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Cyclohexanone-aniline-formaldehyde resins — synthesis and characterization

Summary — Cyclohexanone-aniline-formaldehyde resins, which contain functional groups in the polymeric chain, were prepared by acid catalysis condensation. Mixture of toluene and N-methylpyrrolidone was used both as reaction medium and as carrier for aqueous condensation. The resins were characterized by determination of melting points, viscosity measurement and elemental analysis (contents of nitrogen, N%). Their structure was established by means of IR and ^{1}H NMR spectroscopy. The obtained polymers have low molecular weights and a moderate solubility in medium and highly polar organic solvents. Thermal studies pointed out that these polymers undergo 2—5% weight loss up to 210°C for resins with low content of aniline, whereas weight loss starts at 220—240°C for resins with low content in cyclohexanone. Activation energy for the thermal degradation is observed to be within the range 37.6—41.7 kJ/mol.
Key words: aniline, cyclohexanone, formaldehyde resins.

Formaldehyde resins represent a major class of polymers with a large variety of applications in the field of coating, mechanical, electrical and electronical industries, because of their good thermal, mechanical and electrical properties. These important properties are directly dependent on chemical structure of monomers used in synthesis. A wide variety of monomers, such as phenols, substituted phenols, aromatic amines, polyphenols, cyclohexanone, urea, melamine and so on, were used as raw materials in the preparation of these polymers [1—4].

Acid and base catalysts were used in the preparation of formaldehyde resins and polymers with or without reactive groups resulted. Presence of reactive groups in the polymeric chain allows to modify properties of high molecular weight polymers when used in different blends.

Literature data indicate that a large majority of aniline-formaldehyde resins are obtained through acid catalysis at a molar ratio formaldehyde:aniline ≥ 1 [5—10]. Usually, cyclohexanone-fomaldehyde resins are synthesized in the presence of a base catalyst [10—19]. Only a single literature citation was found on the synthesis of a cyclohexanone-fomaldehyde resin through acid cataly-sis [20]. The syntheses of a cyclohexanone-aniline-fomaldehyde resin have not been presented, yet.

This paper describes the synthesis and characterization of a new type of formaldehyde resins, which contain both cyclohexanone and aniline in their structure. Our interest in those resins results from their application as cross-linking agents for epoxy resins, hence we investigated their thermal properties.

EXPERIMENTAL

Materials

Cyclohexanone (CH_x), N-methylpyrrolidone (NMP) and toluene (solvents) as well as p-toluene sulfonic acid monohydrate (PTSA) were analytical grade products. Paraformaldehyde (p-FA, source of formaldehyde), was 98% purity. Aniline (AN, analytical grade) was distilled before use.

Synthesis of cyclohexanone-aniline-formaldehyde resins

Synthesis of the resins was conducted in acid catalysis (PTSA, 3% w/w). Condensation conditions are summarized in Table 1. In a representative experiment, a three-necked reaction flask fitted with mechanical stirrer, thermometer and water condenser was charged with

48 g (0.5 mole) cyclohexanone, 46.6 g (0.5 mole) aniline, 30 g (1.0 mole) p-formaldehyde and 25 g of mixture of toluene and NMP (1:1) (20% w/w), heated in a thermostatic oil bath at 80°C, and the catalyst was added. An exothermic effect was observed after a short time, and temperature rose up to 95°C. The reaction mass was kept at reflux for 1.5 hours. Then, a Dean-Stark separator was fitted at the top of the water condenser and the mixture was refluxed for another 1.5 hours. Removal of reaction water caused temperature to increase up to 130°C. Finally, the reaction mass was washed with distilled water to neutral reaction, and decanted. Residual water and toluene were distilled under vacuum at 120°C.

Measurements

IR spectra were recorded by means of a Specord M80 (Carl Zeiss) spectrophotometer using KBr pellets.

^{1}H NMR spectra were carried out with the aid of JEOL-JNMC 60HL (Japan) equipment at 50°C in CDCl$_3$ or DMSO d$_6$, using tetramethylsilane as internal standard.

Relative viscosity was determined in a 0.5% g · mL^{-1} DMSO solution, at 20°C with an Ubbelhode viscometer.

