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The Reaction Mechanism of the Transetherification and Crosslinking of Melamine Resins

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Summary: Melamine formaldehyde resins (MFR) are well known resins in the wood board and paper coating market. Etherified MFR´s are applied as crosslinkers in the automotive coating industry. In Europe the growth of the market and the research activities are relatively small. On the other side in comparison to other polymers outstanding properties are possible to realize. So the development of new melamine ether resins (MER) was started. MER is a partly methylolated and fully etherified resin with a highly stable "thermoplastic" processing range. The MER´s themselves are transparent granulates with enough stability for storage and transport. The crosslinking reaction can be started either by thermal or acidic catalytic activation, without losses of formaldehyde. Transetherifications with oligomeric diols can lead to more elastic and higher molecular melamine polyether resin (MPER) structures. The reaction mechanism and the crosslinking kinetics of the partly methylolated melamine ethers of methanol in comparison to the fully methylolated hexamethylol melamine ether will be discussed in this paper.

Keywords: crosslinking; FT-IR; kinetics; melamine formaldehyde resin; transetherification

Introduction

Melamine (2,4,6-triamino-1,3,5-triazine) was first prepared by J. v. Liebig in 1834. The structure of melamine and isomelamine was given by A.W. v. Hofmann (1885). The NH_2-groups of melamine - as well as those of urea - are highly reactive with aldehydes. The first developments of resins with formaldehyde were phenolic resins from the Bakelite corporation in 1910. Between 1940 and 1950 the start up of the first production plants of melamine

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formaldehyde resins (MFR) can be noted. The market profile was developed in the 1960s to 1980s and the product quality enhanced in this time. In the following years the progress in new MFR´s was modest.

The main application fields nowadays are wood particle boards and paper coatings for furniture, floors and as crosslinkers in automotive surface coatings.[1-4] The target to come to new applications assumes the development of new MFR grades with higher qualities, for instance increased elasticity and outdoor stability and the avoiding of the separation of free formaldehyde.

Recent developments are composite materials using natural fibers or glass fibers. New moulding materials can be processed by means of conventional fusion methods, as hot-melt adhesives and for producing plates, tubes, profiles and even injection moulded parts. [5] Today even MFR based fibers or foamed materials can be produced. The key to such new products is based in the knowledge of the structure-property relationships and the reactivities of the melamine resins.

Structure and Reactivity

The initial reaction of melamine with formaldehyde (FA) in aqueous solutions is possible in the whole pH-range (Fig. 1). Only the reaction rates of the several reaction steps are different. The addition of FA is always slow or very slow. In acidic medium the crosslinking reaction is very fast in comparison to the neutral or alkaline reaction medium. It is further to be mentioned that all the reactions follow an equilibrium condition so that the MFR in a water solution is a so called “living structure”, which means that the methylol groups can change positions on the different –N-H groups - they can crosslink or hydrolyse again. At defined temperature, concentrations and pH of the reaction we obtain a structure which can be defined by thermodynamic and kinetic parameters, but it remains stable only over a certain period of time. [6] With longer reaction times or even during storage the condensation reaction leads to resins with higher molecular masses. When this molecular mass is high enough, the condensates become insoluble. The precipitation leads to a shift of the whole equilibrium of the FA-addition to the insoluble resin.

So the storage time of the water based methylolated melamine is limited and they can only be stabilized by transformation into the solid state by the spray drying technology.

