

Addition of H₃PO₄ to Diglycidyl Ethers of Bisphenol A: Kinetics and Product Structure

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ABSTRACT: The preparation of the addition products of H₃PO₄ to bisphenol A based epoxy resins is described. These products are considered modifiers of the epoxy resins and for the further formation of useful networks (coatings and related products). Depending on the ratio of H₃PO₄ to epoxy groups and other reaction variables, a family of oligomers with acidic end groups has been formed. The major reaction is the addition of H₃PO₄ to epoxy groups. Among the side reactions, the acid-catalyzed addition of the >CH—OH (and/or —CH₂OH) groups to epoxy groups dominates. The —OH groups, if not present in the starting resins, are emerging from the P—OH to oxirane ring addition. The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry analysis of the starting epoxy resins has revealed their structural diversity. In the kinetic measurements and determination

of the ester composition, diglycidyl ether of bisphenol A (BADE) as a model compound has been mostly applied. The kinetics of the H₃PO₄–BADE reaction is described, and the structures of the final products are analyzed with ³¹P{¹H}-NMR, which gives (at pH ~ 12) quantitatively the proportions of the monoesters, diesters, and triesters as well as the unreacted H₃PO₄. The conditions have been found leading exclusively to the monoester, and this indicates that an increase in the reaction temperature enhances the selectivity of the reaction; that is, it depresses the proportion of the acid-catalyzed —OH and epoxy group reaction. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 246–254, 2007

Key words: esterification; functionalization of polymers; MALDI; NMR; resins

INTRODUCTION

The modification of epoxy resins into the esters of phosphoric acid is providing a new family of products that by themselves or as additives can be applied to coatings and related final products converting epoxy groups.

In our previous studies, it has been shown that close to the stoichiometric ratio (P—OH/oxirane ≈ 1) in the reaction of H₃PO₄ with diepoxides, insoluble gels are formed.¹ Indeed, three acidic functions of H₃PO₄ and two epoxy groups give a typical A₃ + B₂ system that should lead to network formation. The gels are further converted into soluble, highly branched macromolecules by simple hydrolysis because the hydrolysis of triesters (knots in gels) is much faster than the hydrolysis of diesters and monoesters.^{1–3} In these macromolecules, there are diesters of phosphoric acid (linear units), triest-

ers of phosphoric acid (branching points), and monoesters of phosphoric acid (end groups; see Scheme 1).

It has also been observed that in certain basic solvents (e.g., dimethyl ethers of oligoethylene glycols), the third acidic group of H₃PO₄ is becoming less reactive, and triesters are less extensively formed.

In another series of our works, we studied the kinetics and mechanisms of H₃PO₄ addition to simplest epoxides, mostly ethylene oxide.^{4–6} We established that the reaction stops with the complete consumption of the acid at the conversion stage of ~ 1.25 mol of ethylene oxide per mole of the P—OH groups. Addition to every next acidic group proceeds faster than that to the previously reacted group, the ratio of rates being equal to 1 : 1.9 : 4. This is in contrast to our aforementioned work, in which the reaction was carried out in polyethers as solvents. The elementary reaction of addition involves activated epoxide and dimeric H₃PO₄. The activated epoxide is either H-bonded or protonated (Scheme 2).

The proportions of various esters that form may vary considerably, mostly depending on the oxirane ring/—POH ratio and on other conditions of the reaction. We applied this knowledge to an attempt to prepare simple addition products of H₃PO₄ to diglycidyl ether of bisphenol A (BADE).

This article is dedicated to the memory of Professor Marian Kryszewski.

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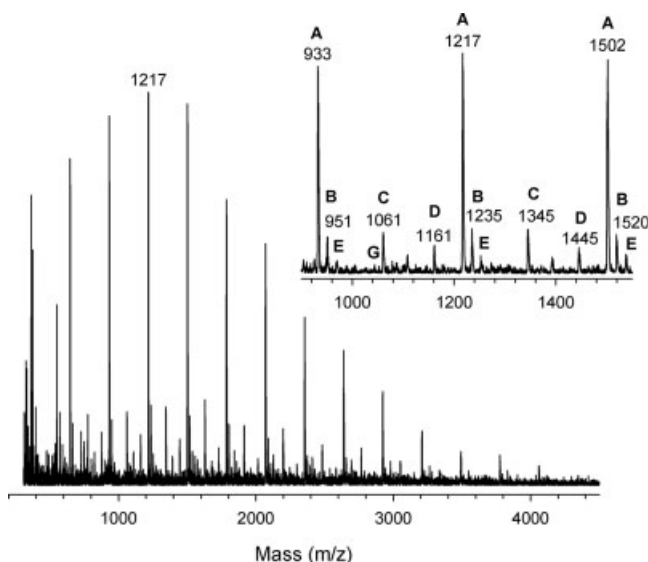


Figure 1 MALDI-TOF MS of Epidian 1. The capital letters over the peaks denote the corresponding structures shown below them. The matrix was DHB/NaI.

various times, small samples of the reaction mixture were taken and poured into an excess of Na_2CO_3 in a water solution. The ^{31}P -NMR spectra in a strong alkaline solution (after the additional adding of NaOH directly before the measurement) were recorded. A relaxation delay of 20 s was used.