A Hungarian MOM derivatograph of Paulik, Paulik-Erdey type at heating rate of 12°C · min^{-1} in air was used to perform thermal studies.
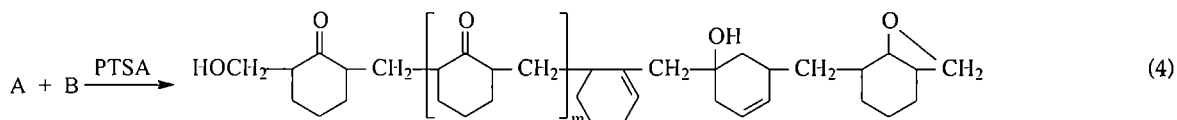
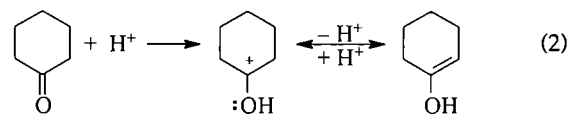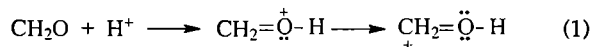Melting points were determined by means of a microscope with heated plate.

RESULTS AND DISCUSSION

Condensation reaction between cyclohexanone, aniline and formaldehyde in acid catalysis (PTSA) was conducted at various molar ratios, in the presence of mixture of toluene:NMP (1:1) as solvents and carrier for reaction water. Condensation conditions and the main characteristics of the obtained resins are summarized in the Table 1.

T a b l e 1. Synthesis and physical properties of cyclohexanone--aniline-formaldehyde resin[*]

Sample	Molar ratio (AN:CH$_x$:p-F)	Nitrogen content %	Color	Relative viscosity	Melting point °C
1	1:0:1	13.91	dark red-brown	1.046	114
2	0.75:0.25:1	8.03	red-brown	1.020	129
3	0.5:0.5:1	5.56	pale red-brown	1.021	123
4	0.25:0.75:1	2.80	pale red-brown	1.036	121
5	0:1:1	0.00	white	1.016	140

[*] Solvent (toluene:NMP = 1:1) — 20% w/w, catalyst (PTSA) — 3% w/w.

$$CH_2O + H^+ \longrightarrow CH_2=\overset{+}{\underset{..}{O}}\text{-}H \longrightarrow CH_2=\overset{..}{\underset{+}{O}}\text{-}H \qquad (1)$$

$$(2)$$

First stage of the reaction proceeds with both substrates reacting with catalyst proton [reactions (1) and (2)] in the presence of small quantities of PTSA and at stoichiometric ratio of cyclohexanone and formaldehyde (sample 5). The methylenic component transforms into an enol derivative capable of reacting with the carbonyl component at the double bound. The resulting alcohol eliminates water and probably reacts into a cyclic ether or an aldol [reaction (3)]. Those products are rapidly transformed into a long chain through polycondensation

$$(3)$$

$$(4)$$
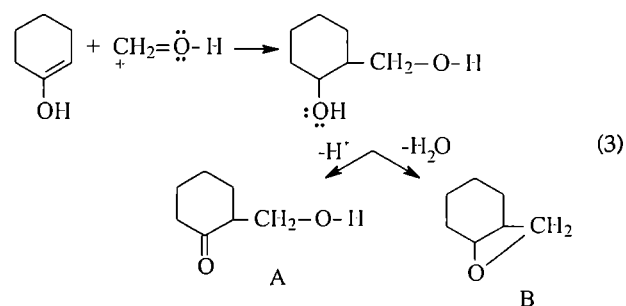
by splitting off water, resulting in a cyclohexanone-formaldehyde resin. Probably, the resins contain a cyclic ether group at end of the polymeric chain [reaction (4)].

Condensation of aniline with formaldehyde at molar ratio 1:1 (sample 1), in the presence of small amount of acid catalyst initially proceeds through formation of an unstable N-methylol aniline compound that rapidly rearranges into "anhydroformaldehyde aniline" by splitting off water [6, 7]. Next, the product reacts with another aniline molecule and rearranges into a polymer with methylene bridges between aromatic rings [reactions (5) and (6)].

$$(5)$$
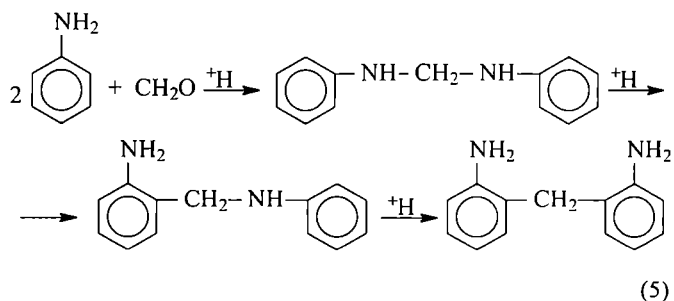
A system consisting of cyclohexanone, aniline and formaldehyde undergoes the following reactions:

(6)

n = 0—2

(10)
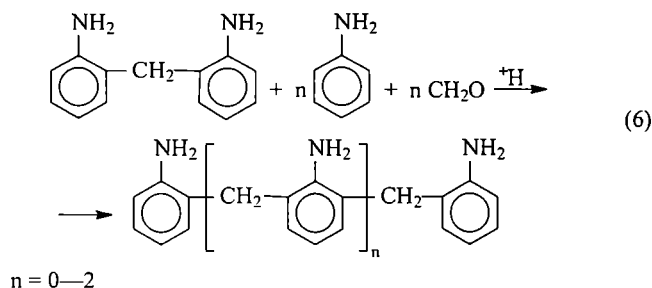
— Initially acidic catalysis causes the enolic forms of cyclohexanone [see reaction (2)] to react with methylene ammonium salt to form mono (A) and bis (B) Mannich type bases [reactions (7)—(9)]. Formation of a mono

(7)

(11)

(8)

A

(9)

B
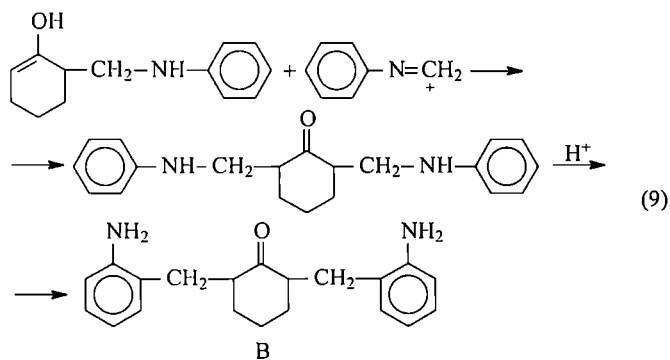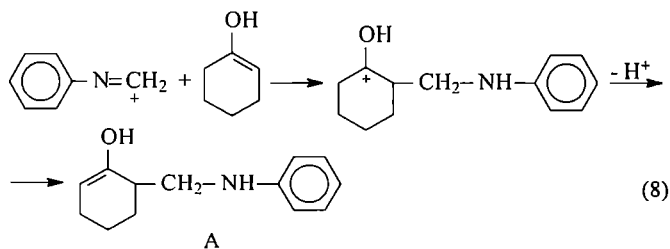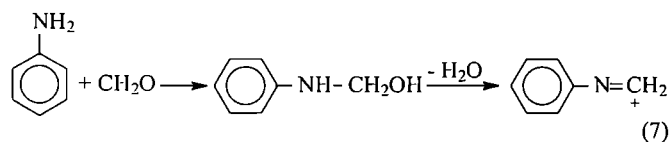
Mannich base is more probable when the cyclohexanone:aniline ratio is ≥ 1. A mixture of mono and bis Mannich bases is formed when the aniline is in high excess [21, 22].

— Next, the mono and bis Mannich type bases, react (in presence of acid catalysis) with CH_2O and with the excess of cyclohexanone or aniline, rearranging into a polymer with methylene bridges between aromatic rings and/or cyclohexanone rings [reactions (10) and (11)]. Polymers obtained from mono and bis Mannich bases and aniline are the most probable alternate polymers [reaction (11)]. Polymers obtained from mono Mannich base and cyclohexanone are random copolymers [reaction (10)].

