Influence of Polycondensation Type on Structure of Resorcinol Formaldehyde Resin Studied by Molecular Simulation

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Abstract : Resorcinol formaldehyde resins are synthesized by polycondensation of resorcinol with formaldehyde and have various structures by the condensation type. The influence of polycondensation type on the stability and structure of the resorcinol formaldehyde resin was studied by molecular mechanics and molecular dynamics. The resins formed by 2,6-polycondensation and 4,6-polycondensation with head-to-tail orientations have structures of intramolecular hydrogen bonds between 1-hydroxyl groups and between outer hydroxyl groups of the adjacent resorcinols, respectively. The resin formed by 2,6-polycondensation with head-to-head orientation has a structure that inner hydroxyl groups cluster in the center of the molecule. Energetical stability of the resin is affected by both the intramolecular hydrogen bonds and the steric hindrance by phenyl group.

Introduction

Phenolic resins are interesting materials because of their high thermal stability, excellent resistance to combustion, high dimensional stability, good mechanical properties, and high chemical stability.[1-9] Phenolic resins have a variety of uses, depending on their types, as bonding agents,[10] tackifiers,[9,11] vulcanizing agents,[12] photoresists,[13] and so forth.

Resorcinol formaldehyde resins (RF resin) are synthesized by polycondensation of resorcinol with formaldehyde.[14,15] RF resins have been of great importance to the rubber industry. Rayon, nylon, fiber glass, polyester, steel, and aramid cords have been successfully bonded to rubber with resorcinol based adhesives.[16,17] Resorcinol reacts with formaldehyde to produce various hydroxymethylated resorcinols of 2-hydroxymethylresorcinol, 4-hydroxymethylresorcinol, and 6-hydroxymethylresorcinol. The hydroxymethylated resorcinols react with a resorcinol and then a dimer of the resorcinol formaldehyde resin is formed by autocondensation and dehydration. The dimer of the resorcinol formaldehyde resin can have various structures depending

on the hydroxymethylated resorcinol type and the reaction site (2, 4, or 6 position of a resorcinol). The different structures by the condensation type are shown in Figure 1. The Resin-A and Resin-B are formed by the 2,6- and 4,6-polycondensations with head-to-tail orientation, respectively. The Resin-C is formed by the 2,6-polycondensation with head-to-head orientation.

Commercially available RF resins have various types of structures. It is hard to synthesize the RF
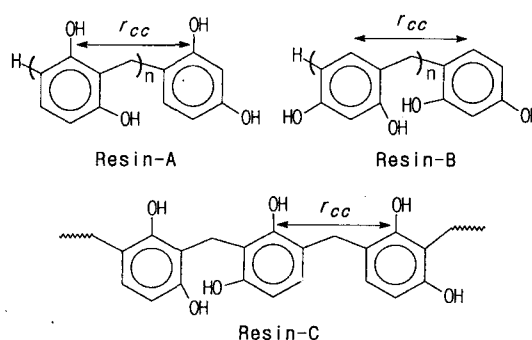
Figure 1. General formulae of resorcinol formaldehyde resins formed by 2,6-polycondensation with head-to-tail orientation (Resin-A), 4,6-polycondensation with head-to-tail orientation (Resin-B), and 2,6-polycondensation with head-to-head orientation (Resin-C).

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resin with uniform constituents. It is also hard to separate the various resins with different structures using chromatography such as gel permeation chromatography and liquid chromatography. Using molecular modeling, however, it is possible to investigate structural charactersitics of new materials and pure materials which are not available to obtain by synthesis and by separation techniques. In the present work, the influence of polycondensation type on the stability and structure of RF resins was studied by molecular mechanics and molecular dynamics.

Modeling and Calculation

The initial structures of input molecules were generated by the *Insight II* package. 2-Methylresorcinol, 4-methylresorcinol, and 6-methylresorcinol (or 2-methylresorcinol) were used as the repeat units of the Resin-A, Resin-B, and Resin-C, respectively. The input molecules were constructed by linking the repeat unit with head-to-tail (for Resin-A and Resin-B) or head-to-head (for Resin -C) orientation. Dimer to decamer of the resorcinol formaldehyde resins were calculated. Calculations were carried out by molecular mechanics and dynamics with CFF91 force field.[18] 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.*[19] 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 employed. Potential cutoff distance of 10.0 Å and distance dependent dielectric constant were employed. The energy-minimized structures of the resorcinol formaldehyde 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. Of the 200 conformers, the conformer with the lowest total energy was determined as the energy-minimized structure.

