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ASSOCIATION PHENOMENA IN SOLUTIONS OF PHENOL-FORMALDEHYDE NOVOLAC RESINS OF ORTHO-REGULAR STRUCTURE

(Presented by Academician V. A. Kargin, June 19, 1963)

It is known that phenol-formaldehyde resins, while being low-molecular substances, in a number of cases exhibit properties characteristic of high-molecular compounds. V. A. Kargin, G. L. Slonimskii, and L. I. Golubenkova (1) explain the presence of a region of high elasticity on the thermomechanical curves of resol-type resins by the existence of a mobile network of hydrogen bonds. At small shear stresses in such low-molecular systems as glycerol—water, irreversible deformations develop, which I. A. Dumanskii and L. V. Khailenko (2) explain by spatial reorientation due to hydrogen bonds. Studying dilute solutions of alkylphenolic resins in carbon tetrachloride, Richards and Thompson (3) concluded that intramolecular hydrogen bonds predominate, which may pass into intermolecular ones under the influence of temperature. Sprengling (4) came to an analogous conclusion in studying *p*-cresol novolacs, as did King (5) in work devoted to the investigation of ortho-novolac phenol-formaldehyde resins. However, these studies do not give a complete picture of the influence of the type of hydrogen bonds on the structure of phenol-formaldehyde resins.

The occurrence of intramolecular hydrogen bonds in resins can take place only when the methylene bridges between phenolic nuclei are located in the ortho position with respect to the hydroxyl group. Only in this case is the distance between the hydroxyl oxygens O—H···O sufficient for the formation of an intramolecular hydrogen bond. Therefore, to elucidate the role of different types of hydrogen bonding in phenol-formaldehyde resins, it is of interest to study resins of regular structure, in which the methylene groups occupy the ortho position relative to the phenolic hydroxyl.

[structural formula]

$R = H;\ CH_3;\ C(CH_3)_3,$

n from 1 to 6

We studied the infrared spectra of solutions of these resins and their models at various concentrations and temperatures in the region of the stretching vibrations of the hydroxyl group. The spectra were recorded on a double-beam infrared spectrograph H-800 with a LiF prism. The phenol-formaldehyde resin of ortho structure was obtained by condensation of phenol with formaldehyde in the presence of zinc acetate (^{6}). The presence of only the ortho structure was verified spectroscopically (^{7}). The model compounds used by us, 2—2 and 2—4 dioxydiphenylmethanes, were also identified spectroscopically.

The principal spectroscopic criterion for assigning a hydrogen bond to the intramolecular or intermolecular type is the behavior of the contour of the band of stretching vibrations of hydroxyl groups upon dilution of the solution with a nonpolar solvent. Preservation of the band contour in

in the spectrum of the solution indicates the presence of an intramolecular bond, whereas the disappearance of the band makes it possible to regard the hydrogen bond as intermolecular.

As is seen from Fig. 1*A*, in the spectrum of a 0.1% solution of 2—2 dioxydiphenylmethane in CCl_4, in the region of the stretching vibrations of the OH group there are three bands: 3300, 3460, and 3610 cm^{-1}. The broad band at 3300 cm^{-1} disappears when the solution of the isomer is diluted to a concentration of 0.006% (Fig. 1*B*); therefore it may be associated with the manifestation of an intermolecular hydrogen bond formed by a polymer chain of hydroxyl groups (^{8}).

Beginning at a concentration of 0.006%, the contour of the 3460 cm^{-1} band does not change upon further dilution and the corresponding change in the thickness of the absorbing layer (Fig. 1*B*); raising the temperature to 90° likewise does not change its contour. Therefore the 3460 cm^{-1} band can confidently be associated with the presence of intramolecular hydrogen bonds. Spatial considerations, as well as calculation of the integral intensities for solutions of concentrations 0.1%, 0.05%, and 0.025%, indicate that the breaking intermolecular hydrogen bonds are converted into intramolecular bonds and partly into free hydroxyl groups.

