Studies on the Aging Process of a Highly Condensed Resol Resin

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Synopsis

The nature of the structure changes of a highly condensed resol resin during its aqueous solution storage was considered. To this end, the curing process of the resin was investigated by means of DTA and its structure was analyzed by means of NMR. The hypothesis relative to stability of the hemiformal bonds was made.

INTRODUCTION

In spite of many years studies, the phenol–formaldehyde resins still remain an interesting object of research. The most interesting problem is to determine the resin structure and to examine their curing process.

In the structure studies, a variety of analytical methods were used. Among them, NMR provides the most data on the main functional groups which are present in the resin and it gives the possibility to determine the average molecular weight.[1-6]

The studies on the curing process of phenol–formaldehyde resin using DTA technique were initiated by White and Rust[7] and by Katovič.[8,9] The introduction of pressure-proof crucibles in the thermal analysis[10] resulted in a general application of DSC (DTA) in the studies on curing processes of phenol–formaldehyde resins, and particularly of resol resins.[3,12-16]

In the precited works a kinetic analysis of the curing process is carried out, an account is given on the effect of pH of resin, of the catalysts, and of the modifying additives on the process. However, in the works which were published up to the present, there is a scarcity of information on the studies on the aging process of the resins when they are stored in the form of a solution at room temperature.

The latter subject has been taken into consideration in the present work. The aqueous solution of the highly condensed resol resin was investigated. The nature of the changes which take place in the resin during storage was educed on the ground of:

—the curing process of heat measurements by DTA
—the quantitative assignations of the structural elements by NMR

EXPERIMENTAL

The object of the studies on the aging process was a highly condensed resol-type resin which had been prepared on a bench scale, according

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to a process developed by the Institute of Heavy Organic Synthesis "Blachownia."[17] The latter process has been applied on a commercial scale to produce some adhesives. The synthesis of the said resin consists in a few stages of phenol and formaldehyde addition (in a molar ratio of 1 : 2.4) in an aqueous solution in presence of an NaOH catalyst. The resin obtained in form of a ca. 37% aqueous solution having an initial viscosity of 358 cP was stored at room temperature in a closed bottle made of a dark glass.

Differential Thermal Analysis

The run of the curing process of the resin was examined using DTA method. TA 2000A Mettler DTA apparatus with stainless steel, pressure-proof crucibles (vol 0.5 cm^3) was used. The DTA experiments were carried out in a closed crucible at a temperature range of 30–200°C. The heating rate was 2°C/min. The resin solution was put into the crucible in an amount of 100 mg. Water in a closed crucible was used as a reference, to prevent the DTA base line drift owing to the heat necessary to keep the vapor–liquid quasiequilibrium inside the sample crucible.[18,19] To calibrate the DTA apparatus, indium was used. The total heat capacities of the both crucibles as well as in calibration procedure and in measurements of the cure process were the same.

Nuclear Magnetic Resonance

The NMR analyses of the resin were made using a R-24A-type spectrometer (Hitachi-Perkin-Elmer). These analyses required an adequate preparation of samples. To this end, the resin was dehydrated at 5°C under a vacuum of 5 mm Hg during several hours. The dehydrated resin was subjected to an acetylation process using acetic acid anhydride in pyridine according to the prescription given by Higginbottom et al.[20] The acetylated resin was extracted by carbon tetrachloride. The extract was analyzed by means of ^{1}H-NMR.

RESULTS AND DISCUSSION

The resin curing process which proceeds during the warming up of an aqueous solution of the resin is visible on the DTA curve in the form of two overlapping exothermic peaks (Fig. 1):

(I) at a temperature range of 60–180°C.
(II) at a temperature range of 100–120°C.

The shape and the size of these peaks change with the storage time. Initially, in a fresh resin, the stage II proceeds with a small intensity. It becomes more and more pronounced when storage time increases. The dependences of the total heat of the curing process (Q_t as a sum of effects I and II) and of the heat of the separated effect II (Q_1) on the resin storage time are shown in Figure 2. It was found that Q_t decreased in a directly proportional way to the time:

$$Q_t = Q_{t,0} - at$$

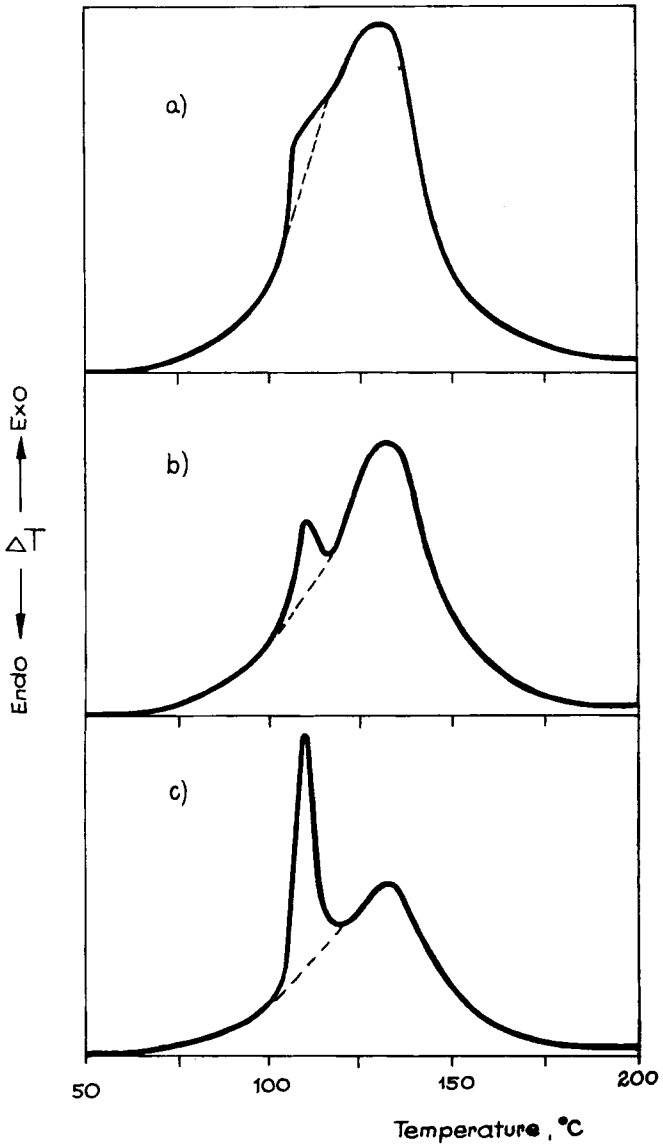


Fig. 1. DTA curves of the resin: (a) at the day of synthesis; (b) 45 days after synthesis; (c) 115 days after synthesis.

where $Q_{t,0}$ is the resin curing heat at the day of the synthesis, whereas the direction coefficient a represents the aging rate. At the gelation moment of the resin solution (vanishing of the liquid behavior), Q_t has a magnitude of $Q_{t,g} = 105$ kJ/kg, which is characteristic for the resins of this type.[21] Thus, the knowledge of this value and the determination of $Q_{t,0}$ and of the coefficient a provides a possibility of foreseeing the time during which the resol resin will keep a liquid form.

The decrease of the total heat effect of the cure process of the resin is a result of some polycondensation reactions which proceed during the storage.

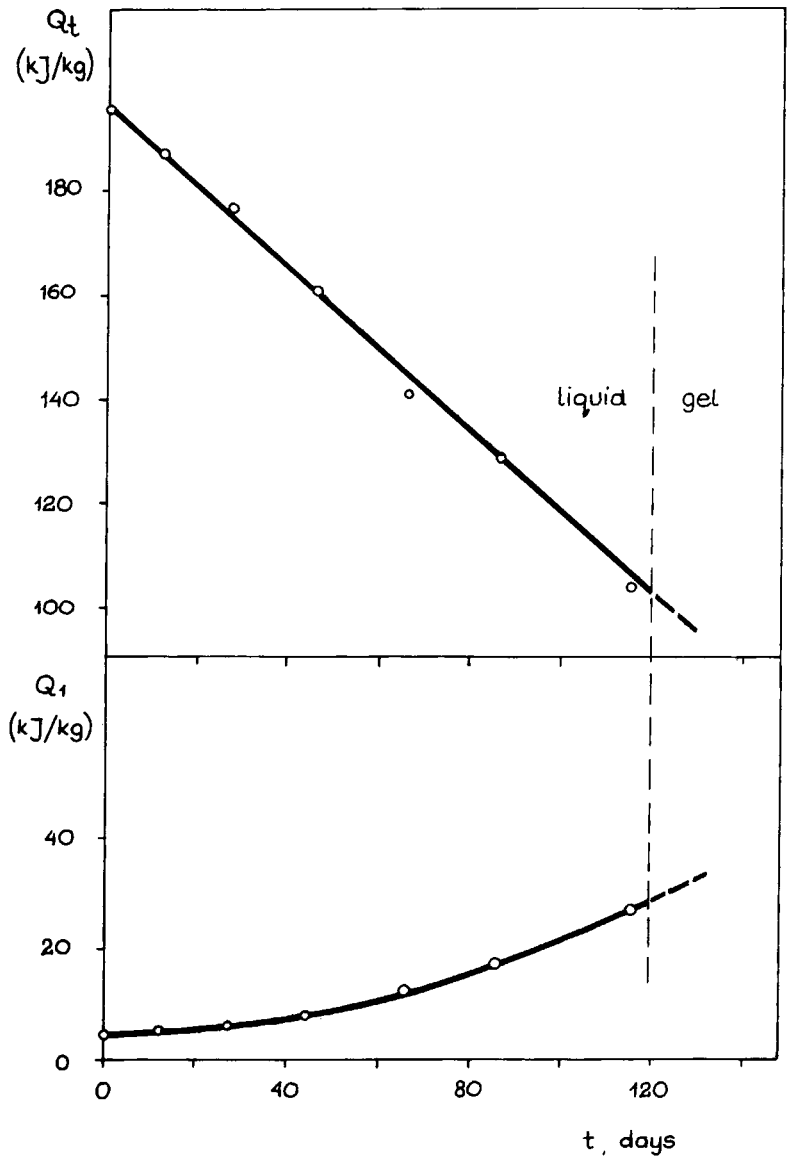


Fig. 2. Dependence of the total heat effect of the curing process (Q_t) and of the heat effect at a temperature range of 100–120°C (Q_1) on storage time.