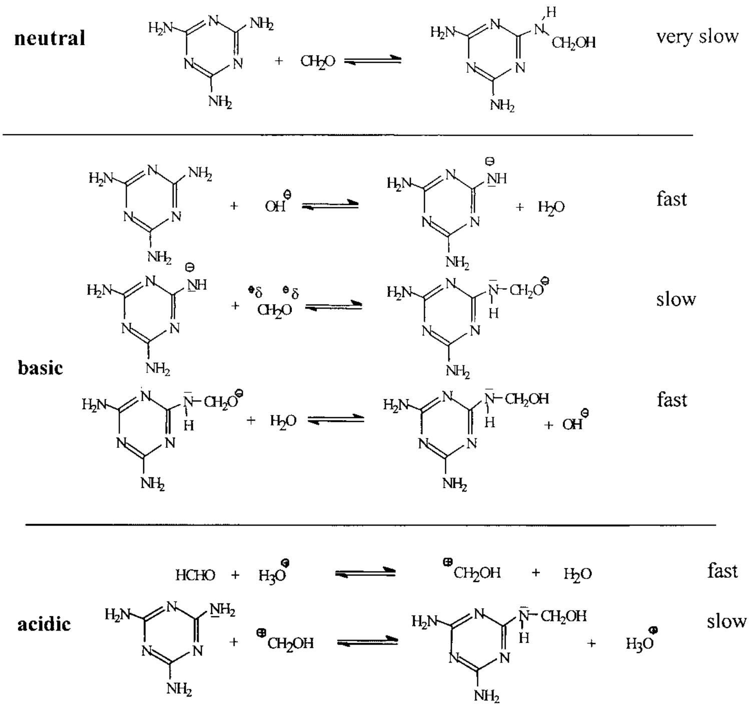
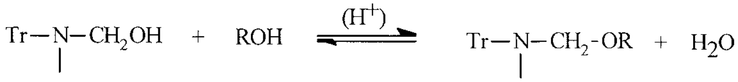


Figure 1. Reaction of melamine with formaldehyde

The reaction mechanism of the synthesis of MER and of the transetherification reaction

The structure of the water soluble methylol melamines can be stabilized by etherification (or acetalization) with alcohols. In most cases the used alcohol is methanol, followed by i-, n-butanol, i-, n-propanol, hexanol and octanol. The reaction is performed in acidic medium with a high excess of alcohol.

(1)



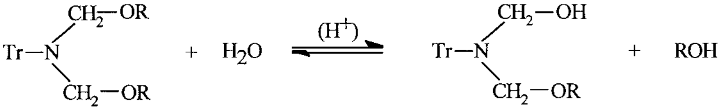
$$\mathrm{Tr{-}\underset{|}{N}{-}CH_2OH} + \mathrm{ROH} \xrightleftharpoons{(H^+)} \mathrm{Tr{-}\underset{|}{N}{-}CH_2\text{-}OR} + \mathrm{H_2O}$$

with Tr ... residual triazine ring

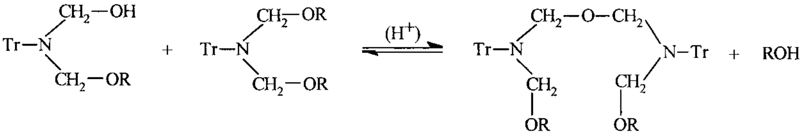
Depending on the methylol content of the basic MFR resins with three to six methylol ether groups can be synthesized. Hexa-(methoxymethyl-)melamine is a well defined crystalline chemical compound. Etherified resins are more hydrophobic and soluble in polar organic solvents. From this it is well to understand, that the etherified hexamethylol melamines, especially with higher alcohols are preferred as crosslinker in the car coating recipes. To yield hydrophobic structures and for good compatibility with the polyacrylic or the polyester resin a high content of ether groups is necessary. In comparison to tri-(methoxymethyl-)melamine they have a lower reactivity, therefore strong acid catalysts have to be applied for the crosslinking and coupling reactions with OH-groups of the polymer component in the varnishes.

It is well known that the crosslinking reaction in water starts with a splitting off of one ether group (2) and the possibility to crosslink (3):

(2)

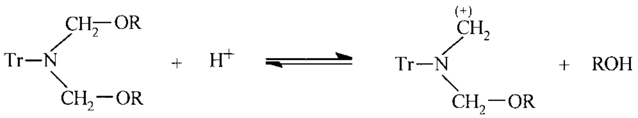


(3)



The reaction mechanism leads in the first step to a methylene cation as demonstrated in equ. (4). [7,8] In water the reaction leads to methylol groups (2). With polymeric alcohols (POH) the mixed polyether structure in equ. (5) is the result, that means a transetherification reaction has occurred. This reaction is very useful to synthesize melamine polyether resins (MPER).

