

Transesterification of Melamine–Formaldehyde Resin Methyl Ethers and Competing Reaction of Self-Condensation

V. N. Pavlyuchenko,¹ S. S. Ivanchev,¹ M. Rätzsch,² H. Bucka,² O. N. Primachenko,¹ P. Leitner,² S. Ya. Khaikin¹

¹Saint Petersburg Department of the Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences, 14 pr. Dobrolyubova, St. Petersburg 197198, Russia

²AMI Agrolinz Melamine International GmbH, St. Peter Str.25, A-4021 Linz, Austria

Received 28 March 2005; accepted 14 August 2005

DOI 10.1002/app.23540

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Transesterification of methyl ethers of melamine-formaldehyde resins (MER) with monophenyl ethers of ethylene glycol or propylene glycol (ROH) and competing reaction of self-condensation are studied depending on MER composition (amounts of CH_3O —, $-\text{CH}_2\text{OH}$, and NH_2 — groups), ROH type, MER/ROH molar ratio, presence or absence of acid catalysts, and temperature. High rates of self-condensation processes prevent a complete conversion of CH_3O — into RO-groups. It turned out MER free of methylol groups were not able to be transesterified with high yields due to a premature gelation taking place prior to attaining 50% conversion of methoxy groups (~ 4 mol/kg) even at low MER/ROH ratios. In contrast, transesterification of MER with methylol groups content up to 3 mol/kg

affords the incorporation of RO-groups into the resin up to 8 mol/kg owing to direct etherification of $-\text{CH}_2\text{OH}$ groups. The following factors are responsible for the growth of etherified product yield: presence of methylol groups in MER in some amounts without deterioration of MER–ROH compatibilization; CH_3O —/ROH molar ratio no higher than 1; primary alcohols (ROH) is more preferable compared to secondary ones; thermal activation of the process is more efficient in comparison with acidic catalysis. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2977–2985, 2006

Key words: chromatography; FTIR; kinetics; polycondensation; resins

INTRODUCTION

Curing of conventional melamine–formaldehyde resins (MFR) yields brittle and nonelastic products. One of the most efficient approaches to MFR modification is based on their etherification with alcohols. Etherified resins are featured with elastic properties and ability to dissolve in organic solvents. These properties determine the main application areas for such modified products as varnish resins, for obtaining coatings onto furniture, automobiles, and other machines,¹ for imparting fibers with water resistance (nonpermeability),² plasticizer-free production of elastic composites with other polymers.³ Another promising way of transesterified MFR application relates to obtaining materials suitable for processing into commercial articles using methods intrinsic to thermoplastic polymers such as

extrusion, injection molding, or blow molding. The thermoplastic processability makes MFR convenient for highly productive technologies with crosslinking being combined with the processing step. The main application of such kind of MFR is the production of the fiber reinforcing materials for automotive parts by extrusion technologies.⁴

The etherified resin properties depend on the alcohol type. MFR solubility in organic solvents, plasticization degree, and elasticity of the coatings and other articles prepared therefrom grow with the increase of aliphatic or alkylaromatic substituents in the alcohol molecule. However, MFR etherification with higher alcohols is complicated due to a poor compatibility of these reactants. Therefore large substituents are incorporated into the resins preliminarily etherified with low alcohols commonly using methylated MFR. The main problem in this approach is the simultaneous side reaction of MFR condensation taking place in the case of performing transesterification at elevated temperatures. This competing process leads to a premature gelation of the reaction system often preventing the achievement of the required transesterification degree. The temperature can be reduced provided the transesterification is carried out in the presence of

Correspondence to: S. S. Ivanchev (ivanchev@SM2270.spb.edu).

Contract grant sponsor: Agrolinz Melamin International GmbH.

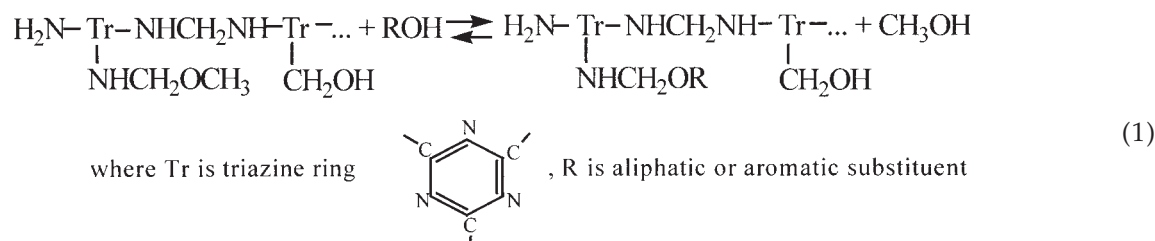
acidic catalysts, although this way seems doubtful, as the resin self-condensation is also catalyzed by acids.