Determination of the ester composition

The reaction was studied at 25 and 100°C. The dioxane solutions of $[\text{BADE}]_0 = 0.495$ mol/L and $[\text{H}_3\text{PO}_4]_0 = 2.18$ mol/L were prepared. A solution of BADE was added dropwise for 10 min to the solution of H_3PO_4 in such a way that the final $[\text{H}_3\text{PO}_4]_0/$

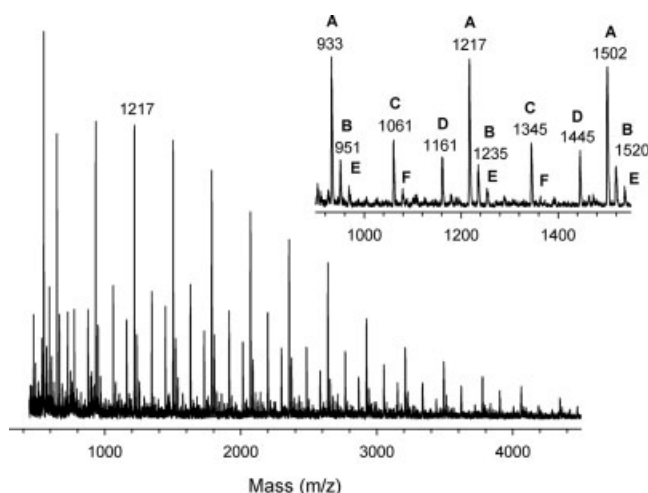


Figure 2 MALDI-TOF MS of Epidian 012. The capital letters over the peaks denote the corresponding structures shown below them. The matrix was DHB/NaI.

$[\text{BADE}]_0$ ratio was varied from 0.5 to over 11.5. The reaction mixture was then kept overnight. The ^1H -NMR spectra did not change after this time; no epoxy groups were present in the reaction mixture. The composition of the esters in each reaction mixture was determined on the basis of ^{31}P -NMR spectra in the water solution at $\text{pH} \sim 12$.

NMR spectra were recorded with a Bruker (Karlsruhe, Germany) AC 200 spectrometer operating at 200 MHz for ^1H spectra, at 50.33 MHz for ^{13}C spectra, and at 81.01 MHz for ^{31}P spectra.

Mass spectrometry measurements were performed with a Voyager Elite (Framingham, MA) time-of-flight instrument. 2,5-Dihydroxybenzoic acid (DHB) as a matrix and NaI as an ionizing agent were used.

RESULTS AND DISCUSSION

The addition of H_3PO_4 to the epoxy resin consists of a series of consecutive, parallel reactions.

