On the Structures of *p-tert*-Butylphenol Resin and α-Naphthol Resin. III. Infrared Absorption Spectra of Resins of *p-tert*-Butylphenol and α-Naphthol

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Polymer synthesized from *p-tert*-butylphenol and formaldehyde with ammonia was used as a suitable material for coating the fiber of a dust respirator to raise its efficiency; it showed an anomalous behavior in benzene solution[1]. Infrared spectra of the polymer in solid and in various solutions have been observed and its structure discussed[1], but there

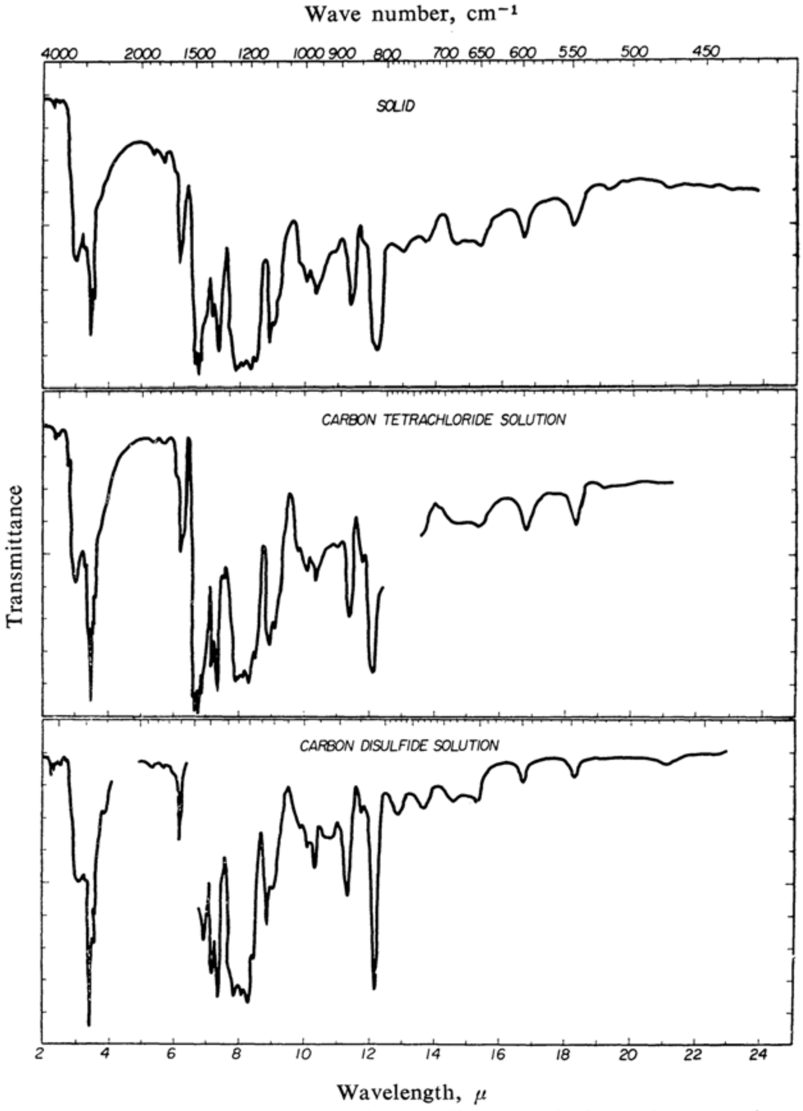

Fig. 1. Spectra of *p-tert*-butylphenol resin in solid and solutions. Spectrum is cut off in the region of interference due to solvents. Concentration of solution is about 15% in carbon tetrachloride and 10% in carbon disulfide.

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[1] R. Soda, *Bull. Nat. Inst. Ind. Health*, No. 3, 40 (1960).