This article presents the study of MFR methyl ethers (MER) transesterification kinetics with the estimation of the contribution from the simultaneous resin self-condensation depending on the process conditions (presence or absence of a catalyst, temperature, and ratio between the reactant concentrations). In addition

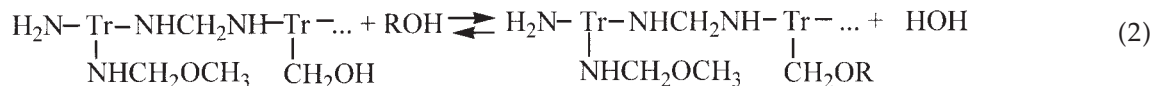
to the considered factors, the observed differences in the reaction kinetics and mechanisms were also attributed to the application of different MER either containing residual methylol groups or completely methylated.

Due to the presence of various functional groups in the resins (CH_3O —, $-\text{CH}_2\text{OH}$, $-\text{NH}_2$, $-\text{NH}-$), the following reactions can proceed at their transesterification.

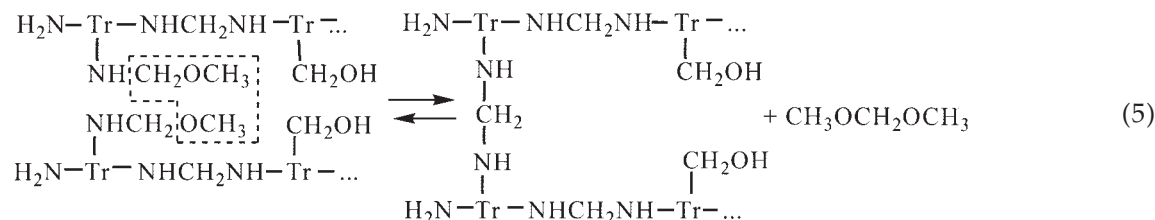
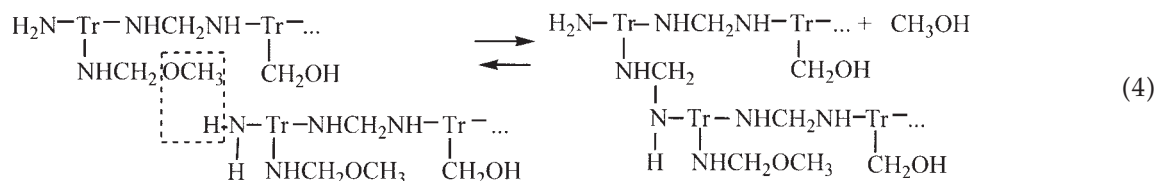
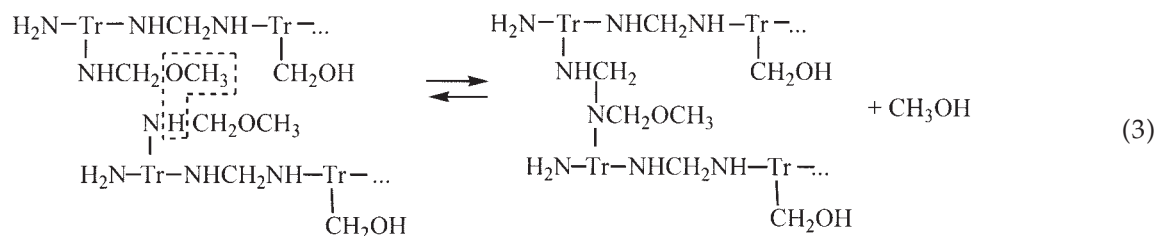
Transesterification

