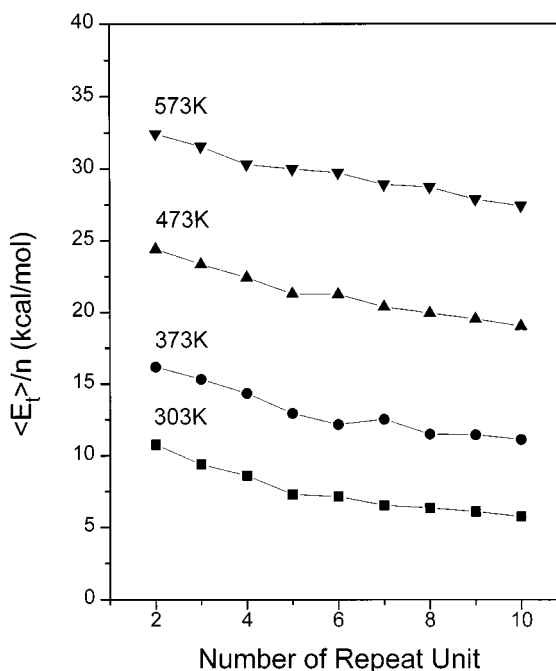

Figure 9. Variation of average total energies for 300 ps per repeat unit, $\langle E_t \rangle/n$, of the *p*-*t*-butylphenol formaldehyde resin (BF resin) depending on the number of repeat unit.

2.38-4.73, 8.81-10.89, 17.91-20.14, and 26.51-29.21 kcal/mol, respectively, while those of the BF resin are 5.75-10.78, 11.13-16.19, 19.04-24.42, and 27.43-32.43, respectively, and those of the BP resin are 4.66-7.46, 11.61-13.78, 21.54-23.25, and 31.11-32.15 kcal/mol, respectively. This means that the BA resin has a more stable structure than the BP resin as well as the BF resin at 303-573 K. This may be
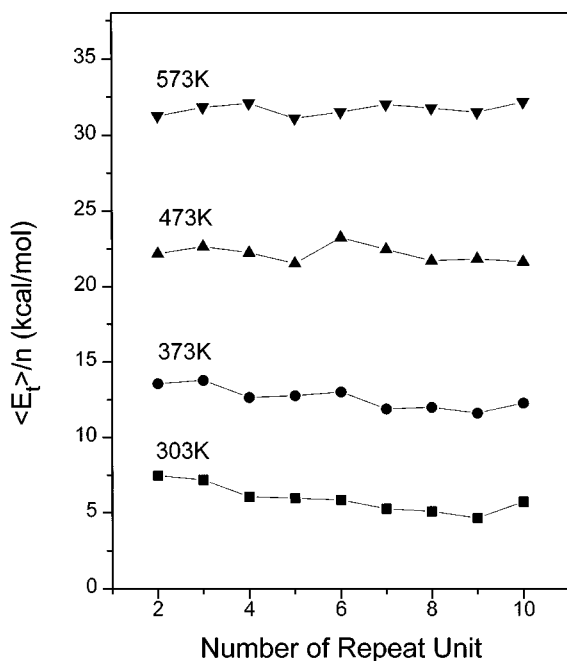
Figure 10. Variation of average total energies for 300 ps per repeat unit, $\langle E_t \rangle/n$, of the *p-t*-butylphenol propionaldehyde resin (BP resin) depending on the number of repeat unit.
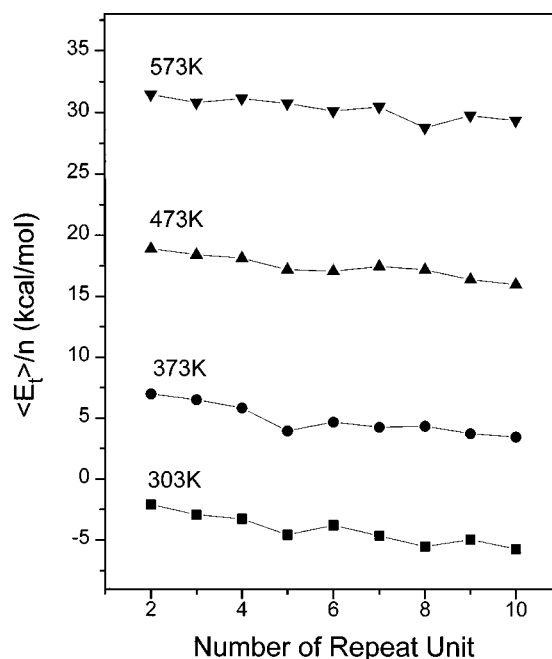