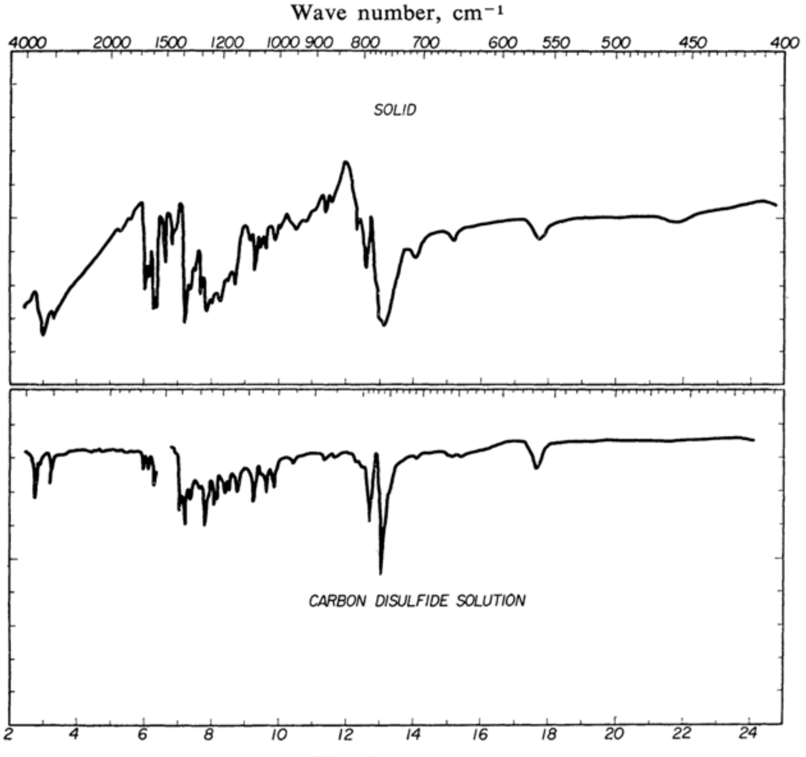

Fig. 2. Spectra of α-naphthol resin in solid and solution. Spectrum is cut off in the region of interference due to solvent. Concentration of solution is about 2%.

still remain some ambiguities in the assignment of those spectral bands. In order to eliminate the doubtfulness in the previous paper, infrared spectra of phenol, *p*-*tert*-butylphenol and α-naphthol were observed in more detail, and the band assignment and their structures were discussed more precisely2). The present paper deals with the band assignment of the spectra of the polymers of *p*-*tert*-butylphenol and α-naphthol, comparing them with information obtained already2), particularly about the O–H deformation vibrations of those polymers.

Experimental

p-*tert*-Butylphenol formaldehyde resin and α-naphthol formaldehyde resin were supplied from S. Koshi. The former was synthesized from *p*-*tert*-butylphenol and formaline with ammonia as catalyst, and the latter, from α-naphthol and formaline. These polymers were purified from their benzene solutions. The color of *p*-*tert*-butylphenol polymer was yellowish brown, while that of α-naphthol polymer was dark brown or black.

The solvents used were benzene, acetone, carbon tetrachloride and carbon disulfide, each being distilled once. Only benzene and acetone were used as solvents for *p*-*tert*-butylphenol polymer. Spectra of the solvents were the same as those reported in the literature.

Solid spectrum of *p*-*tert*-butylphenol polymer was observed by sandwiched film which was resolidified between two window plates. α-Naphthol polymer did not fuse without decomposition; therefore, its solid spectrum was observed by potassium bromide disk alone. Some spectra of *p*-*tert*-butylphenol polymer were also obtained with this potassium bromide disk.

A Perkin-Elmer Model 137 infracord spectrophotometer, a Perkin-Elmer Model 21 spectrophotometer (cesium bromide region), and a Perkin-Elmer Model 221 spectrophotometer were used in the present experiment.

Results

***p*-*tert*-Butylphenol Polymer.**—Spectra of *p*-*tert*-butylphenol polymer in solid and in solutions of carbon tetrachloride and carbon disulfide are shown in Fig. 1. Solid spectrum of the polymer in cesium bromide region is shown in Fig. 3. The solution spectrum of *p*-*tert*-butylphenol polymer is almost the same as its solid spectrum, and no significant change in the bands is found when the concentration is altered, except a little change in the 3 and 8 μ regions, as is shown in Figs. 5 and 6. In solid the polymer gives rise to a broad

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2) R. Soda, This Bulletin, 34, 1842 (1961).

band near 3300 cm^{-1} which shows no appreciable change even if the polymer is dissolved in several solvents and the concentration of the solution varies. Only in the cases of carbon tetrachloride and benzene solutions is a weak but sharp band observed near 3600 cm^{-1} as a shoulder of the broad 3300 cm^{-1} band. In other solvents, such as acetone and carbon disulfide, it does not give rise to any band at 3600 cm^{-1}. The intensity of the band at 3600 cm^{-1} increases slightly as the concentration decreases, but the increment is so small that the quantitative relation with the concentration cannot be confirmed.