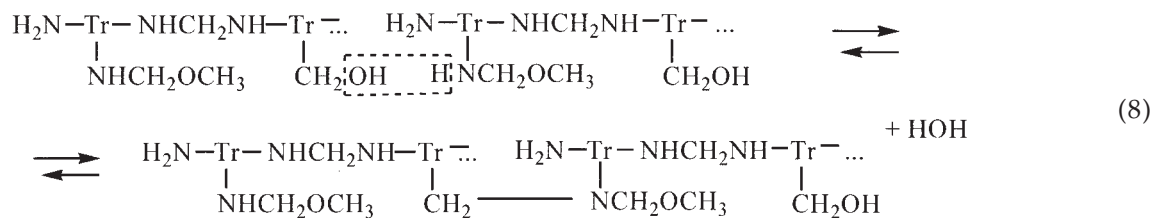
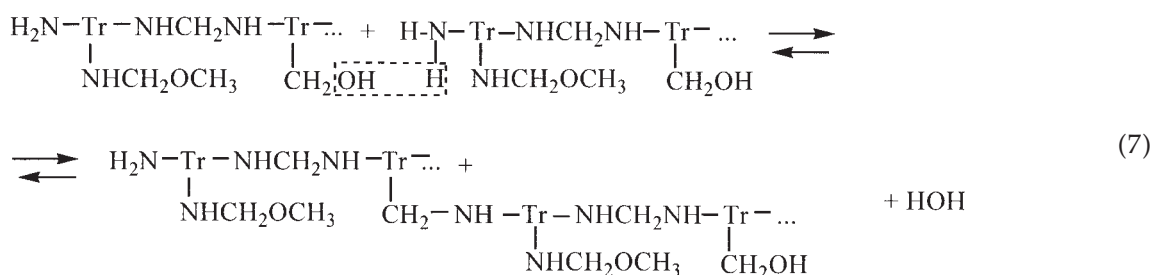
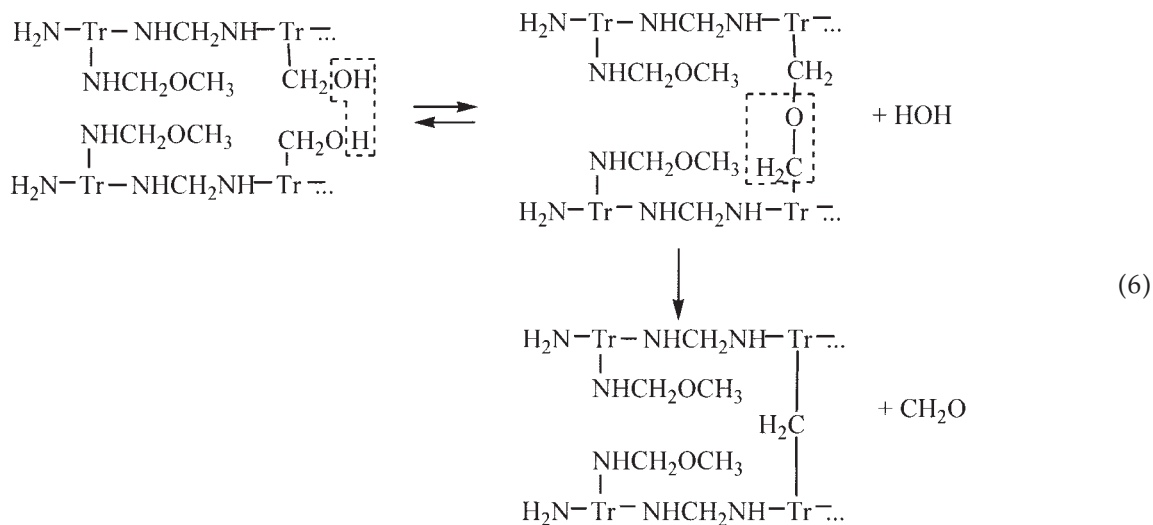


Direct etherification in the case residual methylol groups are present in the resin.



Self-condensation reactions involving methoxy-groups:





Because during transeetherification the yielded low molecular products were permanently removed, the reactions involving these compounds can be neglected and the processes (1–8) can be considered irreversible.

EXPERIMENTAL

Reactants

Methyl ethers of melamine resins (MER) were prepared by a direct route. Both reactions (melamine methylation with formaldehyde and etherification with methanol) were carried out under acidic conditions in a single reactor. Melamine (1 mol), formaldehyde (30 wt % aqueous solution, 4–5 mol) and methanol (8–10 mol) were mixed. pH value was adjusted to 5–6 by the addition of *p*-toluenesulfonic acid. After 30–60 min heating the reaction was stopped by the addition of sodium hydroxide (to pH 8–10).

Volatile compounds (water, residual formaldehyde, and methanol) were eliminated by short heating of the resin at 250°C.

MER performances are summarized in Table I.

Transeetherification was carried out using monophenyl ether of ethylene glycol (MPEEG) (purity 99.5% wt, produced by FERAX, Germany) and monophenyl ether of 1,2-propylene glycol (MPEPG) (t_m 11°C, t_b 241–246°C, d 1.059–1.069, produced by Seppic, France).

Phthalic anhydride (PA) (purity 98%, t_m 131–133°C) and *p*-toluenesulfonic acid (purity 99%) both supplied by MERCK Co. were used as catalysts.

Analytical procedure

Determination of CH₃O-groups content in the initial MER and transeetherification products

Before the analysis the transeetherification products were purified from residual nonreacted MPEEG or

TABLE I
MER Performances

MER	Melamine: formaldehyde : methanol molar ratio	CH ₃ O—, mol/kg	—CH ₂ OH, mol/kg	—NH ₂ , mol/kg	M _n	M _w
A	1 : 4 : 8	8.30	1.3	1.9	1300	1800
B	1 : 4 : 8	6.19	0.4	2.1	700	950
C	1 : 4 : 8	7.56	0.8	2.0	1234	1918
D	1 : 4 : 8	7.74	0.0	2.2		
E	1 : 5 : 10	7.87	2.7	2.3		
F	1 : 5 : 10	7.81	3.1	2.4		