(4)

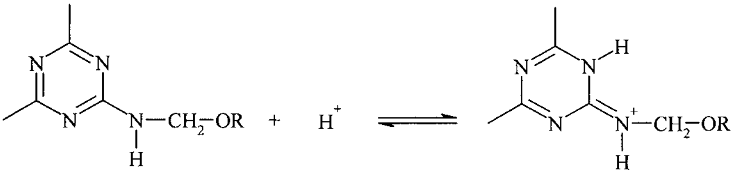


(5)

Contrary to the hexamethylol ethers of melamine, trimethylol ethers of melamine are reactive with a different reaction mechanism. Strong acids are not necessary for the crosslinking of those resins, actually at higher catalyst concentrations the reactivity of the resins is even reduced. One explanation for this at the first sight incomprehensible behaviour of the trisubstituted melamines is the salt formation between the melamine molecules and the strong acid. J. K. Dixon[9] measured the dissociation constants of different methylolated and etherified melamine resins (MER) and demonstrated a decrease in basicity with increasing methylolation and etherification with methanol in comparison to pure melamine.

The reaction of melamine with strong acids leads to stable adducts. The partially unsubstituted MER with free NH-groups reacts with protons of the strong acids to the isomelamine structure as demonstrated in equ. (6).

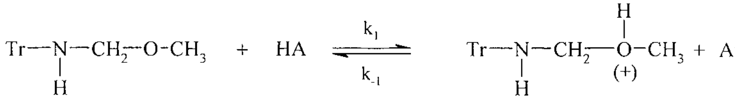
(6)



The protonation of the basic nitrogen in the triazine ring destroys the quasi aromatic structure of the melamine and reduces the possibility to split off methanol because of less potential to stabilize the methylene cation.

In contrast a weak acid catalyst leads to formation of an azomethin structure (equ. (7) and (8)), followed by the two possibilities of self condensation (9) and transetherification with another alcohol molecule ROH (10).

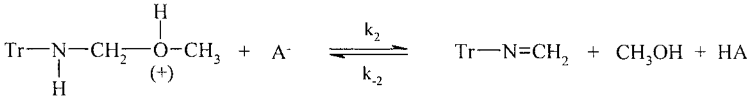
(7)



$$\underset{\displaystyle H}{Tr-N}-CH_2-O-CH_3 + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\displaystyle H}{Tr-N}-CH_2-\underset{(+)}{\overset{\displaystyle H}{O}}-CH_3 + A^-$$

fast

(8)



$$\underset{\displaystyle H}{Tr-N}-CH_2-\underset{(+)}{\overset{\displaystyle H}{O}}-CH_3 + A^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Tr-N{=}CH_2 + CH_3OH + HA$$

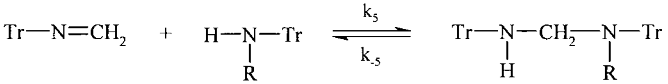
fast

(9)

$$Tr-N{=}CH_2 + ROH \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \underset{\displaystyle H}{Tr-N}-CH_2-OR$$

fast

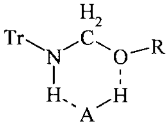
(10)



$$Tr-N{=}CH_2 + \underset{\displaystyle R}{H-N}-Tr \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \underset{\displaystyle H}{Tr-N}-CH_2-\underset{\displaystyle R}{N}-Tr$$

fast

The reaction step (7) may start from a good imaginable cyclic intermediate structure:



Provided that the reaction orders of the elementary reactions are equal to the stochiometric factors of the components involved in the reaction, and using steady state kinetics for the intermediate products, it is possible to express the effective reaction rates for transetherification (r_4) and self condensation (r_5) in the following form:

$$r_4 = k_4 * C_{NCH_2} * C_{ROH}$$

$$r_4 = \frac{k_4 * k_2 * k_1^* * C_{OCH_3} * HA * C_{ROH}}{k_4 * C_{ROH} + k_5 * C_{\mathbf{Resin}}} \approx k_4^* * C_{OCH_3} * HA * C_{ROH}$$

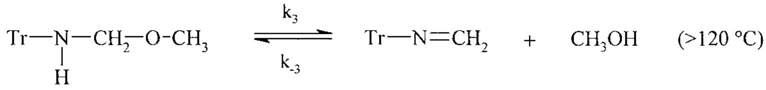
$$r_5 = k_5 * C_{NCH_2} * C_{\mathbf{Resin}}$$

$$r_5 = k_5 * \frac{k_2 * k_1^* * C_{OCH_3} * HA * C_{\mathbf{Resin}}}{k_4 * C_{ROH} + k_5 * C_{\mathbf{Resin}}} \approx k_5^* * C_{OCH_3} * HA * C_{\mathbf{Resin}}$$

Thermal activation of the crosslinking and transetherification reactions

An interesting mechanism of the etherified, partially methylolated structures (for instance tri-(methoxymethyl-)melamine) is that a thermal activation can also lead to splitting off of methanol like demonstrated in equ. (11).

