Synthesis of novolac resins: 2. Influence of the reaction medium on the properties of the novolac oligomers

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The polycondensation of *m*-cresol with formaldehyde catalysed by oxalic acid in the presence of water-miscible organic solvent was investigated. The influence of the reagents' molar ratio and the effect of the nature and quantity of the solvent used on the molecular weight characteristics of the oligomers formed and on the content of free (waste) cresol therein and their softening temperatures were studied. It was established that the presence of water-miscible organic solvent causes a significant change in the viscosity of the reaction mixture and strongly affects the characteristics of the polycondensation process. The possible reasons for this influence are discussed. On the basis of the experiments performed an attempt was made to survey the interconnection between different individual factors affecting the polycondensation of cresols and formaldehyde.

(Keywords: polycondensation; reaction medium; *m*-cresol; novolac resins; properties)

INTRODUCTION

The novolac oligomers are widely used in contemporary microlithography as a key component in photoresist compositions[1]. Important technological characteristics of the photoresists (sensitivity, contrast, thermal durability etc.) are influenced by the physical and chemical properties of their novolac ingredients[2,3]. On the other hand, the features of these polymers are affected by the synthetic route used for their formation. In a previous study[4] we published data on the influence of the isomeric composition of cresol mixtures on cresol–formaldehyde polycondensation.

There are different opinions regarding the effect of organic solvents on the rate and yield of polycondensation[5] and the influence of methanol content in the formaldehyde solution on the characteristics of the phenol–formaldehyde polycondensation process[6,7]. There have been few studies on the synthesis of cresol–formaldehyde oligomers in the presence of water-miscible organic solvents and their influence on the properties of the products obtained.

The aim of the present investigation was to study the influence of the composition of the reaction medium on the yield, molecular weight characteristics and softening temperature of oligomers formed during the polycondensation of *m*-cresol and formaldehyde. In the experiments different amounts of several solvents and their mixtures were used.

EXPERIMENTAL

Materials

m-Cresol (Riedel de Haen) was distilled prior to use. Paraformaldehyde (Merck), oxalic acid (Factory for Pure Reagents 'Krasnaya Zvezda', Vladaya, Bulgaria), methanol, ethanol, dioxane (Poch, Poland) were p.a. grade and were used without additional purification.

Methods

The polycondensation was performed as described previously[8]. The organic solvents or their mixtures were introduced into the reaction vessel 30 min after the system reached boiling temperature. The oligomers formed were isolated from the reaction mixture by precipitation in water and successive filtration and desiccation according to ref. 4.

The molecular weights ($\bar{M}_w$) and molecular weight distribution (I_p) of the polymers were determined by gel permeation chromatography (g.p.c.) using Waters GPC III apparatus with an automatic injector (WISP 712) and set of three Shodex columns (GPC/KT 801, 802.5, 803). The analyses were carried out at 40°C. Tetrahydrofuran was used as an eluent at flow rate 1 ml min^{-1}. The data were calculated using polystyrene standards and Waters Expert™ Software, version 6.2 on Waters M860 data station.

The content of free (waste) cresol was established using the bromide–bromate method[9], and the softening temperature was determined by the ball and ring method[10].

RESULTS AND DISCUSSION

Formalin stabilized with different amounts of methanol is commonly used as a formaldehyde source in the synthesis of novolac oligomers. The influence of the concentration of the formalin solution and the content of methanol therein on the degree of conversion and rate of polycondensation has been described[6,7], but there are

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no data concerning the influence of those factors on the molecular weight characteristics of the oligomers formed.

The first series of experiments investigated the influence of a water-miscible organic solvent (ethanol) on certain properties of novolac cresol–formaldehyde oligomers. Comparative experiments without added solvent were also carried out. Oxalic acid in quantities of 0.001 mol per mol cresol was used as catalyst. The results are presented in *Figures 1* and *2*. Obviously the addition of ethanol to the reaction mixture causes an increase in the molecular weight and polydispersity of the novolac oligomers obtained. This effect is particularly pronounced at near equimolar ratios of cresol to formaldehyde (*Figure 1*). The reactivity of the cresol component during polycondensation is higher; the molecular weight is significantly increased as is the softening temperature of the polymer formed (*Figure 2*). The positive influence of the