MPEPG by dissolving in 1,4-dioxane followed by reprecipitation in toluene or toluene:hexane (1:3 vol. parts) mixture, several times treatment with toluene and drying at ambient temperature. The thus-prepared sample (0.1 g) was dissolved in the mixture containing dimethylsulfoxide (4.275 g) and phosphoric acid (85% solution, 0.225 g) and hydrolyzed in a sealed ampoule at 80°C within 6 h. CH₃O-groups content was evaluated according to the yielded methanol amount determined by gas-liquid chromatography using headspace GC technique with *n*-propanol as an internal standard. The chromatographic analysis was carried out in a column with the length 60 cm and diameter 3 mm filled with a polymeric fluoro-containing sorbent at the following parameters: temperature 90°C, evaporator temperature 110°C, carrier gas (He) flow rate 30 cm³/min, flame-ionization detector (hydrogen flow rate 30 cm³/min, air flow rate 300 cm³/min).

PhOCH₂CH₂O- and PhOCH₂CH(CH₃)-O-groups content in the transesterification products was determined using FTIR-spectroscopy (Shimadzu 8300 FTIR-spectrometer) according to the ratio between the integral absorption for the vibration band of a mono-substituted benzene ring at 692 cm⁻¹ and vibration band of the triazine cycle at 816 cm⁻¹. Samples for characterization were prepared as films of 20-μm thickness deposited onto substrates from 3% solutions in 1,4-dioxane.

The contents of —CH₂OH and —NH₂ groups were estimated using FTIR spectroscopy. The concentration of —NH₂ groups in MER A was evaluated by ¹H-NMR-spectroscopy with Bruker Avance DPX 200 NMR Spectrometer. Deuterated dimethyl sulfoxide (d₆-DMSO) was used as a solvent. Calcium chloride was used as a shift reagent for quantification of the functional groups. Pyrazine (99%, Merck) was used as an internal standard. For quantitative determination of NH₂-groups a broad multiplet (6.0–6.5 ppm) was applied.

Volatiles were determined using FTIR spectroscopy of the gas phase by measuring the intensity of absorption bands at 1032, 1148, 1745, and ~1600 cm⁻¹ characterizing the vibrational transitions for methylol

groups, methylal, formaldehyde, and water correspondingly.

Molecular weights of the resins were determined by GPC technique in THF solutions using miniDAWN instrument. The reaction system viscosity was determined using a Brookfield viscometer (model DV-1+) with spindle #3, RPM 50.

Transesterification technique

The reaction was carried out in a 100 cm³ glass vessel equipped with a stirrer and inlet for inert gas (nitrogen) purged through the reaction mixture with the rate 150–600 cm³/min to remove the volatile products. The reactor entrance was equipped with a capillary device for gas flow rate measurement. The outlet line was also provided for volatiles evacuation and

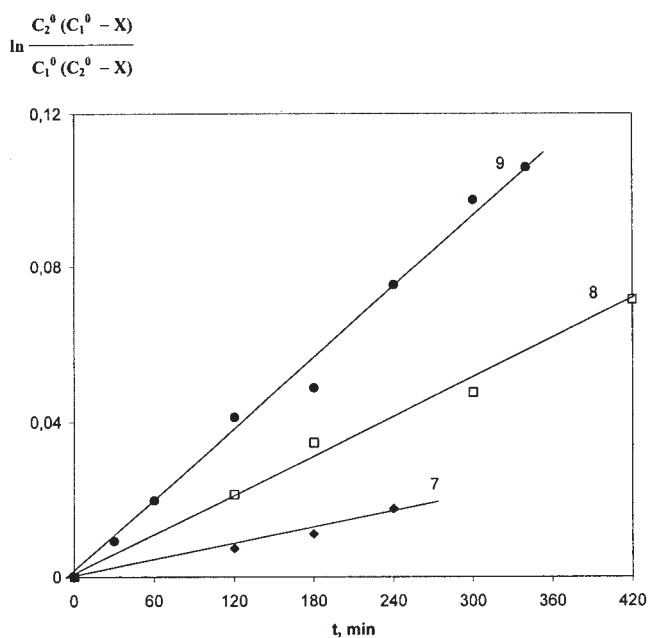


Figure 1 Second order transesterification kinetic plots. C₁⁰ and C₂⁰; initial contents (mol/kg_{reaction mixture}) of CH₃O-groups and ROH correspondingly; X—concentration of MER bonded RO-groups (mol/kg_{reaction mixture}). The plot numbers relate to the corresponding trials in Table II.