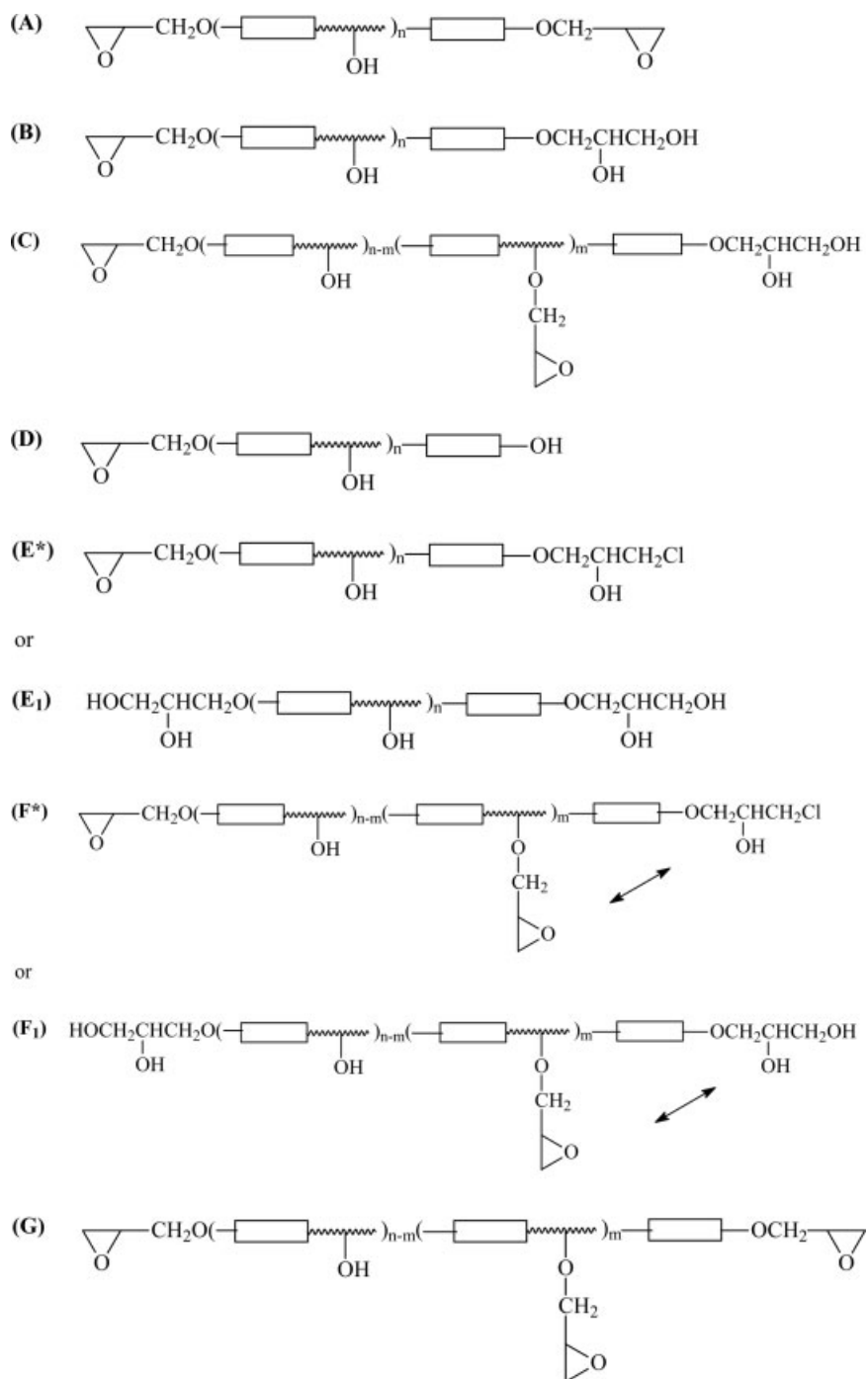
The major reaction is shown in Scheme 3 (in higher molar mass epoxy resins based on bisphenol A, there are also hydroxyl groups). The structures shown in the scheme are the dominant species; several side products are formed during the industrial synthesis of epoxy resins. These are described in the next paragraph.

Structures of the epoxy resins

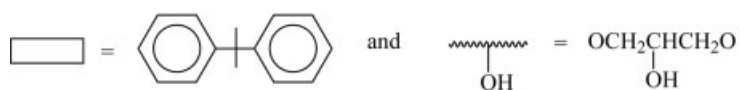
Several epoxy resins were used, having at least nominally the structure of diglycidyl ethers. Pasch et al.⁷ analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) epoxy resins (technical products provided by Dow Deutschland, Inc., Rheinmünster, Germany)

TABLE I
Assignments of the Selected Signals Shown in the Expanded MALDI-TOF Mass Spectra (Figs. 1 and 2)

Structure	m/z	n	m	Calculated molar mass of the structure cationized with Na^+
A	933	2	—	932.11
	1217	3	—	1216.46
	1502	4	—	1500.81
B	951	2	—	950.11
	1235	3	—	1234.46
	1520	4	—	1518.80
C	1061	2	2	1062.25
	1345	3	2	1346.60
D	1161	3	—	1163.41
	1445	4	—	1447.76
E	970	2	—	968.58
	1253	3	—	1252.93
	1538	4	—	1537.28
F	1080	0	2	1080.72
	1365	1	2	1365.72
G	1044	0	2	1044.26



where



* Cl was also found in the technical products by elemental analysis

Scheme 4

TABLE II
Comparison of the $\langle M_n \rangle$ Values of the Epoxy Resins
Given by the Producer and Determined from the
 $^1\text{H-NMR}$ Spectra

Resin	$\langle M_n \rangle$	
	Producer	$^1\text{H-NMR}$
Epidian 1	1000	1050
Epidian 012	2000	1850
Epidian 014	3100	3100
Epidian 016	6600	4500

and established that there are several structural imperfections. Depending on the source of the epoxy resins, these imperfections could differ, as the manufacturing processes also differ. Thus, we analyzed by MALDI the molecular structures of the epoxy resins used throughout this work (technical products of Organika-Sarzyna). In Figures 1 and 2, the MALDI-TOF spectra of the epoxy resins with molar mass ($\langle M_n \rangle$) values equal to 1000 and 2000 (data from producer) are shown.