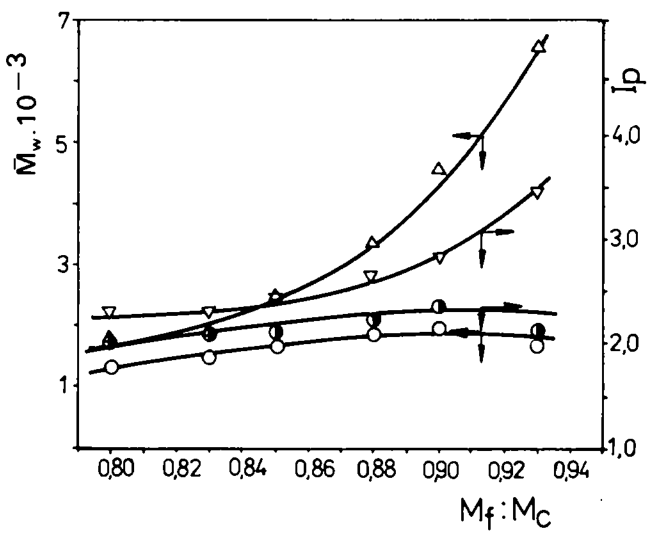


Figure 1 Dependence of the weight average molecular weight ($\bar{M}_w$) and polydispersity index (I_p) of cresol–formaldehyde oligomers, formed in the presence of ethanol (△, ▽) and without ethanol (○, ◑) in the reaction mixture, on the ratio of formaldehyde to cresol (M_f:M_c)

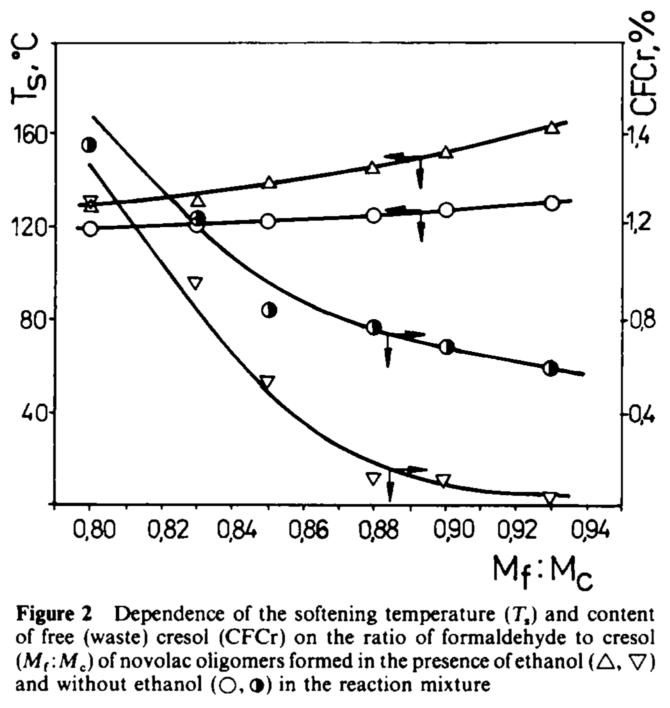


Figure 2 Dependence of the softening temperature (T_s) and content of free (waste) cresol (CFCr) on the ratio of formaldehyde to cresol (M_f:M_c) of novolac oligomers formed in the presence of ethanol (△, ▽) and without ethanol (○, ◑) in the reaction mixture

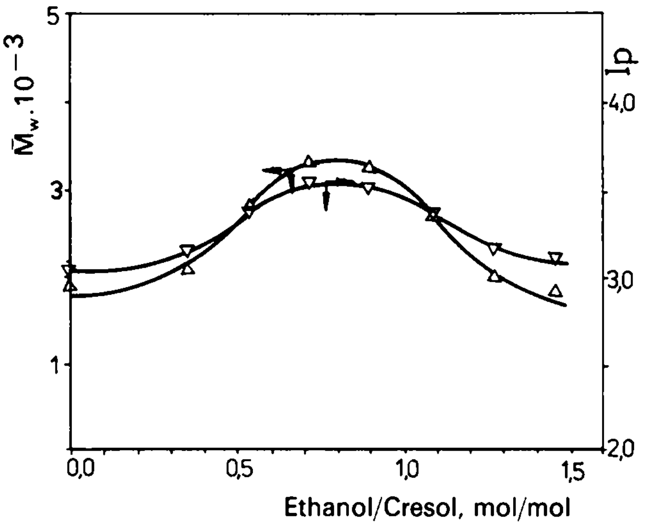


Figure 3 Dependence of the weight average molecular weight ($\bar{M}_w$) and polydispersity index (I_p) of cresol–formaldehyde oligomers on the quantity of the ethanol added to the reaction mixture