In the 8 μ region, this polymer gives rise to the bands at 1425, near 1232 and 1205 cm^{-1} in solid and in solution. Those bands in the 3 and 8 μ regions may be concerned in O–H vibration modes, but as far as the present experiment shows, a solvent cannot be found in which all O–H bonds are set free by dilution.

In the region of 600 to 400 cm^{-1}, and some

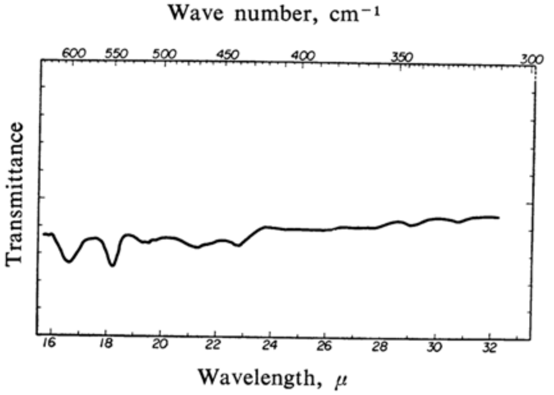

Fig. 3. Spectrum of *p-tert*-butylphenol resin in CsBr region (fused film).

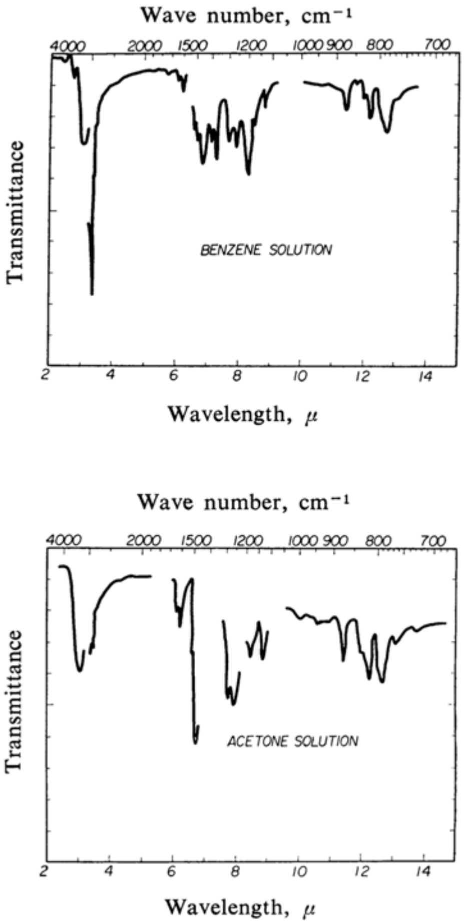

Fig. 4. Spectra of *p-tert*-butylphenol resin in benzene and acetone. Spectrum is cut off in the region of interference due to solvents. Concentration of solution is about 5% in benzene and 5% in acetone.

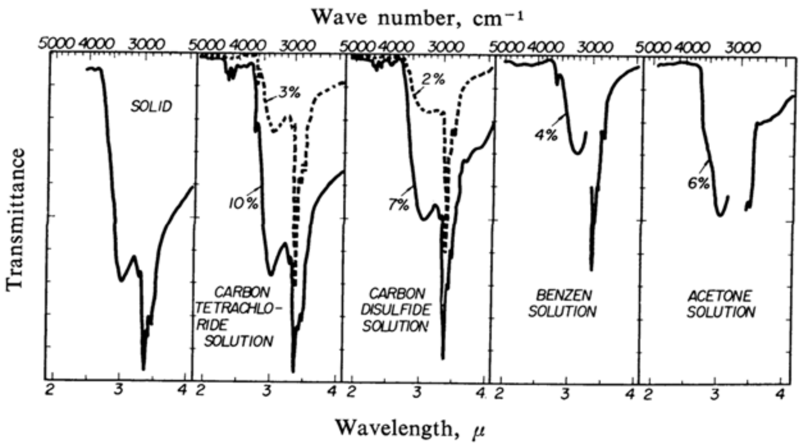

Fig. 5. Spectra of *p-tert*-butylphenol resin in 3 μ region. Spectrum is cut off in the region of interference due to solvents.