By a comparison with data published by Pasch et al.,⁷ we have found similar structures, denoted by us as **A**, **B**, and **E₁**. On the other hand, we have found in our samples (Sarzyna) structures **C**, **D**, **F**, **F₁**, and **G**, which were not observed by Pasch et al. in the Dow resins.

To comprehend better the original MALDI-TOF MS results, there are inserts in the corresponding figures indicating the structures in more detail. In Table I, the assignments of the selected signals shown in the expanded MALDI-TOF mass spectra are given. The structures are shown in Scheme 4. Whenever the chlorohydrin structure is observed, it could be present in one of the two positions, as indicated by an arrow.

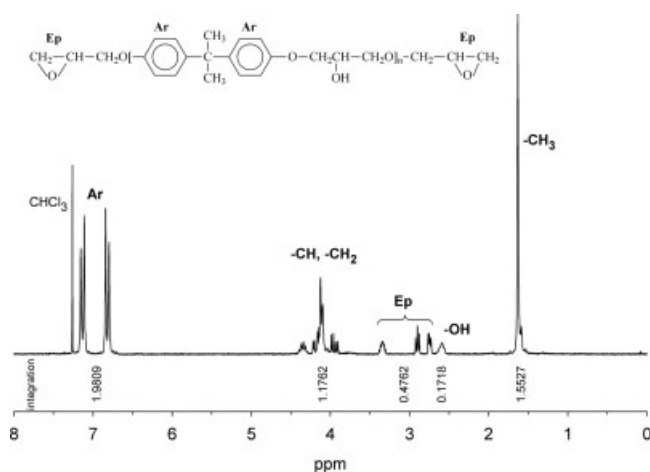


Figure 3 $^1\text{H-NMR}$ spectrum of Epidian 1.

The actual proportions of the given structures are not exactly known because the MALDI response could differ with the structure. Nevertheless, particularly for the higher molar mass, the influence of these differences may be less evident.

In Table II, the $\langle M_n \rangle$ values determined from the epoxy content (data given by producer) are compared with our $^1\text{H-NMR}$ measurements, assuming a simple structure without side products. The disagreement observed for the highest molar mass product 6600 (4500) indicates that in this product there is more branching than in the lower mass resins. This is understandable if the chemistry of the synthesis is taken into account.

In Figure 3, the $^1\text{H-NMR}$ spectrum of the epoxy resin (Epidian 1) is shown, indicating the corresponding groups (electronic integration is given, being used in the calculations). From this and similar spectra, $\langle M_n \rangle$ could also be calculated under the same assumption described previously.

Phosphorylation processes

First, the dependence of the structure of phosphorylated products (i.e., the ratio of the monoesters, diesters, and triesters) on the $[\text{H}_3\text{PO}_4]_0/[\text{Epoxy Group}]_0$ ratio was studied. Thus, we determined the proportions of the monoesters, diesters, and triesters as well as the concentration of the H_3PO_4 left and other structures (e.g., pyrophosphates) related to this ratio in the starting reaction mixture.

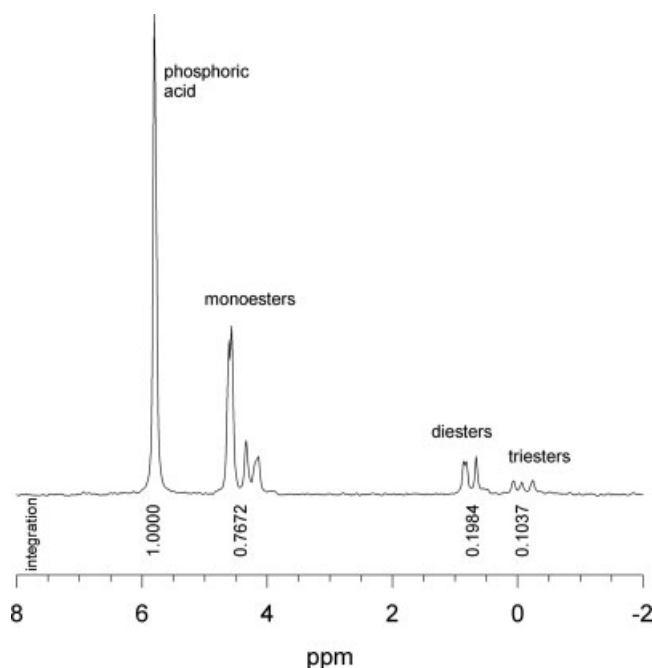
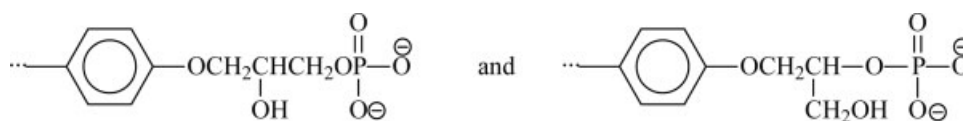


Figure 4 $^{31}\text{P-NMR}$ spectrum of the reaction mixture of BADE with H_3PO_4 in dioxane at 25°C after 25 h (reaction conditions: $[\text{H}_3\text{PO}_4]_0/[\text{Epoxy Group}]_0 = 1 : 1$).