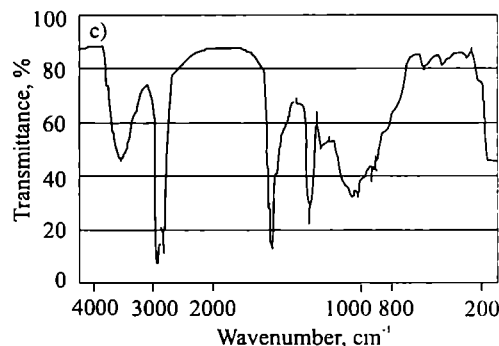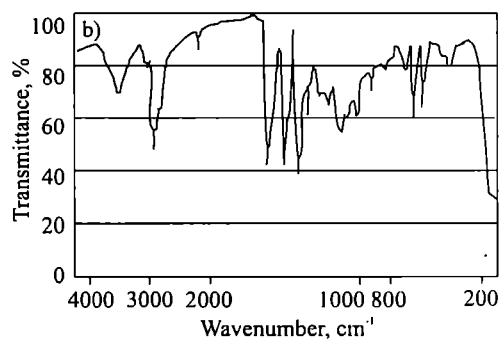Condensation products are solid materials, brittle, color changing from white (cyclohehanone-formalde-
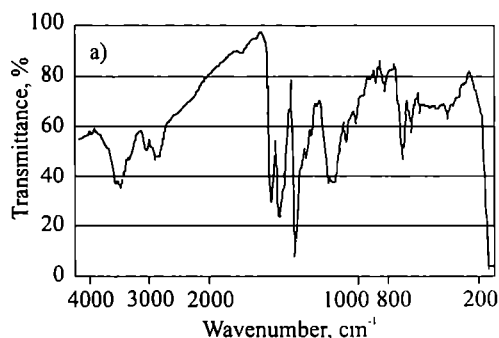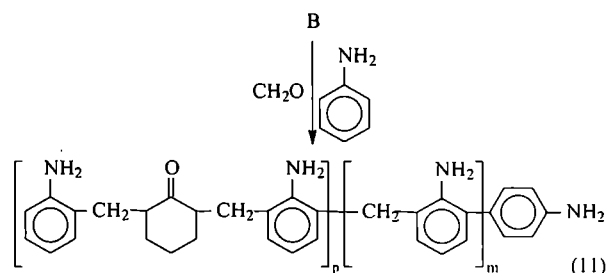

Fig. 1. IR spectra: aniline-formaldehyde resin (a, sample 1); cyclohexanone-aniline-formaldehyde resin (b, sample 3); cyclohexanone-formaldehyde resin (c, sample 5)

hyde resin — sample 5, *cf.* Table 1) to dark red-brown (sample 1) with the increase of aniline content. The resins are well soluble in polar solvents (CHCl3, DMSO, DMF, NMP), soluble in aromatic solvents and insoluble in MeOH and petroleum ether.

Structures of these resins were confirmed using IR, ^{1}H NMR spectroscopy and elemental analysis (N%). IR spectra (Fig. 1) show an intense band situated at 3450 cm^{-1}, which is specific for OH, NH, NH2 groups present in the structure of the resins. The specific peak to the symmetric and asymmetric vibrations of CH2 groups located in the cyclohexanone ring is situated at 2850—2950 cm^{-1} and appeared only in the resins that contain cyclohexanone in the structure. Resins containing aniline in the structure exhibit specific vibrations characteristic for substituted benzene at 820, 750, 700 cm^{-1}.
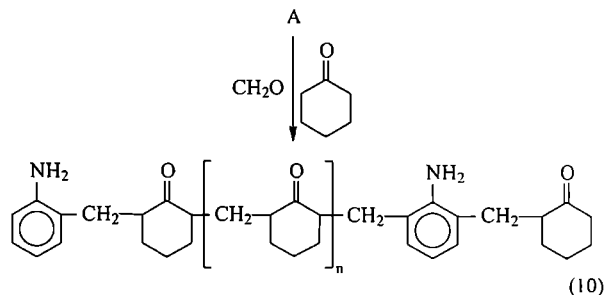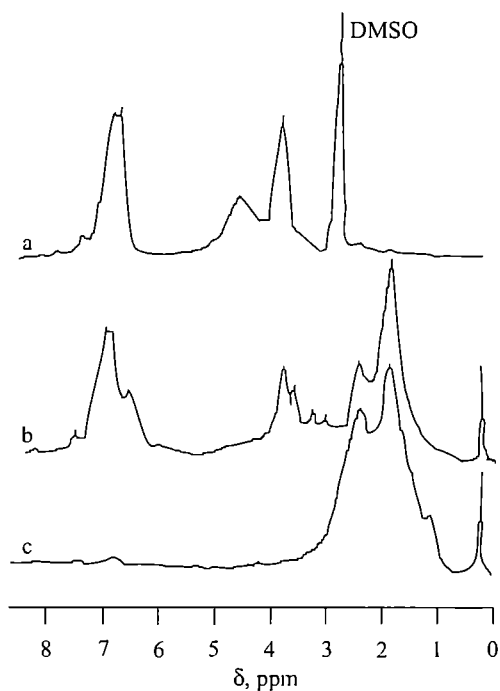