Results and Discussion

Of the energy-minimized structures of the RF resins obtained from the conformational search, tetramers of the three resins were displayed representatively in Figure 2-4. Figure 2, 3, and 4 represent the structures of tetramers of the Resin-A, Resin-B, and Resin-C, respectively. The RF resins, irrespective of the polydensation type, have common structural characteristics of intramolecular hydrogen bonds between hydroxyl groups of the adjacent resorcinols. The intramolecular hydrogen bonds lead to a cyclic structure that hydroxyl
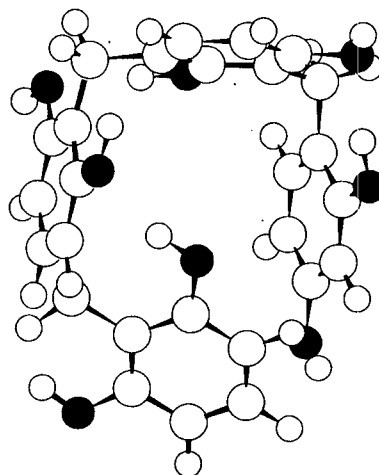
Figure 2. Structure of the energy-minimized Resin-A tetramer. Solid circles indicate oxygen atoms.
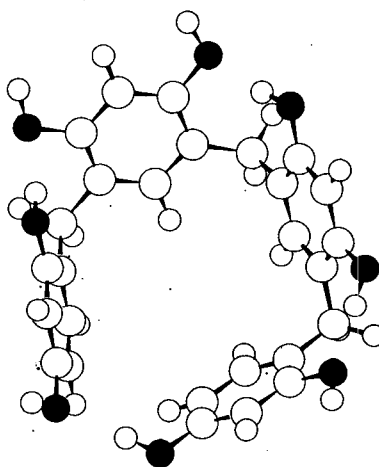
Figure 3. Structure of the energy-minimized Resin-B tetramer. Solid circles indicate oxygen atoms.
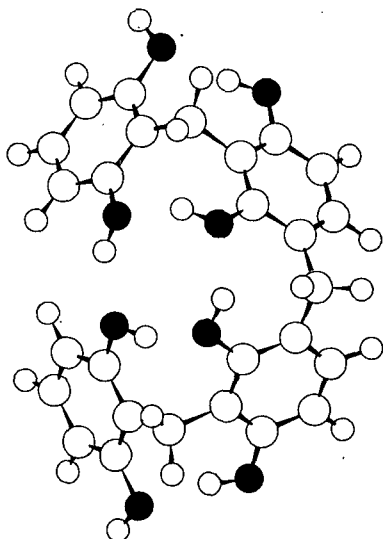
Figure 4. Structure of the energy-minimized Resin-C tetramer. Solid circles indicate oxygen atoms.

groups or hydrogen atoms cluster in the center of the molecule. The Resin-A has a structure of intramolecular hydrogen bonds between 1-hydroxyl groups of the adjacent resorcinols (Figure 2), while the Resin-B has a structure of the intramolecular hydrogen bonds between 1-hydroxyl and 3-hydroxyl groups of the adjacent resorcinols (Figure 3). The Resin-C has a structure of intramolecular hydrogen bonds not only between 1-hydroxyl groups but also between 3-hydroxyl groups of the adjacent resorcinols (Figure 4). The Resin-B has a structure that hydrogen atoms linked to 5-carbon atoms of the resorcinols cluster in the center of the molecule by intramolecular hydrogen bonds between outer hydroxyl groups of the adjacent resorcinols. The Resin-C also has a cyclic structure that inner hydroxyl groups cluster in the center of the molecule by intramolecular hydrogen bonds between outer hydroxyl groups as well as between inner hydroxyl groups of the adjacent resorcinols. The intramolecular hydrogen bonds of a phenolic formaldehyde resin were studied using an X-ray crystallography and a molecular simulation.[6,13,20] 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 hydro-

gen 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. Structure and stability of p-t-butylphenol formaldehyde resin depending on tacticity were studied using a molecular simulation.[20] The p-t-butylphenol formaldehyde resin has structural characteristics that hydroxyl groups cluster in the center of the molcule by intramolecular hydrogen bonds between hydroxyl groups of the adjacent p-t-butylphenols and t-butyl groups are extended out.

Distances between ortho-carbon atoms to the methylene linkages of the adjacent resorcinols, r_{cc}, (Figure 1) were measured from the energy-minimized structures of the resins in order to investigate the structural difference of the three resins depending on the condensation type. Table I gives the r_{cc} of the Resin-A, Resin-B, and Resin-C. The average r_{cc} from dimer to decamer of the Resin-A, Resin-B, and Resin-C are 3.95, 3.82, and 3.83 Å, respectively. It can be considered that the resin with a short r_{cc} has a stronger intramolecular interaction than the resin with a long one. The r_{cc} of the Resin-B and Resin-C are shorter than those of the Resin-A. This can be explained by the intramolecular hydrogen bonds between outer hydroxyl groups of the adjacent resorcinols of the Resin-B and Resin-C. Since the inner hydrogen atoms linked to 5-carbon atoms of the resorcinols of the Resin-B and the inner hydroxyl groups of the Resin-C cluster in the center of the molecule, the r_{cc} of the Resin-B and Resin-C are shorter than those of the Resin-A.