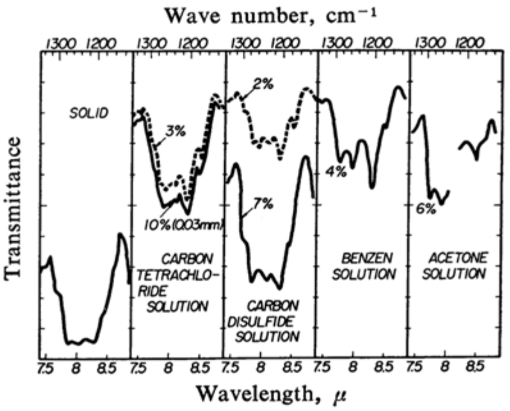

Fig. 6. Spectra of *p-tert*-butylphenol resin in the region near 1200 cm^{-1}. Spectrum is cut off in the region of interference due to solvents.

other regions, such a change of spectra with phase cannot be observed. The observed bands and their assignments are summarized in Table I.

α-Naphthol Polymer. — α-Naphthol polymer is insoluble or scarcely soluble in a non-polar solvent such as carbon tetrachloride; therefore, only a spectrum of a dilute solution of carbon disulfide was observed, as is shown in Fig. 2. The solution spectrum is considerably different from that of solid. This difference is so large that it cannot be explained as an impurity effect due to insufficient purification. In the region of the bands concerned with the C–H out-of-plane vibration mode, the strong bands occur at 765 and 755 cm^{-1}. In 3 μ, the solid gives rise to a very broad band near 3380 cm^{-1}, but the solution gives rise to a sharp (strong) band at 3600 cm^{-1} and a broader (weak) band at 3450 cm^{-1}. In the 8 μ region, several bands are observed, and the bands at 1441 and 1240 cm^{-1} in solid are considered to shift to 1385 or 1370 and 1176 cm^{-1} in solution respectively. In the lower wave number regions, no significant shift or chang is observed between solid and solution.

Discussion

***p-tert*-Butylphenol Polymer.** — *p-tert*-Butylphenol polymer is composed of *p-tert*-butylphenol and a methylene bridge at the ortho positions of phenol ring, and both sides of the linear polymer chain are probably *p-tert*-butylphenol residues[1,3-5]. The polymer has in it a methylene group, 1, 2, 3, 5-tetra- and 1, 2, 4-tri-substituted benzene rings, aromatic O–H and a *tert*-butyl group. *p-tert*-Butylphenol has in it a 1, 4-di-substituted benzene ring, aromatic O–H and a *tert*-butyl group. The polymer gives rise to the bands concerned with those group vibration modes, and the spectral difference between the polymer and *p-tert*-butylphenol may be attributed to the difference between groups or ring structures in these compounds.