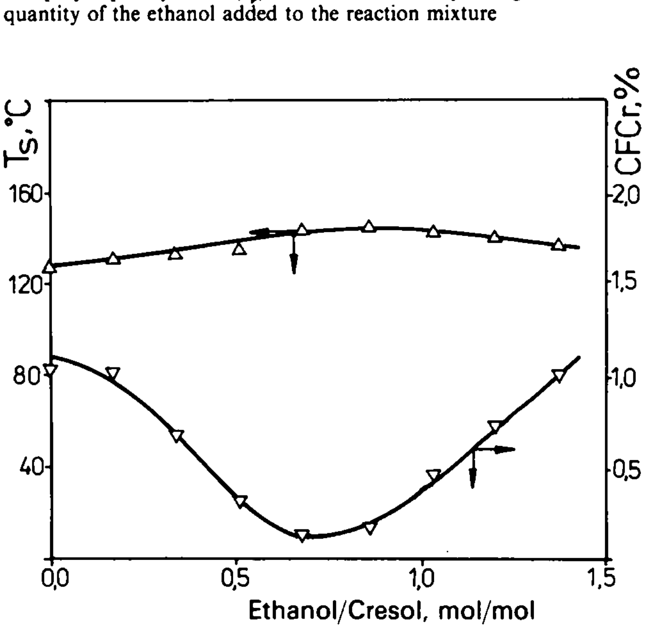


Figure 4 Dependence of the softening temperature (T_s) and content of free (waste) cresol (CFCr) on the quantity of ethanol added to the reaction mixture

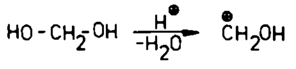
alcohol on the polycondensation process could be explained by its ability to improve the homogeneity of the reaction mixture and to decrease its viscosity.

In the experiments without added ethanol, the viscosity of the reaction medium is much higher, especially near equimolar reagent ratios. This probably decreases the mobility of the reacting molecules and leads to insufficient interaction of species resulting in lower molecular weights of the oligomers (*Figure 1*).

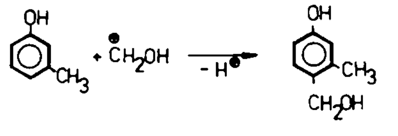
In the next series of experiments, the influence of the concentration of ethanol introduced into the reaction mixture on these parameters was studied in some detail. The experiments were performed at a formaldehyde/cresol ratio of 0.88. The results are presented in *Figures 3* and *4*.

The dependences established (*Figures 3* and *4*) have clearly expressed maxima in the region around 0.34 mol ethanol per mol cresol. This suggests that two types of competitive process are taking place, with opposite influences on the polycondensation.

The first group of processes, united by the so-called first factor, include the formation of methylol cations and methylol derivatives of cresol, from which novolac oligomers are formed via many parallel and consecutive reactions (reactions (1)–(3)). Decreasing the viscosity of the reaction mixture favourably influences these reactions.



(1)



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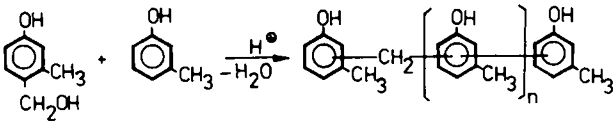
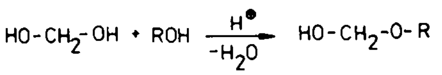


(3)



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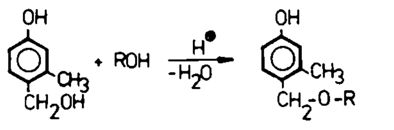

(5)

The second group of processes, united around the so-called second factor, includes the side reactions (reactions (4) and (5)) which hinder the formation of novolac end products. The negative action of processes included in the second factor is enhanced with the decrease in the concentration of reagents, i.e. with the increase of the amount of solvent added.

In *Tables 1* and *2* an attempt is made to summarize the individual elements of both factors and to explain their influence on the characteristics of novolac oligomers. On this basis the dependences shown in *Figures 5* and *6* might be explained as follows.