(11)



$$Tr-\underset{H}{\underset{|}{N}}-CH_2-O-CH_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Tr-N=CH_2 + CH_3OH \quad (>120\,°C)$$

In the literature experts are discussing the catalytic effect of impurities as for instance the rest of salts from the synthesis process. This effect can not be excluded by now. We found high reaction rates at conditions at pH-values to 9.5 and temperatures between 180 to 200 °C.

The derivation for the effective reaction rates for transetherification and self condensation reactions leads to similiar results as in the catalytic process (the assumptions to be made are the same as aforementioned):

$$r_4 = k_4 * C_{NCH_2} * C_{ROH}$$

$$r_4 = \frac{k_4 * k_3 * C_{OCH_3} * C_{ROH}}{k_4 * C_{ROH} + k_5 * C_{\mathbf{Resin}}} \approx k_4^{**} * C_{OCH_3} * C_{ROH}$$

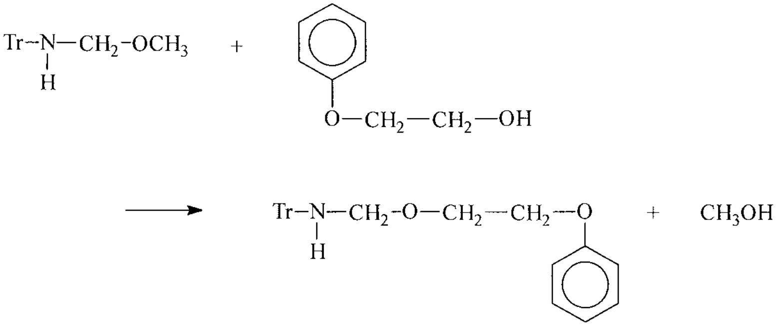
$$r_5 = k_5 * C_{NCH_2} * C_{\mathbf{Resin}}$$

$$r_5 = \frac{k_5 * k_3 * C_{OCH_3} * C_{\mathbf{Resin}}}{k_4 * C_{ROH} + k_5 * C_{\mathbf{Resin}}} \approx k_5^{**} * C_{OCH_3} * C_{\mathbf{Resin}}$$

Experimental results and discussion

We investigated the transetherification reaction of the methyl ether of trimethylolmelamine (tri-(methoxymethyl-)melamine, TMMM) with the monophenyl ether of ethylene glycol (12). Pure monomeric TMMM is actually very hard or even impossible to synthesize. For our purposes, a very low molecular MER provided by the AMI, having a melamine:formaldehyde ratio of 1:3 was an adequate model substance. The monophenyl ether of ethylene glycol (MPEEG) was used in 99.5 % commercial purity. For acidic catalyzed reactions p-toluenesulfonic acid was used in a concentration of $5.58.10^{-3}$ mol/kg.

(12)



The reactions were carried out in a glass reactor equipped with a mechanical stirrer and inlets for gas and liquid sampling. Methanol was removed in a continuous flow of nitrogen. The off-gas was analyzed with FT-IR spectroscopy. The quantification of the samples was also done with an FT-IR method. The resin is dissolved in 1,4-dioxane and then precipitated in toluene or iso-propanol (for higher conversion rates) to separate unreacted MPEEG (soluble in toluene). The procedure is repeated a second time, then the resin is dried at reduced pressure and ambient temperature.

IR spectra were measured in a 3 % dioxane solution on a KBr support (Film thickness ~20 μm, Shimadzu 8300 FTIR spectrometer). For the quantification the ratio between the integral intensities of the bands at 698 cm^{-1} (mono-substituted benzene ring vibrations) and 812 cm^{-1} (triazine cycle vibrations) was used. The calibration was carried out using standard MER-MPEEG mixtures.