The change of the bands concerned in the

TABLE I. BAND POSITIONS AND ASSIGNMENT OF SPECTRUM OF *p-tert*-BUTYLPHENOL RESIN

Bands, cm^{-1}		Assignment
Solid	Solution	
	(3610)	ν(O–H), free ?
3300	3311 to 3200	ν(O–H), bonded
3030	3030	ν(C–H), aromatic
2950	2960	ν(C–H), $-CH_3$
2910	2910	ν(C–H), $-CH_2-$
2870	2870	ν(C–H), $-CH_3$
2830	2830	ν(C–H), $-CH_2-$
1613	1613	Ring vibration
1598	1597	Ring vibration
1534	1536	Ring vibration
1511	1513	Ring vibration
1484	1484	δ(C–H), $-CH_3$
1462	1462	δ(C–H), $-CH_3$ or $-CH_2-$
1450	1453	δ(C–H), $-CH_3$ or $-CH_2-$
1425	1427	δ(O–H), bonded and ν(C–O)
1394	1395	δ(O–H), $-CH_3$ or $-CH_2-$
1362	1363	Skeletal vibration
1328	1327	$-CH_2-$ Twisting
1294	1294	$-CH_2-$ Twisting ?
1270	1273	Skeletal vibration
1257	1258	C–CH_3 Rocking
1238	1233	δ(O–H), bonded and ν(C–O)
1206	1204	δ(C–H), aromatic ?
1181	1179	δ(C–H), aromatic
1125	1125	δ(C–H), aromatic
1106	1107	δ(C–H), aromatic
1010	1015	δ(C–H), aromatic
990	992	Skeletal vibration
968	970	Skeletal vibration
920	918	ν(C–C), C–CH_3
880	882	δ(C–H), out of plane
848	850	ν(C–C), C–CH_3
822	825	δ(C–H), out of plane
818	820	δ(C–H), aromatic or ν(C–C), C–CH_3
778	777	
730	730	$-CH_2-$ Rocking
685	685	Substituent characteristic
654	653	Substituent characteristic
600	600	
550	548	δ(O–H), out of plane
521	522	δ(O–H), out of plane
474	475	

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3) R. J. Grisemthwaite and R. F. Hunter, *J. Applied Chem.*, **6**, 324 (1956).

4) W. J. Wurke and S. J. Ruetman, *J. Polymer Sci.*, **32**, 22 (1958).

5) A. Rosenthal, F. Lederer and K. Gilson, *Can. J. Chem.*, **34**, 679 (1956).

O–H vibration modes in the polymer with the phase or the concentration of solution is different from that of *p-tert*-butylphenol. The spectrum of the polymer shows no obvious difference between solution and solid. Solid and acetone solutions give rise to a broad band at 3300 cm^{-1} but carbon tetrachloride and benzene solutions give rise to a weak band at 3600 cm^{-1} near the 3300 cm^{-1} band. *p-tert*-Butylphenol gives rise to the broad band at 3300 cm^{-1} in solid and a sharp band at 3600 cm^{-1} besides the broader band at 3400 cm^{-1}. These bands are assigned to the O–H stretching vibration mode, the band at 3600 cm^{-1} is assigned to the vibration of free O–H, and the band at 3400 to 3300 cm^{-1}, to that of bonded O–H. Therefore, the O–H bond in the polymer is considered to be bound by very strong intramolecular H–bonding; this H–bonding cannot be easily broken into a free O–H bond in the solution. Only in a non-polar solvent, with interaction between the non-polar group of the polymer and the solvent, can the polymer chain extend to some extent and some O–H bond perhaps exist in a free state. The hydrogen bonded O–H bond of the polymer cannot be loosened by a hydrogen acceptor solvent such as acetone. Accordingly, in the case of the *p-tert*-butylphenol polymer, an appreciable change by the phase change cannot be expected in the bands concerned with O–H vibration modes.

The bands are assigned by comparing them with spectral data of various aromatic O–H compounds[4-6], particularly that of *p-tert*-butylphenol[2]. The assignment in Table I is carried out in such a way.

p-tert-Butylphenol in solid gives rise to the bands at 1389 and 1222 cm^{-1}, and those are assigned to the O–H in-plane deformation vibration, coupled with a C–O stretching vibration. Therefore, the bands at 1425 and 1232 cm^{-1} in the polymer are assumed to be assigned to those vibration modes. In a similar way, the bands at 548 and 520 cm^{-1} are assumed to be concerned with O–H out-of-plane deformation vibration.

The other bands at 600 to 400 cm^{-1} may be attributed to characteristics of 1, 2, 4, 6-tetra- and 1, 2, 4-tri-substitutions.

α-Naphthol Polymer.—Polymerization of α-naphthol and formaldehyde may take place at various positions of the α-naphthol nucleus. Position 1 of naphthalene ring is occupied by the O–H group, and there are two types of adjacent free hydrogen atom groups in α-naphthol. The methylene bridge can occupy several positions of the α-naphthol ring, for example, 2, 4, 6 and 8. The type of adjacent free hydrogen atom group is assumed to be as shown in Fig. 7.