Figure 12. Variation of average total energies for 300 ps per repeat unit, $\langle E_t \rangle/n$, of the *p-t*-octylphenol acetaldehyde resin (OA resin) depending on the number of repeat unit.
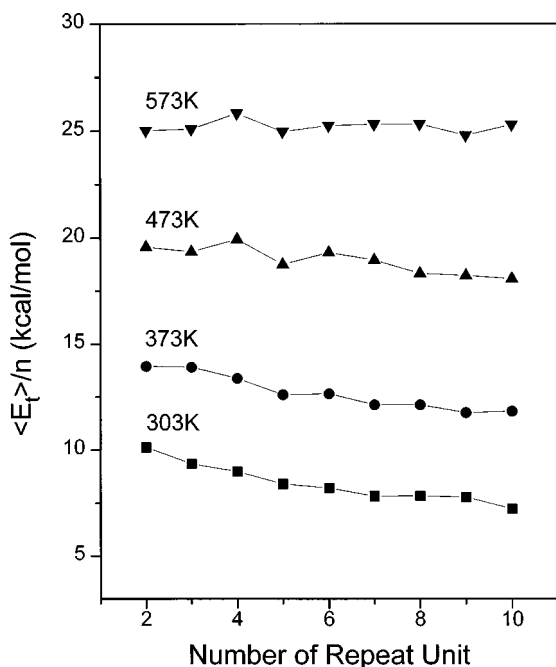

Figure 11. Variation of average total energies for 300 ps per repeat unit, $\langle E_t \rangle/n$, of the *p*-methylphenol acetaldehyde resin (MA resin) depending on the number of repeat unit.

explained by the pseudo-helical structure of the BA resin as discussed above.

Of the BA resin dimer to decamer, the E_t^m/n and $\langle E_t \rangle/n$ of the octamer is lower than those of the others. This means that the BA resin octamer has a specific stability. The stability of the BA resin octamer was reported in the previous work.[15] The $\langle E_t \rangle/n$ at 303-573 K of the BF

resin increases with an increase of the molecular size. This may be due to an increase of the intramolecular hydrogen bonds of the BF resin with an increase of the molecular size. However, the $\langle E_t \rangle/n$ at 303-573 K of the BA resin and BP resin are nearly same irrespective of the molecular size. This may be due to the steric hindrance of the linkage. The methylene linkage of the BF resin is smaller than the ethylidene (BA resin) and propylidene (BP resin) linkages so that the hydrogen bonds between hydroxyl groups of the adjacent *p-t*-butylphenols of the BF resin are less inhibited by the linkage than those of the BA resin and BP resin. The methyl (BA resin) and ethyl (BP resin) will inhibit the hydrogen bonds by their rotation and vibration when the temperature is high.

Effect of the *p*-substituent on energetic stability. The E_t^m/n of the *p*-alkylphenol acetaldehyde resins (MA resin, BA resin, and OA resin) decrease with an increase of the *p*-substituent size from methyl to *t*-octyl as shown in Figure 7. This is the reason why the van der Waals interactions between *p*-substituents of the *p*-alkylphenols increase by increasing its size. Absolute values of the E_t^m/n of the MA resin, BA resin, and OA resin are 6.22-9.39, 19.91-22.27, and 36.86-39.42 kcal/mol, respectively.

The $\langle E_t \rangle/n$ at 303-473 K of the OA resin (Figure 12) are lower than those of the BA resin (Figure 8) and MA resin (Figure 11), while those at 573K of the OA resin are higher than those of the others. The $\langle E_t \rangle/n$ of the MA resin at 303, 373, 473, and 573 K are 7.23-10.13, 11.76-13.95, 18.09-19.94, 24.80-25.83 kcal/mol, respectively, and those of the OA resin are -5.72~-2.09, 3.46-6.97, 15.98-18.90, and 28.76-31.46 kcal/mol, respectively. This means that the van der Waals interactions between *t*-octyl groups of the OA

resin are more favorable at the temperatures = 473 K than those between methyl groups of the MA resin or *t*-butyl groups of the BA resin since the *t*-octyl is more bulky than the methyl and *t*-butyl.

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