Scheme 5

A typical ^{31}P -NMR spectrum, with assignments for the major chemical shifts, is given in Figure 4. This and all other ^{31}P -NMR spectra were taken in H_2O as the solvent at $\text{pH} \sim 12$ because under these conditions there is no overlap of the monoesters, diesters, and triesters, which are known to overlap under neutral or acidic conditions.

Depending on the reaction conditions, various ratios of monoesters, diesters, and triesters are observed. In Figure 4, all of the major groups of the structures are identified, although we are not in a position to discriminate more subtle structures within the monoesters, diesters, and triesters. Perhaps, for instance, within monoesters, the major peak is related to the product of regular additions, without side processes in its vicinity (Scheme 5).

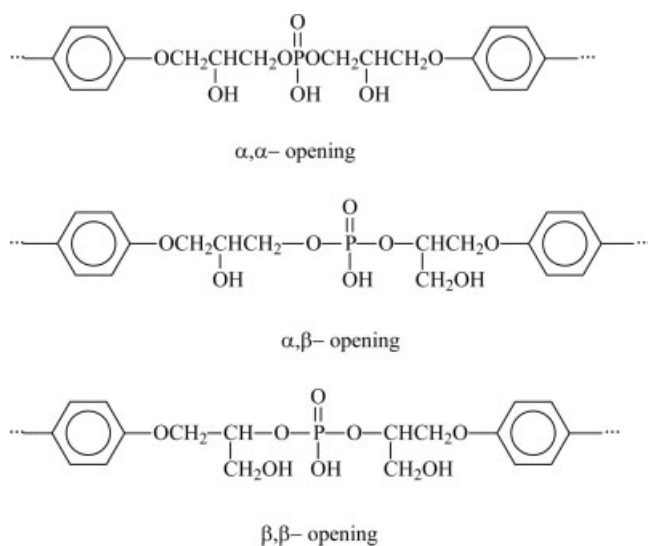
The major peak is split into two, apparently because of the two different ways of ring opening. Actually, in our work on the reaction of propylene oxide (methyl oxirane) with H_3PO_4 , the α - and β -ring openings were found to proceed with almost the same probability.⁵ The other peaks in this region, usually two smaller singlets (one of these is further split), can be related to the end group having in its vicinity the $-\text{OH}$ substituted during synthesis, by either a reaction with an epoxy group or phosphorylation. During the course of the reaction, the ratios of the peak areas (from electronic integrations) of these three signals, located within the chemical shifts

of the monoesters, change from 9.2 : 2.6(3.5) : 1 at the beginning (first recorded spectrum) to 6.2 : 1.9(3.3) : 1 at the end of reaction. In the angle brackets, the ratio of the first two signals are given.

Thus, the changes in these proportions are not substantial, at least for the first two peaks, in the course of the reaction. In the region of the diesters, there are products of a lower degree of phosphorylation, mostly two singlets: one split into two, very close to one another at $\delta = 0.83$ ppm and $\delta = 0.67$ ppm. In the later stages of the reaction, the third peak at $\delta = 0.50$ ppm appears.

The most probable structures are α,α -opening and other isomers, in which the first and second ring openings may be of the α or β type, giving the structures shown in Scheme 6.

Thus, at 0.43–0.87 ppm, we may have products resulting from the α,α -, α,β -, and β,β -opening. The major peak, split into two, differing only by $\delta = 0.04$ ppm, may be due to the α,α -opening and α,β -opening, whereas the next singlet, at $\delta = 0.67$ ppm, could be due to the β,β -ring opening. The ratio of these peaks is close to 1.5, whereas for the equal probabilities of product formation, a 2 : 1 ratio could be expected. The third small peak may result from the diester having in its vicinity substituted hydroxyl groups [$-\text{CH}(\text{OH})-$] existing from the beginning or