Both thermal activation and acidic catalysts were studied and we received nearly linear dependencies of the conversion versus reaction time. Fig. 2 demonstrates this behaviour of the thermal activation at 120-150 °C. At low temperature the shift of the transetherification reaction can be explained by the evaporation and the transport processes of the methanol out of the equilibrium in the melt.

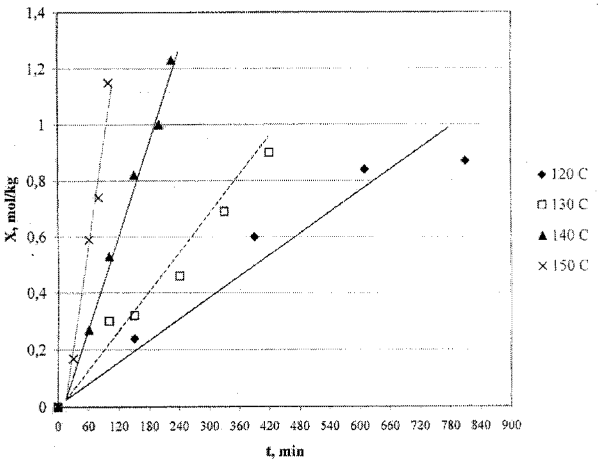


Figure 2. Transetherification of TMMM with MPEEG. Conversion vs. reaction time, thermal activation

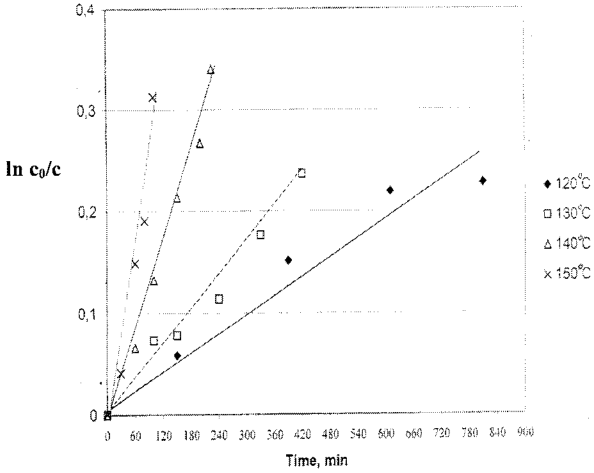


Figure 3. Transetherification of TMMM with MPEEG. First order reaction kinetics, thermal activation

The interpretation of the kinetic dependence as a first order reaction in Fig. 3 and a second order reaction in Fig. 4 allowed no conclusions to the mechanism.

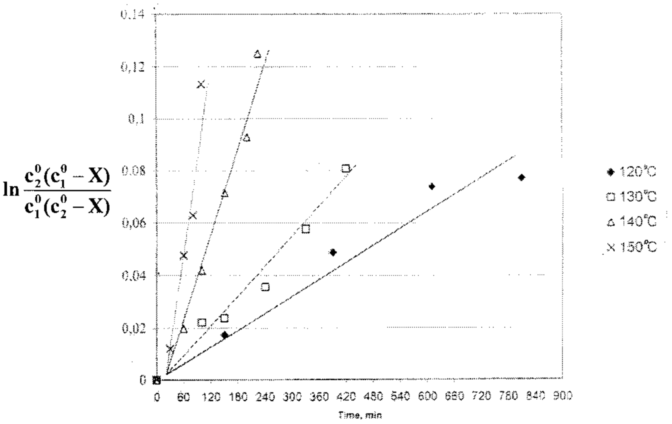


Figure 4. Transetherification of TMMM with MPEEG. Second order reaction kinetics, thermal activation

In contrast to this we got an answer to the reaction mechanism when the reaction rates of the transetherification were compared at different concentration ratios of the ether groups and the MPEEG. The following figures show the results for thermal and catalytic transetherification reactions. In Fig. 5 we found a strong dependence of the first order rate constants from the concentration ratio, whereas in Fig. 6 for second order kinetics no dependence of the rate constants from the concentration ratio can be found. This result provides some experimental evidence for the kinetic considerations presented above.

In agreement with the expectations from the etherification reaction, the reaction rate constants show a good correlation with the reaction temperature of the process. Fig. 7 demonstrates the activation energy of the thermal transetherification reaction with a value of E_a = 96-109 kJ/mol.