TABLE II
Kinetic Parameters of MER Transeetherification

Trial No.	MER type (amount, g)	ROH type (amount, g)	CH ₃ O—: ROH molar ratio	Catalyst (amount, g; concentration, mol/kg)	T (°C)	$k \cdot 10^5$ [kg/(mol · s)]	E_a (kJ/mol)	A [kg/(mol · s)]
1					80	0.27		
2	A (22.62)	MPEEG (20.00)	1.29	p-TSA (0.068; $5.58 \cdot 10^{-3}$)	100	0.70	60	$1.91 \cdot 10^3$
3					110	1.83		
4					130	3.07		
5	A (22.62)	MPEEG (20.00)	1.29	PA (0.045; $3.58 \cdot 10^{-3}$)	110	0.56	65	$5.53 \cdot 10^3$
6					130	1.57		
7	A (22.62)	MPEEG (20.00)	1.29	No	110	0.10	96	7.18
8					120	0.29		
9					130	0.53		
10	D (18.71)	MPEPG (20.00)	1.10	No	130	0.18		

subsequent collection in a running-flow cell with a KBr window for analysis and a capillary for taking liquid samples. The process was carried out as long as stirring of the reaction mixture remains possible. As gelation occurs the reaction mixture becomes nonfluent and sticks to the stirrer. The transeetherification level (degree of CH₃O-groups conversion into RO—) determined at this moment was considered as a threshold value $D_\infty\%$. Taking into consideration one more way of RO-groups incorporation in MER due to a direct etherification of methylol groups (reaction 2)

the threshold transeetherification degree was also evaluated as RO-groups content in MER in moles per 1 kg of the initial MER (D_∞).

RESULTS AND DISCUSSION

In our previous studies⁵ the considered transeetherification reactions were shown to follow the second-order reaction kinetics. This conclusion relates to both catalyzed by weak (PA) or strong (TSA) acids and thermally activated processes. The second-order kinetic plots are illustrated in Figure 1 for all these cases. Table II summarizes the calculated transeetherification rate constants that according to ref. 5 remain almost constant at [CH₃O—]:[MPEEG] molar ratio variation at least in the range from 0.5 to 2.0. Similar results were also obtained for transeetherification in the presence of MPEPG although the reaction rate constants were lower in agreement with reduced reactivity of secondary alcohols in such reactions.¹ The Arrhenius equation coefficients are also indicated in Table II. As expected, the catalytic reactions are featured with relatively low activation energies.

The considered kinetic data were obtained at small degrees of methoxy groups conversion assuming the

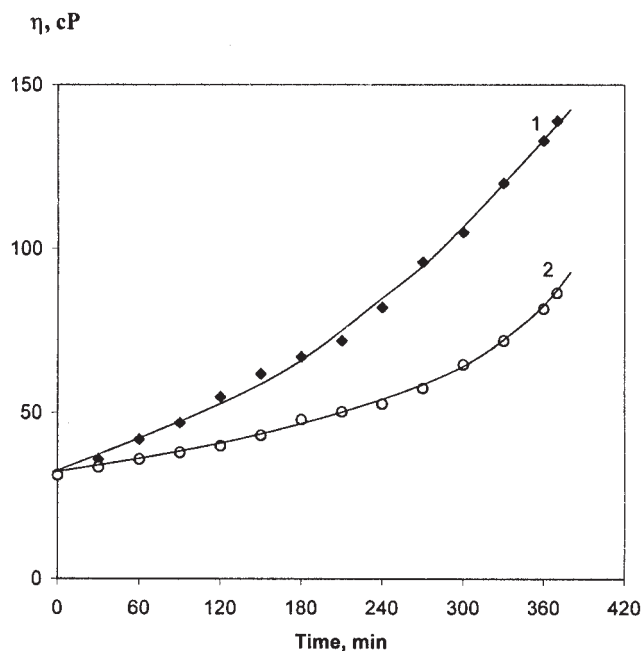


Figure 2 Reaction mixture viscosity change for MER A-MPEEG during the process. Reaction conditions are shown in Table II. 1—trial No. 4; 2—trial No. 9.

TABLE III
Molecular Properties of MER A Transeetherification Products Depending on the Reaction Conditions

Trial No.	Catalyst	CH ₃ O-groups conversion (%)	M_n	M_w
4	p-TSA	33.1	118,000	153,000
6	PA	30.6	118,000	133,000
9	No catalyst	28.1	32,000	43,000

Trial numbers correspond to the data in Table II.

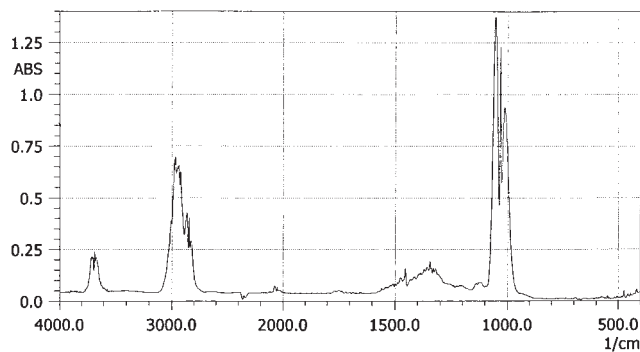


Figure 3 IR spectrum of the volatiles yielded at MER D transesterification.

contribution of self-condensation at this stage of the reaction is negligible, that is, a possible CH_3O -groups consumption for self-condensation was not taken into

account. However, the reaction system viscosity growth observed during the transesterification (Fig. 2) suggests the self-condensation onset already at the early steps of the process. A direct evidence of self-condensation is a high molecular weight (MW) of the yielded products (Table III), with MW increasing at similar $\text{CH}_3\text{O} \rightarrow \text{RO}$ conversions ($\sim 30\%$) being more prominent for catalytic processes. This phenomenon has determined the preferential use of thermal activation in our subsequent kinetic studies.