Scheme 6

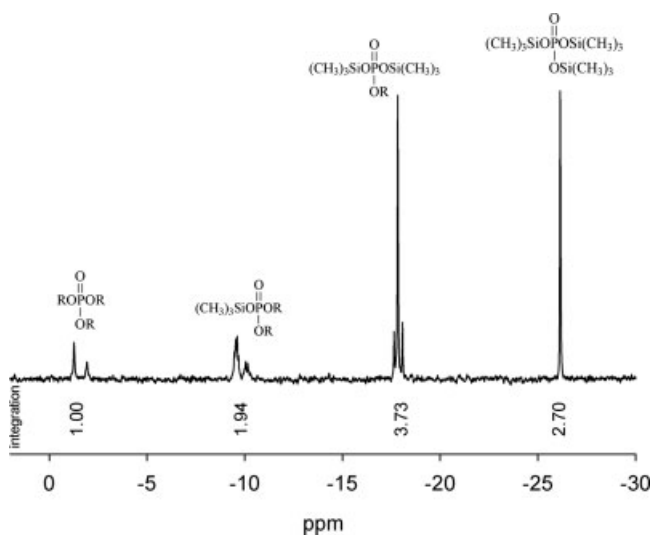


Figure 5 ^{31}P -NMR spectrum of a typical silylated reaction mixture of BADE with H_3PO_4 in a dioxane solvent at 25°C after 25 h (reaction conditions: $[\text{H}_3\text{PO}_4]_0/[\text{Epoxy Group}]_0 = 1 : 1$).

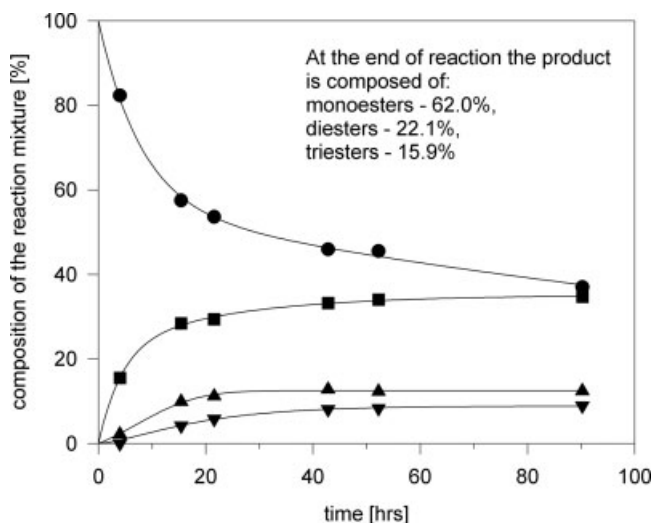


Figure 6 Kinetics of the reaction of H_3PO_4 (0.68 mol/L) with BADE (0.34 mol/L) in 1,4-dioxane at 25°C: (▼) triesters, (▲) diesters, (■) monoesters, and (●) H_3PO_4 .

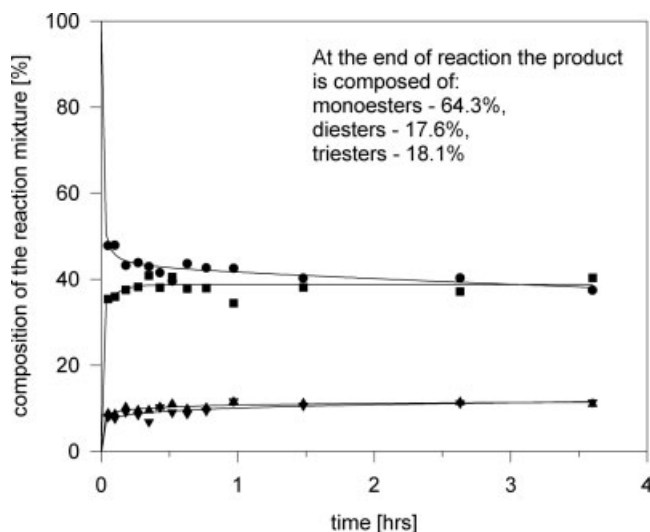


Figure 8 Kinetics of the reaction of H_3PO_4 (0.68 mol/L) with BADE (0.34 mol/L) in 1,4-dioxane at 100°C: (▼) triesters, (▲) diesters, (■) monoesters, and (●) H_3PO_4 .

formed during the phosphorylation process. In the region of triesters (from $\delta = -0.23$ ppm to $\delta = 0.08$ ppm), there are three peaks; their peak areas and positions do not change with the conversion. The triesters are formed in the reactions of diesters with epoxy groups from another molecule. The three singlets most likely hide a much more complicated pattern due to the superposition of the differences described for a diester, plus two possible epoxy ring openings.