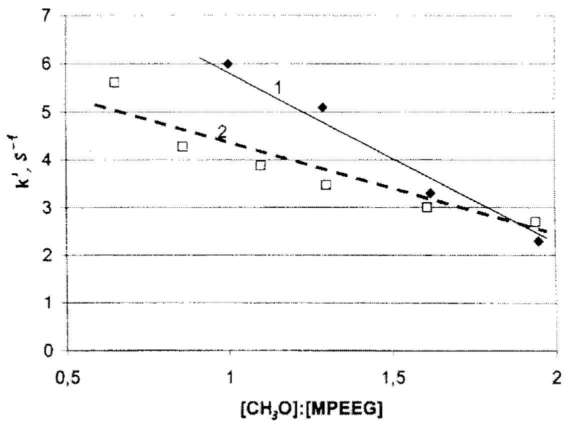


Figure 5. Transetherification of TMMM with MPEEG. First order reaction rate constants vs. concentration ratio. (1- acid catalyst, 110 °C; 2- no catalyst, 140 °C)

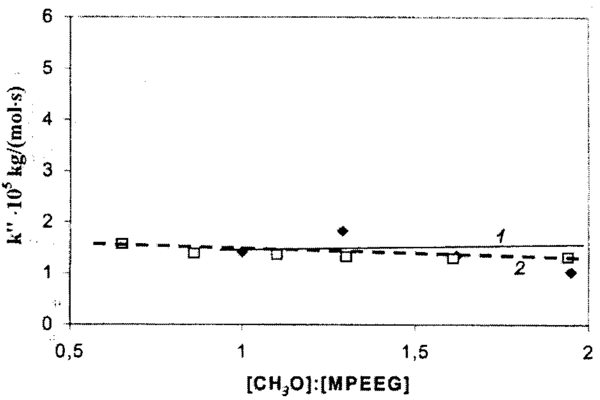


Figure 6. Transetherification of TMMM with MPEEG. Second order reaction rate constants vs. concentration ratio. (1- acid catalyst, 110 °C; 2- no catalyst, 140 °C)

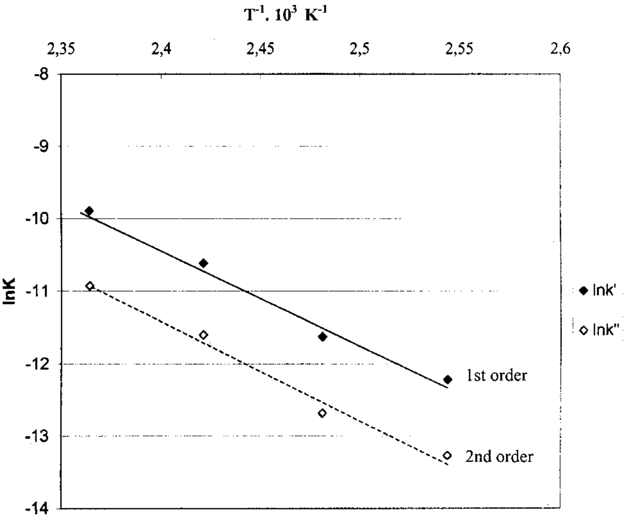


Figure 7. Arrhenius plot of the reaction rate constants vs. T^{-1} for the transetherification of TMMM with MPEEG. $E_a = 96 - 109$ kJ/mol

The activation energy of the acid catalysed process was determined in analogous manner, with a value of $E_a \sim 60$ kJ/mol, which is comparable to measurements with hexa-(methoxymethyl-) melamine from the literature. [8,10] The lower value of E_a gives evidence that via the protonation in equ. (7) the splitting off of methanol is favoured in comparison to the thermal reaction pathway of equ. (11).

Conclusions

The transetherification reaction of TMMM with diols is of practical interest for a new generation of highly reactive thermoplastic melamine resins. Kinetic investigations have been done with the monoalcohol MPEEG to allow measurements of the conversion rate vs. reaction time. The results demonstrate a bimodal reaction mechanism with different activation energies for the thermal and the catalytic transetherification reaction. The activation energies of the thermally activated transetherification reaction are in the same order of magnitude as the activation energies of the crosslinking reaction.

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