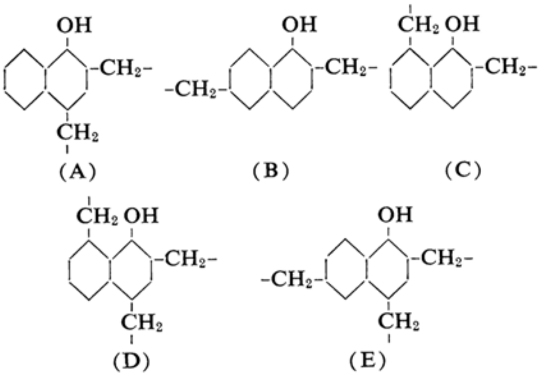

Fig. 7. Diagram regards to several types of methylene bridge in α-naphthol resin.

Out-of-plane bending vibration and some in-plane bending of aromatic C–H bond give rise to bands in the region of 950 to 650 cm^{-1}, and the band positions obey an empirical rule of the spectrum of substituted aromatic derivatives[7-11]. With several substituted naphthalene derivatives in which two sorts of adjacent free hydrogen atom groups exist, the intense band arise in the region of 860 to 800 cm^{-1} and 750 to 700 cm^{-1}. In the case of four adjacent free hydrogen atoms, the compound also gives rise to the bands in the region of 770 to 735 cm^{-1} and 730 to 710 cm^{-1}. With three adjacent aromatic hydrogen atoms, the characteristic bands appear at 810 to 750 cm^{-1} and 730 to 680 cm^{-1}. One isolated hydrogen atom attached to aromatic ring gives rise to the band at 900 to 850 cm^{-1}. From those rules of spectral bands concerned with out-of-plane C–H bending, the polymer may be considered to have a linear but a partly cross-linked chain structure in which the methylene bridge group mainly occupies the 2 and 4 or 6 positions of the naphthalene ring. The main structures may be drawn as shown by I and II in Fig. 8. Bands 850 and 870 cm^{-1} are assigned to out-of-plane bending of the isolated C–H group, bands 810 and 760 or 710 cm^{-1} to that of two adjacent free hydrogen atoms, and bands 770 and 760 or 710 cm^{-1} to that of four adjacent free hydrogen atoms. The band at 790 cm^{-1} is weak, and if the polymer has

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[6] H. Kammerer, *Angew. Chem.*, **70**, 390 (1958).

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Metheu & Co., Ltd., London, J. Wiley & Sons Inc., New York (1954), pp. 64-69 and p. 96.

[8] "Chemical Application of Spectroscopy", Ed. by W. West, Interscience Pub. Ltd., London (1956), pp. 388-434.

[9] H. Kamata and S. Tanaka, *Japan Analyst*, **5**, 98 (1956).

[10] R. W. Bayer and E. J. O'Reily, *J. Phys. Chem.*, **62**, 504 (1958).

[11] H. Luther and H. Gunzler, *Z. Naturforsch.*, **10b**, 445 (1955).

structure I in Fig. 8, this band can be assigned to the vibration of three adjacent free hydrogen atoms in the end of the polymer chain.

In the region of 3 μ, the band at 3380 cm^{-1} is assigned to H–bonded O–H stretching vibration, that at 3450 cm^{-1} to that of weakly H–bonded O–H bond, and that at 3600 cm^{-1} to free O–H stretching vibration. The O–H bonds in the solid polymer may all be bound with each other by intermolecular hydrogen bonding, and in carbon disulfide solution, the polymer has a large number of free O–H bonds and a very small number of H–bonded O–H bonds. It may be assumed that the O–H bonds in the molecule of the α-naphthol polymer find it difficult to approach near enough to each other to build up a strong intramolecular hydrogen bonding.