The previously described structural analysis was based on the ^{31}P -NMR spectra studied in H_2O as a solvent at $\text{pH} \sim 12$. It was possible because products of H_3PO_4 addition to BADE (the lowest molar mass

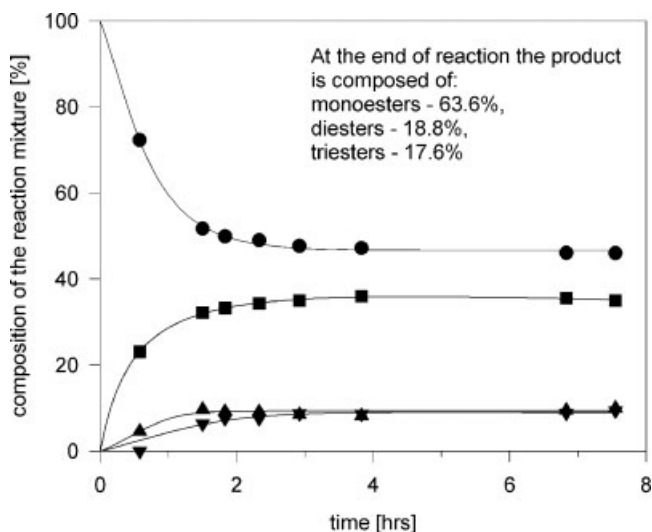


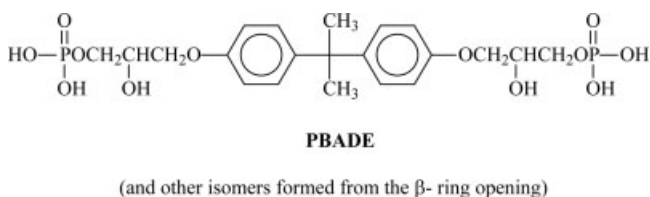
Figure 7 Kinetics of the reaction of H_3PO_4 (0.68 mol/L) with BADE (0.34 mol/L) in 1,4-dioxane at 55°C: (▼) triesters, (▲) diesters, (■) monoesters, and (●) H_3PO_4 .

epoxy resin from bisphenol A) are soluble in H_2O . Similar reaction products of H_3PO_4 with epoxy resins of higher molar masses are not soluble in H_2O . Therefore, the structural aspects of these products had to be studied differently. It is also known that in organic solvents acidic esters of H_3PO_4 of a given alcohol absorb in the same region, excluding any possibility of the structural analysis. Therefore, to distinguish structural units, the required samples of the reaction mixture (still containing H_3PO_4) were silylated. In the reaction with hexamethyldisilazane, the corresponding esters are formed and are known to absorb in the ^{31}P -NMR spectra as follows: $[(\text{CH}_3)_3\text{SiO}]_3\text{P}=\text{O}$ at $\delta = -25$ ppm, $[(\text{CH}_3)_3\text{SiO}]_2\text{P}(\text{O})\text{OR}$ at $\delta = -17$ to -18 ppm, and $[(\text{CH}_3)_3\text{SiO}]\text{P}(\text{O})(\text{OR})_2$ at $\delta = -7$ ppm. A typical spectrum of the product, containing all mentioned previously structures, is shown in Figure 5.

There is a major peak at -17.5 ppm of the silylated monoester, and there are peaks related to diesters and triesters as well as a peak at -25 ppm (H_3PO_4).

TABLE III
Dependence of the Ratios of Various Esters on the Starting $[\text{H}_3\text{PO}_4]_0/[\text{Epoxy Group}]_0$ Ratio at 25°C

No.	$[\text{H}_3\text{PO}_4]_0/[\text{Epoxy Group}]_0$ (mol/mol)	Final composition (%)		
		Monoester	Diester	Triester
1	1.05	59.2	26.0	14.8
2	2.23	74.2	16.1	9.7
3	5.44	84.6	8.8	4.6
4	11.55	92.0	5.3	2.6
5	17.36	~ 100	0	0
6	23.28	~ 100	0	0



Scheme 7

Kinetics of polyaddition

The course of polyaddition was studied on the basis of the $^1\text{H-NMR}$ spectra (disappearance of epoxy groups) and $^{31}\text{P-NMR}$ spectra (appearance of esters). Typical plots, giving the dependence of the H_3PO_4 , monoester, diester, and triester concentrations as a function of time, are shown in Figures 6–8.

At 25°C , the reaction is relatively slow and requires approximately 100 h for completion. However, already at 55°C , a few hours are sufficient, and at 100°C , the reaction is completed in minutes. Clearly, the higher the proportion is of monoesters, the higher the temperature is of the reaction.