The intramolecular hydrogen bonds between hydroxyl groups of the adjacent resorcinols are very important structural characteristics of the RF resins. Table II gives the number of the intramolecular hydrogen bonds and the distance between oxygen atoms formed the hydrogen bonds, r_{oo}, for the different sized oligomers of the Resin-A, Resin-B, and Resin-C. The number of the intramolecular hydrogen bonds of the Resin-C is much larger than that of the Resin-A. This may be due to short distances between outer hydroxyl groups of the Resin-C. Since the Resin-C is

Table I. Distances between *ortho*-Carbon Atoms to the Methylene Linkages of the Adjacent Resorcinols in the Energy-Minimized Resorcinol Formaldehyde Resins, r_{cc}, in Å

Size of Molecule	Resin-A	Resin-B	Resin-C
Dimer	3.76	3.73	3.74
Trimer	3.78-3.79	3.65-3.70	3.73-3.78
Tetramer	4.02-3.77-3.79	3.64-3.79-4.06	3.75-3.80-3.77
Pentamer	3.74-3.77-3.88-3.90	3.61-3.70-3.67-4.66	3.69-3.72-3.70-4.30
Hexamer	3.75-4.73-4.60-3.83-3.74	3.76-3.55-3.52-3.94-3.90	3.66-3.81-3.83-3.90-3.85
Heptamer	3.77-3.76-3.80-3.85-4.06-4.91	3.68-3.61-3.87-3.90-3.49-3.65	3.83-3.82-3.73-4.70-3.83-3.75
Octamer	3.77-3.72-3.80-3.89-4.47-3.64-3.53	3.73-4.80-3.51-4.13-3.77-3.88-3.70	3.80-3.74-4.60-3.71-3.74-3.80-3.74
Nonamer	3.49-3.96-3.76-3.93-4.73-4.78-3.59-3.89	3.98-4.48-3.73-4.33-3.87-3.65-3.93-3.92	3.68-3.67-4.47-3.84-4.39-3.77-3.66-3.77
Decamer	5.51-3.72-3.74-3.73-3.75-3.77-3.76-4.85-3.74	3.59-3.55-3.58-4.83-4.02-3.56-3.95-3.44-3.70	3.77-3.77-3.69-3.65-3.84-3.90-3.87-3.55-3.75

Table II. Distances between Oxygen Atoms of the Hydroxyl Groups Hydrogen-bonded in the Energy-Minimized Resorcinol Formaldehyde Resins, r_{oo}, in Å. Values in the Parentheses are the Number of the Intramolecular Hydrogen Bonds

Size of Molecule	Resin-A	Resin-B	Resin-C
Dimer	(1) 2.98	(1) 2.78	(2) 2.78, 2.77
Trimer	(2) 2.93, 3.05	(2) 2.80, 2.78	(3) 2.76, 2.75, 2.77
Tetramer	(3) 2.93, 3.00, 2.83	(4) 2.81, 2.76, 2.73, 2.82	(6) 2.73, 2.74, 2.73, 2.78, 2.75, 2.77
Pentamer	(5) 2.82, 2.95, 2.80, 2.86, 3.12	(4) 2.81, 2.85, 2.76, 2.78	(7) 2.68, 2.69, 2.78, 2.75, 2.73, 2.74, 2.84
Hexamer	(5) 2.88, 2.88, 2.84, 2.82, 2.98	(6) 2.78, 2.81, 2.79, 2.86, 2.92, 2.87	(8) 2.72, 2.93, 2.84, 2.77, 2.76, 2.74, 2.72, 2.82
Heptamer	(4) 2.83, 2.80, 2.91, 2.92	(6) 2.94, 2.82, 2.80, 2.92, 3.06, 3.01	(9) 2.73, 2.78, 2.76, 2.7., 2.71, 2.76, 2.72, 2.80, 2.75
Octamer	(6) 2.87, 2.84, 2.79, 2.84, 3.03, 2.82	(7) 2.74, 2.80, 2.84, 2.95, 2.94, 2.74, 2.75	(11) 2.76, 3.09, 2.77, 2.75, 2.74, 2.78, 2.78, 2.66, 2.76, 2.79, 2.78
Nonamer	(5) 2.96, 3.01, 2.95, 2.97, 2.89	(10) 2.80, 2.95, 2.71, 2.78, 2.80, 2.90, 2.78, 2.81, 2.95, 2.96	(11) 2.72, 2.68, 2.81, 3.02, 2.69, 2.73, 3.09, 2.77, 3.00, 2.75, 2.76
Decamer	(8) 3.20, 2.83, 3.05, 3.12, 3.12, 2.97, 2.84, 2.83	(9) 2.93, 2.92, 2.79, 2.81, 2.98, 2.85, 2.77, 2.97, 2.83	(14) 2.72, 2.68, 2.86, 2.84, 2.69, 2.86, 2.70, 2.70, 2.71, 2.73, 3.06, 2.78, 2.93, 2.74