However, there is an interesting change in the resin thermal cure process, i.e., the increase of the heat effect (Q_1) at a temperature range of 100–120°C. This proves that some modifications of the resin structure take place during storage.

The structure and the size of the "mean molecule" of the resin were found from NMR analysis. Based on the data given by Woodbrey et al.,[1] the number of rings and the molecular weight of the "mean molecule," as well as the number and the type of functional groups, were found. Table I shows the results of this analysis for a fresh resin as compared with those obtained 45

TABLE I
Structure Characteristics of the Resin According to ^{1}H-NMR

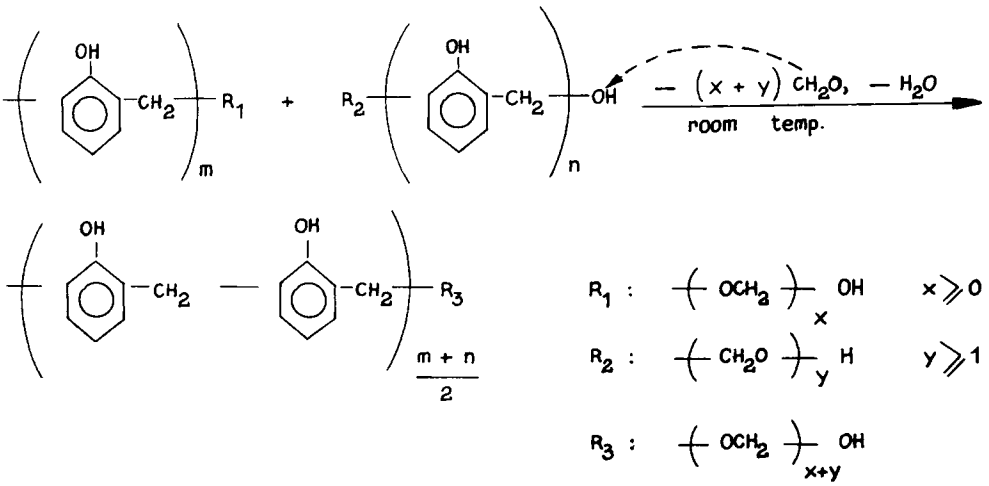
Number of days after synthesis	"Mean molecule"		Number of functional groups per one phenol ring		
	Number of phenol rings	Molecular weight	Methylol groups	Hemiformal groups	Methylene bridges
0	6.06	871	1.23	0.064	0.84
12	7.28	1040	1.18	0.076	0.86
27	8.70	1235	1.08	0.089	0.90
45	10.24	1444	1.01	0.094	0.92

days after. It is evident that the average molecular weight and the number of hemiformal bonds and of methylene bridges increase, whereas the number of the methylol groups decreases during the storage. The presence of any ether bridges was not in evidence.

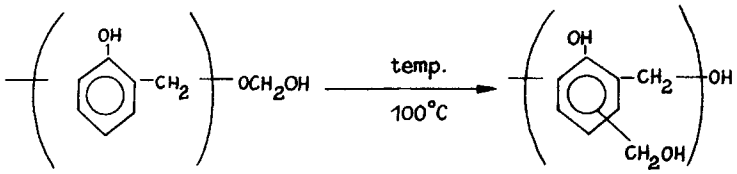
The obtained results confirm that the polycondensation reactions occur in the storage resin at ambient temperature. The reactions between the methylol and/or hemiformal groups must take place. Methylene bridges are formed and water and formaldehyde are eliminated. One should suppose that the formaldehyde is attached to the methylol groups forming hemiformal bonds again.

During warming up, the hemiformals are most probably the subject to a decomposition already at relatively low temperatures. The formaldehyde which is formed during this decomposition may be bonded to the free position of the phenol rings in the partly cured resin. Thus, the methylol bonds are formed which are partly unable, for steric reasons, to enter into further reactions. The above hypothetical interpretation could elucidate the existence of the exothermic effect at a temperature range of 100–120°C.

The study of Woodbrey et al.[1] gives an indirect confirmation of the said reasoning. These authors have ascertained the presence of hemiformals in the



Scheme 1.



Scheme 2.

resin synthesized at a temperature range of 60–95°C, and an absence of hemiformals in the resins synthesized at a temperature of 105°C. These observations and our interpretation of the results of this work let us make a hypothesis that the hemiformal bonds are unstable at temperatures above 100°C.

CONCLUSION

From the described study a conclusion may be drawn that the aging of the highly condensated resol resin is predominantly the consequence of the behavior of hemiformal groups. During the storage of the resin solution at room temperature, hemiformal groups undergo some slow polycondensation reactions and methylene bridges are formed. Formaldehyde which is eliminated during these reactions forms new hemiformal groups that are able to undergo the subsequent polycondensation reactions.

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