Of interest is the manifestation of hydrogen bonds in solutions of the 2—4 isomer of dioxydiphenylmethane (the 2—4 structure is characteristic of phenol-formaldehyde resins of irregular structure). In solutions of 0.1% concentration, the broad band at 3300 cm^{-1} is absent. Consequently, such a configuration of benzene nuclei cannot form a polymer chain of hydrogen bonds, as in the case of the 2—2 isomer. Since, in accordance with the spatial configuration, the formation of an intramolecular hydrogen bond in the 2—4 isomer is impossible, the 3550 cm^{-1} band should be assigned to a special type of intermolecular bond of dimeric character. This associate is so strong that it is not destroyed either on dilution or on raising the temperature of the solution.

Fig. 1. Infrared spectra of solutions of dihydric phenols and phenol-formaldehyde resins in the region 4000-3000 cm^{-1}. *A*—0.1% solution of 2—2 dioxydiphenylmethane in CCl_4 (cell 5 mm), *B*—0.006% solution of 2—2 dioxydiphenylmethane in CCl_4 (cell 20 mm); *V*—0.006% solution of 2—4

dioxydiphenylmethane (cell 20 mm), G—0.01% solution of ortho-novolac resin in CCl_4 (cell 10 mm, temperature 20°), D—0.01% solution of ortho-novolac resin in CCl_4 (cell 10 mm, temperature 90°).

The studies of hydrogen bonds carried out on model compounds made it possible to interpret the bands of the stretching vibrations of hydroxyl groups in the spectra of solutions of phenol-formaldehyde resins. Figure 1G shows the spectrum of a 0.01% solution of an ortho-novolac resin in carbon tetrachloride. As is seen from the spectrum presented, the band of OH groups bound by a hydrogen bond has two maxima: 3300 and 3460 cm^{-1}; in addition, the band of the free hydroxyl group at 3610 cm^{-1} is clearly manifested. Dilution of solutions of the ortho-novolac resin does not lead to a change in the 3300 cm^{-1} band; however, raising the temperature causes a significant change in its contour (Fig. 1D). Paracresol and para-tertiary butylphenol novolacs behave in a similar manner. This phenomenon, as well as the coincidence of the position of the 3300 cm^{-1} band with the band

bound by intermolecular bonding of hydroxyl groups in 2-2 -dioxydiphenylmethane, gives grounds to believe that in solutions of phenolic resins of ortho structure there exist stable associates, formed by intermolecular hydrogen bonding, which are not destroyed even upon considerable dilution.

To confirm the existence of associates in ortho-novolac resins, we carried out electron-microscopic investigations of thin resin films. In the work of Spurr and co-workers (8), globular formations in cured phenol-formaldehyde resins were reported; however, the nature of the molecular forces causing the appearance of such formations was not clarified by the authors. We prepared samples of ortho-novolac resin by applying several drops of a 0.1% solution in acetone and pyridine to the surface of water. The investigation was carried out at direct electron-microscopic magnification of 5000–10 000 on a GEM5-U electron microscope. In Fig. 2a, globules of regular spherical shape are clearly visible. The size of the globules varies within the range 1000–10 000 Å.

We also studied compounds related to phenolic resins—condensates based on benzyl chloride, of the structure

[structural formula: $\mathrm{Ph-CH_2-[Ph-CH_2]_n-Ph-CH_2Cl}$], n from 1 to 6

and ortho-novolac resins acetylated by the method of Vansheidt (11), of the structure:

[structural formula: acetylated ortho-novolac chain with $OCOCH_3$ substituents; $R = \mathrm{H}$; n from 1 to 6]

In both cases no globules were found. The character of the electron-microscopic picture is seen from Fig. 2b. Evidently, the appearance of globular formations is connected with the presence of associates bound by hydrogen bonding.

As our experiments showed, the decrease in the integral intensity of the 3300 cm^{-1} band with increasing temperature of the resin solutions occurs with a simultaneous increase in the integral intensity of the bands at 3460 cm^{-1} and 3610 cm^{-1}. Consequently, the destruction of intermolecular hydrogen bonding is accompanied by the formation of new hydrogen bonds.

The experiments carried out give grounds to believe that in solutions of phenolic resins of ortho structure there exist stable associates formed by intermolecular hydrogen bonding. An increase in temperature leads to rupture of these bonds; at the same time, owing to rotation about the methylene bridge, new intramolecular hydrogen bonds and free hydroxyl groups are formed.

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Note: Figure translations are in progress. See original paper for figures.