The introduction of solvent leads to a decrease in the viscosity of the reaction mixture (*Figures 7* and *8*) and improves its homogeneity. This increases the rate of polycondensation and leads to formation of products

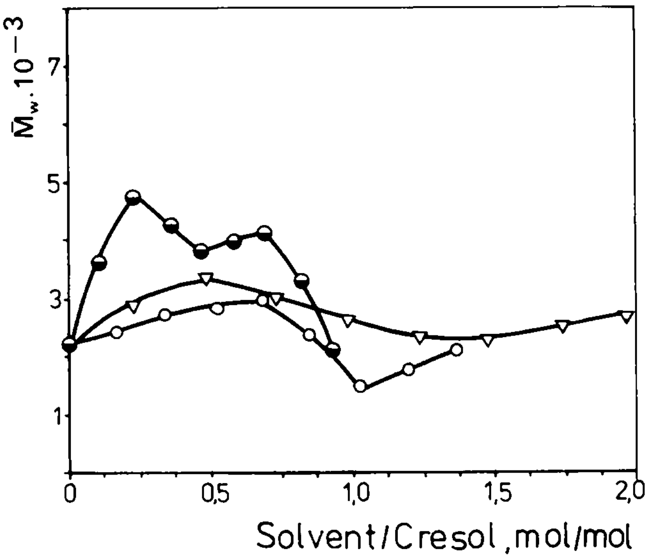

Figure 5 Dependence of the weight average molecular weight ($\bar{M}_w$) on the quantity of ethanol (○), methanol (▽) and dioxane (◒) added to the reaction mixture

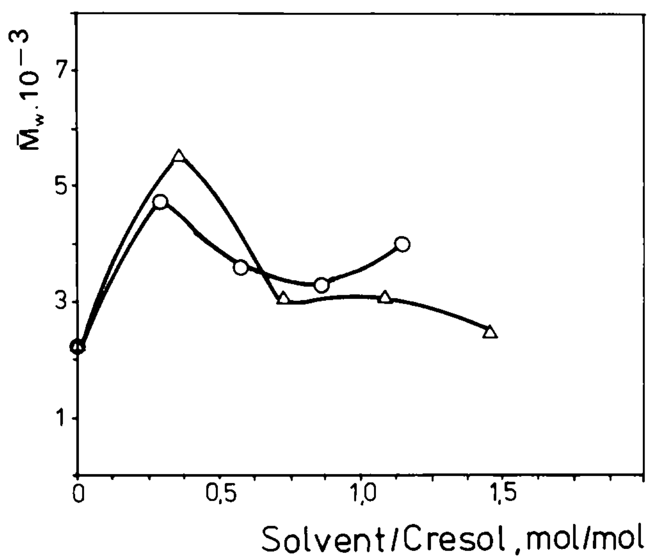

Figure 6 Dependence of the weight average molecular weight ($\bar{M}_w$) on the quantity of the 1:1 mixtures of ethanol/dioxane (○) and methanol/dioxane (△) added to the reaction mixture

Table 1 Dependence of the parameters of reaction mixture on the quantity of organic solvent added[a]

Parameters	Increase in quantity of solvent in the reaction mixture	Increase of ratio solvent/precipitant
Viscosity	<, (+)	>, (+)
Monomer concentration	<, (−)	<, (−)
Effective concentration	>, (+)	>, (+, −)
Side reactions	>, (−)	

[a] > = increases; < = decreases; (+) = improves; (−) = deteriorates

Table 2 Dependence of the properties of novolac oligomers on the parameters of the reaction mixture[a]

Parameters	Concentration of free cresol in the reaction mixture	Softening temperature	M_w (g.p.c.)	I_p (g.p.c.)
Viscosity, <	<, (+)	>, (+)	>, (+)	>, (−)
Monomers concentration, <	<, (+)	>, (+)	>, (+)	<, (+)
Effective concentration, >	<, (+)	>, (+)	>, (+)	<, (+)
Side reactions, >,	>, (−)	<, (−)	<, (−)	<, (−)