formed by the 2,6-polycondensation with head-to-head orientation while the Resin-A is formed by the 2,6-polycondensation with head-to-tail orientation, the distances between the outer hydroxyl groups of the Resin-C are shorter than those of the Resin-A (Figure 1). The total numbers of the intramolecular hydrogen bonds from dimer to decamer of the energy-minimized resins are 39, 49, and 71 for the Resin-A, Resin-B, and Resin-C, respectively. The r_{oo} of the Resin-C are also shorter than those of the Resin-A. This implies that the

intramolecular hydrogen bonds of the Resin-C are stronger than for the Resin-A. The average r_{oo} from dimer to decamer of the Resin-A, Resin-B, and Resin-C are 2.93, 2.84, and 2.78 Å. The number of the hydrogen bonds of the Resin-B is smaller than that of the Resin-C. This may be due to the difference in the structures of the Resin-B and the Resin-C. Since all the hydroxyl groups of the Resin-B are extended out as demonstrated above, it is hard to form a hydrogen bond between the end hydroxyl groups and to form double

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hydrogen bond to one hydroxyl group. On the contrary, the Resin-C has a structure that both inner and outer hydroxyl groups can form hydrogen bonds and a hydrogen bond between the end hydroxyl groups can be formed. For example, the Resin-C dimer has 2 hydrogen bonds formed not only between the inner hydroxyl groups but also between the outer hydroxyl groups. There are four hydrogen bonds formed by the inner hydroxyl groups including a hyrogen bond between the end hydroxyl groups and two hydrogen bonds formed by the outer hydroxyl groups in the Resin-C tetramer as shown in Figure 4.

The total energies of the energy-minimized structures of the resins were calculated to compare energetical stabilities of the three resins depending on the polycondensation type. Figure 5 shows variation of the total energies of the Resin-A, Resin-B, and Resin-C as a function of the molecular size. Both of the Resin-A and Resin-C are formed by the 2,6-polycondensation, however, their orientations are different each other as demonstrated previously. The Resin-C is energetically more stable than the Resin-A as shown in Figure 5. This can be explained by the number of the intramolecular hydrogen bonds and the r_{cc}. The number of the intramolecular hydrogen bonds of

the Resin-C is much higher than that of the Resin-A, and the r_{cc} of the Resin-C are shorter than those of the Resin-A. The Resin-B is energetically more stable than the Resin-A. This can be also explained by the number of the intramolecular hydrogen bonds and the r_{cc} similarly. The Resin-B is also energetically more stable than the Resin-C. This can not be explained, however, by the number of the intramolecular hydrogen bonds and the r_{cc} because the number of the intramolecular hydrogen bonds of the Resin-B is less than that of the Resin-C (Table II) and the r_{cc} of the Resin-B is nearly same that of the Resin-C. The result may come from the steric hindrance. It is considered that the Resin-B has a less sterically hindered structure than the Resin-A and Resin-C since all the hydroxyl groups of the Resin-B are extended out. Though the formation of the intramolecular hydrogen bonds in the Resin-B seems less favorable compared to the Resin-C, the hydroxyl groups of the Resin-B are not hindered by the neighboring phenyl rings. On the contrary, the hydroxyl groups of the Resin-A and Resin-C are, to some extent, hindered by the neighboring phenyl rings as shown in Figure 2 and 4.

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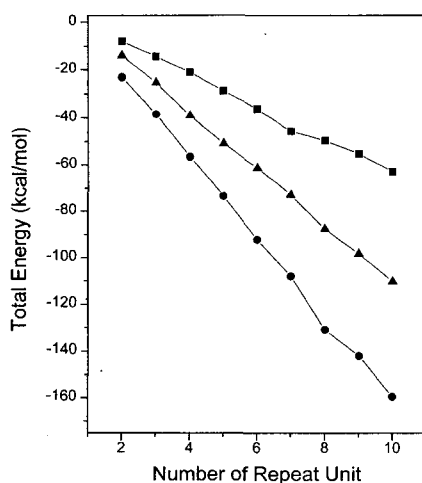
Figure 5. Variation of total energy as a function of the molecular size of the energy-minimized structure of the resorcinol formaldehyde resins with different polycondensation types. Rectangles, circles, and triangles indicate the Resin-A, Resin-B, and Resin-C, respectively.

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