TABLE II. BAND POSITIONS AND ASSIGNMENT OF SPECTRUM OF α-NAPHTHOL RESIN

Bands, cm^{-1}		Assignment
Solid	Solution	
	3600	ν(O–H), free
	3510	ν(O–H), bonded
3380		ν(O–H), bonded
3030	3060	ν(C–H), aromatic
1650	1664	Ring vibration
1626	1629	Ring vibration
1587	1597	Ring vibration
1575	—	Ring vibration
1508	—	Ring vibration
1460	—	δ(C–H), -CH$_2$-
1441	1403 ?	δ(O–H), bonded and ν(C–O)
1385	1385	δ(C–H), -CH$_2$- or skeletal vibration
	1357	δ(O–H), free and ν(C–O)
1353		
1335		-CH$_2$- Twisting or skeletal vibration
1302	1297	-CH$_2$- Twisting or skeletal vibration
1269	1276	Skeletal vibration
1241	1242 and 1233	δ(O–H), bonded and ν(C–O)
1203	1199	δ(C–H), aromatic
1179		
	1176	δ(O–H), free and ν(C–O)
1142	1143	ν(C–C), aromatic
1081	1080	ν(C–C), aromatic
1051	1051	δ(C–H), aromatic
1014	1014	δ(C–H), aromatic
953	955	Skeletal vibration
930		Skeletal vibration
876	876	Skeletal vibration or δ(C–H), out of plane
859	853	δ(C–H), out of plane
809	812	δ(C–H), out of plane
792	788	δ(C–H), out of plane
765	767	δ(C–H), out of plane
755	757	δ(C–H), out of plane
711	710	δ(C–H), out of plane
661	659	Substituent characteristic skeletal vibration
567	568	δ(O–H), out of plane ?

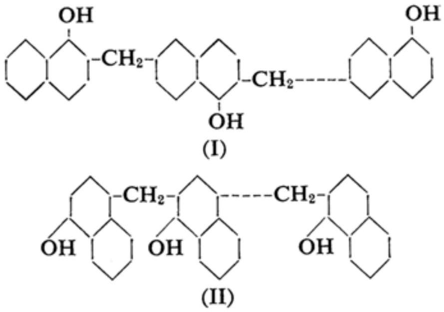

Fig. 8. Possible structures of α-naphthol resin prepared in this work.

From the comparison of the spectra of *p-tert*-butylphenol and its polymer, the bands at 1460, 1385 or 1353, 1335, 1300 and 750 cm^{-1} are assigned to the methylene group vibration6,7). O–H deformation vibration may be coupled with C–O stretching vibration. The bands 1385 or 1353 and 1176 cm^{-1} are assigned to the vibration of the free O–H bond, and the bands at 1441 and 1240 cm^{-1}, to those of H–bonded O–H. The bands at 568 cm^{-1} may be concerned with O–H out-of-plane bending. The other bands are attributed to the vibration of the condensed aromatic ring. The band positions and assignments are summarized in Table II.

Summary

Polymers of *p-tert*-butylphenol with formaldehyde and α-naphthol with formaldehyde have been synthesized, and infrared spectra have been observed in solid and in solutions. The following conclusions have been obtained concerning band assignments and the polymer structures.

(1) *p-tert*-Butylphenol polymer is a linear chain polymer connected with the methylene bridge, and O–H bonds restrict each other by a strong intramolecular hydrogen bonding. This hydrogen bonding is partly loosened in a benzene and carbon tetrachloride solution, but not in an acetone solution.

(2) With *p-tert*-butylphenol polymer the bands at 1425 and 1205 cm^{-1} are assigned to the deformation vibration of the O–H bond coupled with the C–O stretching vibration. Out-of-plane O–H bending is considered to give rise to the bands in the 550 to 500 cm^{-1} region, and the bands at 548 and 520 cm^{-1} are

assumed to be concerned with those vibrations.

(3) The O–H bond in α-naphthol polymer is bound by an intramolecular hydrogen bonding in solid, but in solution almost all the O–H bonds are liberated from the H–bonding. The polymer is considered to be a linear chain molecule whose O–H bonds can only with difficulty interact with each other to make an intramolecular hydrogen bonding.

(4) In-plane O–H deformation vibration coupled with C–O stretching vibration of α-naphthol polymer gives rise to the bands at 1385 or 1357 and 1176 cm^{-1}. The bands at 560 cm^{-1} may be concerned in out-of-plane O–H bending vibration.

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