Fig. 2. ^{1}H NMR spectra: aniline-formaldehyde resin (a, sample 1); cyclohexanone-aniline-formaldehyde resin (b, sample 3); cyclohexanone-formaldehyde resin (c, sample 5)

The resins were also analyzed by ^{1}H NMR spectroscopy (Fig. 2). Thus, major signals for pure cyclohexanone resins (Fig. 2c) are situated in the interval 1.2—2.3 ppm. The peak centered at 1.6 ppm represents ring methylene groups adjacent to the carbonyl group. Methylene groups not adjacent to carbonyl groups, appear as several weak bands in the 2.2—4.4 ppm range. Major peaks for pure aniline-formaldehyde resins (Fig. 2a), are located in the 6.62—7.19 ppm range and are characteristic for aromatic protons of the benzene ring. ^{1}H NMR spectra of resins that contain both cyclohexanone and aniline (Fig. 2b), peaks located in the 1.2—2.3

ppm range are attributed to the cyclohexanone ring and peaks situated in the 6.42—7.3 ppm range are specific to aromatic protons of the aniline moiety. Methylene bridges, specific to formaldehyde resins are present in the 3.6—3.82 ppm range.
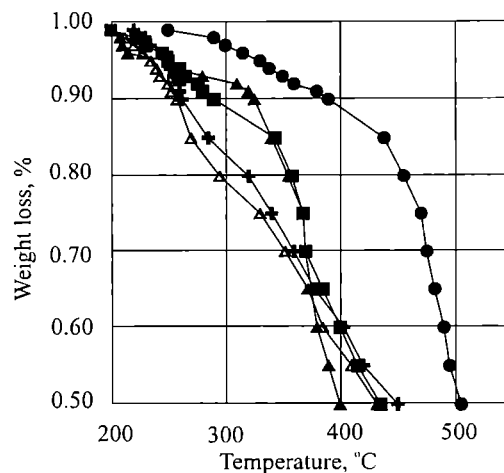

Fig. 3. TG curves for aniline-formaldehyde resin (● — sample 1), cyclohexanone-aniline-formaldehyde resins (△ — sample 2, ■ — sample 3, + — sample 4), cyclohexanone-formaldehyde resin (▲ — sample 5)

Table 2. Thermal parameters of cyclohexanone-aniline-formaldehyde resins

Sample (see Table 1)	Temperature, at which weight loss is equal		Weight loss at 500°C, %	Decomposition activation energy, kJ/mol
	10%	50%		
1	390	505	50	41.75
2	290	435	58	37.59
3	295	428	60	40.10
4	240	440	59	37.11
5	325	400	55	40.79

Figure 3 presents TG curves and the main characteristic parameters for decomposition of these resins are summarized in Table 2. Polymers with higher aniline content in the structure show an increase in weight (2%) in the first stage of decomposition, in the 80—180°C range. A possible explanation of this fact is that NH2 groups in the polymeric chain are oxidized. Such weight increase disappeared along with the increase in content of cyclohexanone moiety in the structure of these resins. TG curves and data presented in Table 2 show that in the 200—500°C range pure aniline-formaldehyde resins (sample 1) exhibit a high thermal stability in comparison with the cyclohexanone-aniline-formaldehyde resins. Decomposition of pure aniline-formaldehyde resins starts at 250 °C and weight loss reaches approximately 5%, up to 350°C. These results can be attributed to the high aromatic ring content of these polymers. However,

cyclohexanone-aniline-formaldehyde resins lose weight rapidly, during the initial stage of heating (between 200—300°C) and subsequently (above 400°C) weight loss exceeds 50%.

Relative thermal stability was quantitatively estimated with the activation energy of decomposition calculated using the Coats and Redfern method for an order of reaction $n = 1$ [23]. The values of $-\log[-\log(1-\alpha) \cdot T^{-2}]$ were plotted against reciprocal of decomposition temperature (K). Activation energies of decomposition were calculated from the slope of the straight lines and presented in Table 2. The data allow to conclude that cyclohexanone-aniline-formaldehyde resins have similar values of relative thermal stability.

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