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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, although 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 resole-type resins by the existence of a mobile network of hydrogen bonds. At small shear stresses in such low-molecular systems as glycerin—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; these may change into intermolecular ones under the action of temperature. Sprengling (4), studying para-cresol novolacs, and also Kin (5), in work devoted to the investigation of ortho-novolac phenol-formaldehyde resins, arrived at a similar conclusion. However, these works do not give a complete picture of the influence of the type of hydrogen bonds on the structure of phenol-formaldehyde resins.

The formation of intramolecular hydrogen bonds in resins can occur only when the methylene bridges between phenolic nuclei are situated in the ortho position relative to the hydroxyl group. Only in this case is the distance between the hydroxyl oxygens O—H···O sufficient for formation of an intramolecular hydrogen bond. Therefore, in order to clarify the role of different types of hydrogen bond in phenol-formaldehyde resins, it is of interest to investigate resins of regular structure in which the methylene groups occupy the ortho position to the phenolic hydroxyl.

[structural formula of an ortho-regular phenol-formaldehyde novolac resin]

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

n from 1 to 6

We studied the infrared spectra of solutions of these resins and of their models at various concentrations and temperatures in the region of stretching vibrations of the hydroxyl group. The spectra were recorded on a double-beam H-800 infrared spectrograph with an LiF prism. The ortho-structured phenol-formaldehyde resin was obtained by condensation of phenol with formaldehyde in the presence of zinc acetate (6). The presence of only ortho structure was verified spectroscopically (7). The model compounds we used, 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 disappearance of the band makes it possible to regard the hydrogen bond as intermolecular.

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Fig. 2. Electron microphotographs. a —ortho-novolac phenol-formaldehyde resin from a 0.1% acetone solution; b —chlorinated benzene condensate from a 0.1% acetone solution

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a —ortho-novolac phenol-formaldehyde resin from a 0.1% acetone solution;
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As can be seen from Fig. 1A, 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. 1B); therefore it may be associated with the manifestation of an intermolecular hydrogen bond formed by a polymeric 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. 1B); 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 integrated intensities for solutions of concentration 0.1%, 0.05%, and 0.025%, indicate that the hydrogen intermolecular bonds being destroyed are converted into intramolecular and, in part, into free hydroxyl groups.

It is of interest to examine the manifestation of hydrogen bonds in solutions of the 2—4 isomer of dioxydiphenylmethane (the 2—4 arrangement is characteristic of phenol-formaldehyde resins of irregular structure). In solutions of concentration 0.1% the broad 3300 cm^{-1} band is absent. Consequently, such a configuration of the benzene rings cannot form a polymeric chain of hydrogen bonds, as in the case of the 2—2 isomer. Since, in accordance with the spatial configuration, 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 upon dilution or upon raising the temperature of the solution.

Fig. 1. IR spectra of solutions of dihydric phenols and phenol-formaldehyde resins in the 4000-3000 cm^{-1} region. 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°).

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The studies carried out on hydrogen bonds in 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 presents the spectrum of a 0.01% solution of ortho-novolac resin in carbon tetrachloride. As can be seen from the spectrum shown, the band of OH groups connected 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 ortho-novolac resin does not lead to a change in the 3300 cm^{-1} band; however, increasing the temperature causes a significant change in its contour (Fig. 1D). Paracresol and para-tert-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

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

To confirm the existence of associates in ortho-novolac resins, we carried out electron-microscopic studies of thin resin films. In the work of Spurr and coworkers ([8]), globular formations in cured phenol-formaldehyde resins were reported; however, the character of the molecular forces causing the appearance of such formations was not clarified by the authors. We prepared specimens of ortho-novolac resin by applying several drops of a 0.1% solution in acetone and pyridine to the surface of water. The study was performed at a 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

$$[\mathrm{Ph} - \mathrm{CH_2} - \mathrm{Ph} - \mathrm{CH_2} - \mathrm{Ph} - \mathrm{CH_2Cl}]_n \qquad n \text{ from 1 to 6}$$

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

$$\mathrm{AcO{-}C_6H_3}(R)\mathrm{{-}CH_2}\,[\mathrm{C_6H_3}(R)(\mathrm{OCOCH_3})\mathrm{{-}CH_2}]_n\,\mathrm{C_6H_3}(R)(\mathrm{OCOCH_3})$$

$$R = H;$$

$$n \text{ from 1 to 6}$$

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

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

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

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