According to the above reaction pathways the transesterification can be accompanied with self-condensation proceeding via different mechanisms.

First, we would like to consider the processes free of complicating reactions (2) and (6)–(8), that is, transesterification of the resins with the absence or small amount of methylol groups. The reaction mechanism can be estimated according to the chemical composi-

TABLE IV
Change of the Reactant and Functional Groups Concentrations in the Course of MER Transesterification with MPEEG

MER type (amount, g)	$[\text{—NH}_2]_0$ mol/kg	$\frac{C_1^0}{C_2^0}$ molar ratio	T (°C)	t (min)	C_1 (mol/kg)	C_2 (mol/kg)	X, (mol/kg)	$C_1^0 - C_1$ (mol/kg)	$C_1^0 - C_1 - X$, (mol/kg)
C (24.13)	1.15	1.29	120	0	4.26	3.28	0.00	0.00	0.00
				150	3.33	3.03	0.25	0.93	0.68
				390	2.90	2.67	0.61	1.36	0.75
				610	2.79	2.44	0.84	1.47	0.63
C (24.13)	1.15	1.29	140	0	4.26	3.28	0.00	0.00	0.00
				60	2.53	3.01	0.27	1.73	1.46
				100	2.46	2.77	0.51	1.80	1.29
				150	2.25	2.45	0.83	2.01	1.18
				200	1.90	2.28	1.00	2.36	1.36
C (16.08)	0.93	0.86	140	225	1.75	2.04	1.24	2.51	1.27
				0	3.45	4.01	0.00	0.00	0.00
				60	2.31	3.71	0.30	1.14	0.84
				100	2.19	3.47	0.54	1.26	0.72
D (20.57)	1.11	1.10	150	170	1.49	3.18	0.83	1.96	1.13
				0	3.92	3.57	0.00	0.00	0.00
				30	2.28	3.42	0.15	1.64	1.49
				120	2.21	2.87	0.70	1.71	1.01
D (36.28)	1.56	1.94	150	180	1.88	2.81	0.76	2.04	1.28
				0	4.99	2.57	0.00	0.00	0.00
				50	3.09	2.18	0.39	1.90	1.51
				60	2.97	2.11	0.46	2.02	1.56
				70	2.95	2.04	0.53	2.04	1.51
				90	2.56	2.03	0.54	2.43	1.89
				120	2.46	1.92	0.65	2.53	1.88
D (74.80)	1.74	4.00	150	130	2.49	1.82	0.75	2.50	1.75
				0	6.11	1.53	0.00	0.00	0.00
				40	4.04	1.32	0.21	2.07	1.86
				50	4.00	1.28	0.25	2.11	1.86
D ^a (18.71)	1.08	1.10	150	0	3.74	3.40	0.00	0.00	0.00
				40	2.32	3.25	0.15	1.42	1.27
				60	2.23	3.16	0.24	1.51	1.27
				80	2.30	3.06	0.34	1.44	1.10
				100	2.42	3.00	0.40	1.32	0.92

All the concentrations are related to 1 kg of the reaction mixture.

Initial MPEEG amount in all trials is 20.00 g.

^a MPEPG.

TABLE V
Kinetic Parameters of MER Transeetherification

MER type (amount, g)	ROH type (amount, g)	CH ₃ O—: ROH molar ratio	T (°C)	$k \cdot 10^5$, [kg/(mol · s)]	$D_x^%$, (%)	D_{∞} , (mol/kg)
A (22.62)	MPEEG (20.00)	1.29	130	0.75	28.1	2.33
B (30.16)	MPEEG (20.00)	1.29	130	0.81	23.2	1.43
C (24.13)	MPEEG (20.00)	1.29	130	0.45	20.1	1.64
		1.29	140	1.33	28.9	2.25
		1.29	150	2.60	26.8	2.09
D (20.57)	MPEEG (20.00)	1.10	130	0.62	23.9	1.85
		1.10	150	2.28	19.4	1.50
		1.10	170	3.78	22.9	1.77
D (18.71)	MPEPG (20.00)	1.10	130	0.19	9.6	0.74
		1.10	150	0.89	10.7	0.83
		1.10	170	1.28	8.1	0.62

tion of the volatiles yielded in the course of the process. IR spectra of the reaction gas phase (Fig. 3) indicate methanol (1032 cm^{-1}) to be the only volatile while methylal is absent because the corresponding band near 1148 cm^{-1} is missing. Therefore, the processes performed using resins free of or containing small methylol group amounts can include only methanol yielding reactions (1), (3), and (4), that is, chemical composition of the volatiles does not allow us to distinguish the transeetherification and self-condensation reactions.