[a] > = increases; < = decreases, (+) = improves; (−) = deteriorates

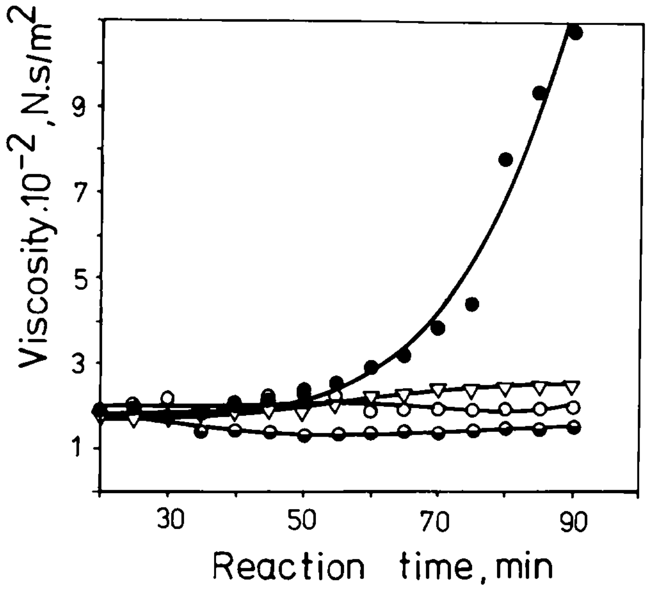

Figure 7 Time dependence of the viscosity of the reaction medium on the type of solvent added: ●, without solvent; ▽, with methanol; ○, with ethanol; ○, with dioxane

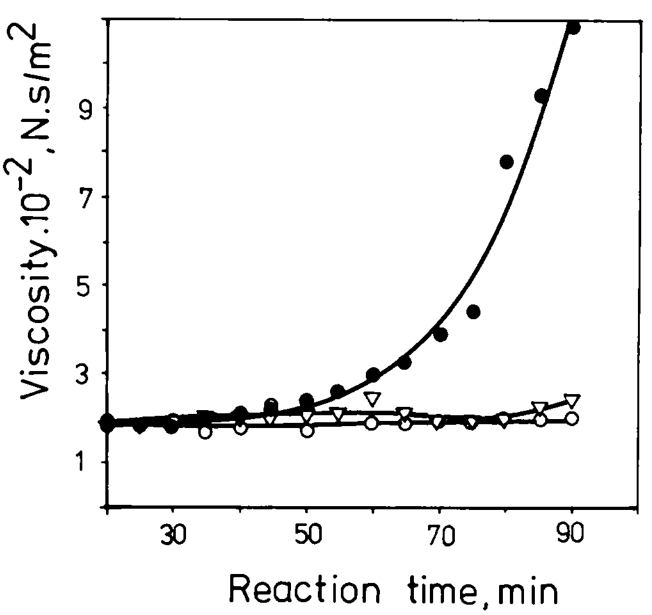

Figure 8 Time dependence of the viscosity of the reaction medium on the type of solvent mixture added: ●, without solvent; ▽, methanol/dioxane (1:1); ○, ethanol/dioxane (1:1)

with higher molecular weights (the first maximum in the curves appears). The following increase in the quantity of solvent added decreases the reagents' concentration and therefore should decrease the rate of polycondensation. This is confirmed by the lower molecular weights of the oligomers obtained. The solvent/precipitant ratio is still not high enough and the macromolecules in the solution are still in a globular form[11]. This hinders diffusion of reagents to the active sites of the polymer chains.

The increase in the quantity of solvent changes the solvent/water ratio in the reaction medium and probably causes swelling of the macromolecular globules. In spite of the decrease in the overall concentration of reagents and oligomer in the reaction mixture, this swelling enables, to a certain extent, the penetration of reagents to more active centres in the propagating polymer chains and increases their effective local concentration. This is the probable reason for the appearance of the second maximum in the molecular weights observed in *Figures 5* and *6*.

The values of the observed maxima decrease in the order dioxane > methanol > ethanol. This could be explained by the different chemical nature of the solvents used, the alcohols being involved in side reactions (4) and (5). That is why the addition of dioxane, which is not able to participate in the side reactions, leads to formation of oligomers with the highest molecular weights.

CONCLUSIONS

The introduction of organic solvents that are miscible with water during the polycondensation of cresol and formaldehyde results in higher conversion of reagents and formation of oligomers with higher molecular weights.

Dioxane, ethanol and methanol might be used as effective regulators of the molecular weight characteristics of the cresol–formaldehyde oligomers formed.

Addition of mixtures of the above-mentioned organic solvents has a synergistic effect on the molecular weights of the polymers obtained.

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