Structure of the products versus the reaction conditions

In our earlier work, it was shown (as indicated above) that the rate of reaction of ethylene oxide with P–OH groups is increasing in the following order: $(\text{RO})_2\text{P}(\text{O})\text{OH} > \text{ROP}(\text{O})(\text{OH})_2 > \text{H}_3\text{PO}_4$. The obvious way to obtain mostly the simple addition products is to use a large enough excess of H_3PO_4 over the epoxy groups. The dependence of the pro-

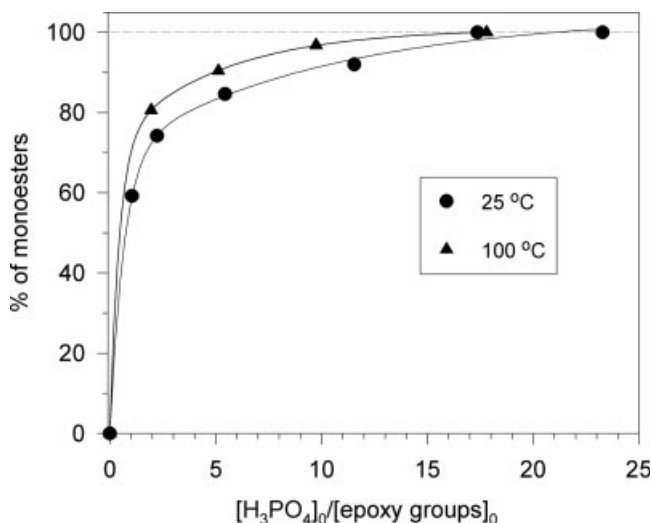


Figure 9 Dependence of the proportion of monoesters on the $[\text{H}_3\text{PO}_4]_0/[\text{Epoxy Group}]_0$ ratio at 25 and 100°C in 1,4-dioxane [reaction conditions: H_3PO_4 (0.68 mol/L) and epoxy groups (0.68 mol/L)].

portions of the various esters as a function of this ratio is shown in Table III.

Thus, for the reaction of BADE, conducted at 25°C in a 1,4-dioxane solvent in such a way that the solution of BADE in the dioxane solvent was slowly introduced to the H_3PO_4 solution in the same solvent, the (practically) exclusive structure of the monoesters (PBADE) was observed when the $[\text{H}_3\text{PO}_4]_0/[\text{Epoxy Group}]_0$ ratio was close to 17 (Scheme 7). In all experiments, the rate of addition was kept constant.

The proportion of monoesters in the mixture of phosphoric acid esters as a function of the $[\text{H}_3\text{PO}_4]_0/[\text{Epoxy Group}]_0$ ratio is given in Figure 9.

When the reaction was performed at 100°C , that is, when a solution of BADE in 1,4-dioxane was introduced slowly into a solution of H_3PO_4 in the boiling dioxane, then the reaction appeared to be more selective, although the difference was rather small. This is shown in Table IV and Figure 9.

This result means, nevertheless, that the temperature coefficients of the reactions of the H_3PO_4 and monoester with epoxy group differ in such a way that the rate constant for the slower reaction (at 25°C) increases faster. This could be expected on the grounds of the general kinetics. We were not exploring higher temperatures, which could give even better results. Another explanation could be that because of the much faster reaction at a higher temperature, the time at which the P–OH/epoxy groups ratio is kept high is relatively longer.

Thus, with a large enough excess of H_3PO_4 over epoxy groups, almost exclusively monoesters of phosphoric acid are formed. Reaction products close to the simple addition products based on BADE are water-soluble. The higher molar mass epoxy resins were phosphorylated in the same way as described for BADE. However, for all of these resins, that is, Epidian 012, Epidian 014, and Epidian 016, the H_3PO_4 /epoxy resin ratio equal to ~ 4.0 was already sufficient to have over 95% monoesters (95% of the P atoms in the phosphorylated resin were in monoesters, and the rest, i.e., 5%, were in the diesters and triesters). The phosphorylated products were simply precipitated from the dioxane solution into water,

TABLE IV
Dependence of the Ratios of Various Esters on the Starting $[\text{H}_3\text{PO}_4]_0/[\text{Epoxy Group}]_0$ Ratio at 100°C

No.	$[\text{H}_3\text{PO}_4]_0/[\text{Epoxy Group}]_0$ (mol/mol)	Final composition (%)		
		Monoester	Diester	Triester
1	1.95	80.6	11.2	8.2
2	5.13	90.4	6.3	3.1
3	9.74	96.8	3.2	0
4	17.80	~ 100	0	0

washed until the neutral pH, dried, silylated, and analyzed by ^{31}P -NMR as described for the silylated product of the BADE- H_3PO_4 reaction (Fig. 5).

CONCLUSIONS

BADE was taken as a model of epoxy resins for the phosphorylation reaction. A relatively high excess of H_3PO_4 over epoxy groups is required at 25°C to have almost exclusively a simple addition product, that is, a monoester. At lower ratios, the phosphorylated products contain also diesters and triesters. Their proportions as a function of the H_3PO_4 /epoxy groups have been determined.

The higher molar mass epoxy resins were studied by MALDI-TOF MS, and it was shown that they contain a large number of isomeric side products. The phosphorylation of these resins is much more

specific than that of BADE; that is, a higher proportion of monoesters is obtained at lower H_3PO_4 /epoxy group ratio.

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