The contribution of self-condensation can be estimated by a simultaneous determination of the concentrations of CH₃O— (C_1) and resin bonded RO-groups (X). The data on the change of each reactant content in the course of the reaction as well as the calculated values ($C_1^0 - C_1 - X$) characterizing CH₃O-groups consumption for self-condensation are summarized in Table IV. The consumption of methoxy groups ($C_1^0 - C_1$) exceeds the accumulation of resin bonded RO-groups suggesting that CH₃O-groups are partially involved in the reactions (3) and (4). It should be noted that self-condensation is featured with a very rapid decrease of CH₃O-groups content with the value ($C_1^0 - C_1 - X$) reaching a certain value in 30–60 min and only slightly changing subsequently. Interestingly, the measured values almost correspond to primary amino-groups content in the reaction system. This process behavior allows us to suppose that at the initial steps of the process self-condensation proceeds predominantly involving the primary amino groups. This assumption is in agreement with higher reactivity of NH₂-groups compared to —NH— with the relative contribution of the latter increasing at deeper steps of the process as the primary amino-groups are exhausted.

The considered results show that the reaction (3) proceeds significantly faster than (1). Actually, we can

suppose that by the first X measurement (usually in 30–60 min) the reaction (3) is almost completed. Hence, the calculation of transeetherification rate constants can be corrected by fixing the initial concentration of CH₃O-groups as ($C_1^0 - C_3^0$), where C_3^0 is the initial content of NH₂-groups. The thus-defined transeetherification rate constants are summarized in Table V. Noteworthy, the constants for these resins determined at the same temperature are close to each other, that is, they do characterize the reaction (1) with the rate depending on the nature of the used alcohol (in the case of MPEEG the rate constants are markedly higher

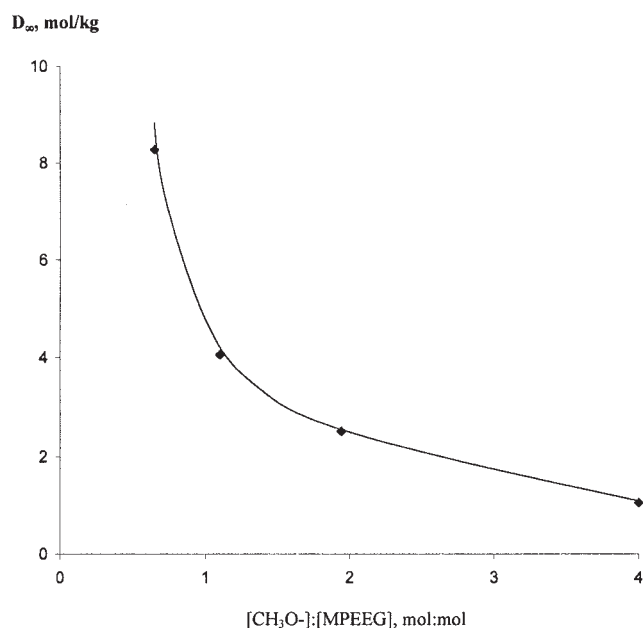


Figure 4 Effect of CH₃O—: MPEEG molar ratio upon the threshold transeetherification degree for MER F at 150°C (trial Nos. 12–15, Table VII).

TABLE VI
Change of Functional Groups and Reactant Concentrations in the Course of MER E Transesterification

t (min)	C ₁ (mol/kg)	C ₂ (mol/kg)	X (mol/kg)	C ₁ ⁰ -C ₁ (mol/kg)	C ₁ ⁰ -C ₁ -X, (mol/kg)
0	3.96	3.60	0	0	0
120	1.63	1.29	2.31	2.33	0.02
160	1.13	0.74	2.86	2.83	-0.03

Reaction conditions: MER E — 20.23 g, MPEEG — 20.00 g, C₁⁰: C₂⁰ molar ratio 1.10, T = 150°C.

relating to the systems containing MPEEG). Table V also contains the threshold transesterification degrees reached by the gelation time. These values are clearly shown to only slightly depend on the temperature and resin type but considerably drop upon MPEEG replacement by MPEEG. Due to a low alcohol reactivity in the latter case self-condensation processes lead to gelation at CH₃O-groups conversions about 10%. CH₃O-groups conversion is strongly affected by the molar ratio between the reactants. As illustrated in Figure 4, even at low CH₃O:ROH molar ratios CH₃O- conversion does not exceed 50%.

The resins E and F with high methylol group content are featured with quite different behavior. The value C₁⁰-C₁-X for MER E is close to zero (Table VI) and the calculated transesterification rate constants (Table VII) are markedly higher relating to those summarized in Table V. These data in combination with low E_a values suggest that for transesterification and self-condensation of MER E and F possible reactions (2), (6)–(8) involving methylol groups should be taken into account and the constants indicated in Table VII should be considered as integral coefficients characterizing the end product yield via simultaneous transesterification (1) and direct etherification (2). A relatively higher rate of the latter determines the increased

rate constants for these resins. A considerable contribution of the direct etherification is also suggested by a high level of CH₃O-groups substitution (Table VII). In one of the trials this value is over 100%, that is, the amount of MER bonded RO-groups exceeds the content of CH₃O-groups.

Self-condensation of the resins E and F proceeds predominantly according to the pathways (6)–(8) while the contribution of the reactions (3) and (4) is probably insignificant in view of the relating C₁⁰-C₁-X values. Hence, we suppose the primary amino-groups are mostly consumed in the interaction with —CH₂OH (pathway 7). A permanent water yield during the process confirms a possibility for this reaction but does not prove it definitely because the direct etherification (2) also leads to water formation. However, the considered self-condensation processes are free of the reaction (6) as clearly indicated by the absence of the absorption band near 1745 cm⁻¹ (formaldehyde) in the FTIR spectra for the reaction gas phase.

Thus, the application of MER containing about 3 mol/kg of —CH₂OH groups affords resins with increased content of RO-groups at similar CH₃O:ROH molar ratios compared to the resins free of methylol groups. This phenomenon is determined by more fa-

TABLE VII
Kinetic Parameters of MER E and F Transesterification

Trial No.	MER type (amount, g)	CH ₃ O:ROH molar ratio	T, (°C)	k · 10 ⁵ , kg/(mol · s)	E _a (kJ/mol)	D _x [%] (%)	D _∞ (mol/kg)
11	E (20.23)	1.10	130	1.73 ± 0.24	61.1 ± 23.4	62.9	4.95
			150	7.02 ± 0.90		72.3	5.69
			170	8.87 ± 1.10		64.9	5.11
12	F (11.97)	0.65	130	2.16 ± 0.33	45.2 ± 2.5	84.2	6.62
			150	4.58 ± 0.40		105.2	8.28
			170	7.30 ± 0.25		90.9	7.15
13	F (20.23)	1.10	130	2.76 ± 0.44	44.0 ± 3.8	60.5	4.76
			150	4.28 ± 0.63		51.6	4.06
			170	9.07 ± 0.71		54.5	4.29
14	F (35.73)	1.94	130	2.64 ± 0.20	42.3 ± 2.5	29.4	2.31
			150	5.37 ± 0.50		32.0	2.52
			170	8.22 ± 0.49		28.9	2.75
15	F (73.66)	4.00	130	3.68 ± 0.24		12.9	1.01
			150	6.69 ± 1.02		13.4	1.06

MPEEG amount in all trials is 20.00 g.

variable ratios between the rates of the end product yielding reactions (pathways 1 and 2) and self-condensation.

CONCLUSION

The study of transeetherification for methyl ethers of melamine-formaldehyde resins with monophenyl ethers of ethylene glycol or propylene glycol has revealed that this process is accompanied with a competing self-condensation reaction. The presence of various functional groups ($\text{CH}_3\text{O}-$, $-\text{NH}_2$, $-\text{NH}-$, $-\text{CH}_2\text{OH}$) determines a variety of chemical reactions resulting in the formation of the etherified product or resin self-condensation. High rates of self-condensation processes prevent a complete $\text{CH}_3\text{O}- \rightarrow \text{RO}-$ conversion due to involvement of methoxy groups in the condensation reactions with amino- and methylol groups. Unexpectedly, MER free of highly reactive methylol groups were found to be unable to turn into transeetherified resins with high yields. In these cases the gelation occurs prior to attaining 50% conversion of CH_3O -groups (~ 4 mol/kg) even at $\text{CH}_3\text{O}:\text{ROH}$ molar ratios below 1. In contrast, transeetherification of MER with methylol groups content up to 3 mol/kg affords the incorporation of RO-groups into the resin in the amounts up to 8 mol/kg due to the direct etherification of $-\text{CH}_2\text{OH}$ groups. Thus, a certain content of methylol groups in MER is an essential factor promoting an increase of the end product yield.

Small amounts of $-\text{CH}_2\text{OH}$ groups cause no obstacles to the alcohol-resin compatibilization and, from other hand, provides an increased RO-groups content in the resulting product.

Thus, to achieve the maximum yield of the required product (MER transeetherified with a higher alcohol) and avoid a premature gelation transeetherification should be performed taking into consideration the following factors: (1) MER should contain a small amount (about 2 mol/kg) of methylol groups; (2) $\text{CH}_3\text{O}:\text{ROH}$ molar ratio should not exceed 1; (3) transeetherification should be carried out using primary alcohols possessing a high reactivity; (4) thermal activation of the process is more efficient compared to acidic catalysis.

The authors would like to thank Agrolinz Melamin International GmbH for financially supporting this study.

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