Mechanisms of Thermal Degradation of Phenolic Condensation Polymers.   III.   Cleavage of Phenolic Segments during the Thermal Degradation of Uncured Epoxy Resins*

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Synopsis

The phenolic cleavage of the uncured epoxy resins is further substantiated by the semi-quantitative study with the aid of the mass spectrometer analysis.   In general, the phenolic cleavage (at 475°C.) of the epoxylated novolac resin, D.E.N. 438 resin, was found to be similar to that of the unepoxylated novolac resin.   For both cases, cresols and phenol were the major products as a result of the homolytic cleavage and the subsequent hydrogen abstraction.   At the same time, a small amount of xanthene or the substituted xanthenes appeared in the mixture presumably due to the dehydration of related phenolic compounds.   A small amount of $C_6H_5OC_3H_3$ or $C_6H_4OC_3H_4$ could indicate that there could be some cyclization of the glycidyl ether side chain of the epoxylated novolac resin.   For the epoxylated bisphenol-A resin, D.E.R. 331 resin, the phenolic cleavage at high temperature appeared to follow two major and one minor scheme.   The first type of cleavage is undoubtedly homolytic to yield isopropylphenol, C_2H_5 phenols, cresols, and phenol.   The second type cleavage was not found in the above two resins and is heterolytic in nature.   This cleavage resulted in the formation of isopropenylphenol.   Due to the presence of $C_6H_5OC_3H_3$ or $C_6H_4OC_3H_4$, it is postulated that the cyclization of the glycidyl ether side chain may also, take place.

INTRODUCTION

The study on the thermal stability and degradation schemes of epoxy resins was reported previously.[1]   The experimental results showed that the phenolic compounds, in addition to the tarry residues, were the major degradation products.   Hence, the data did not support the degradation scheme proposed by Neiman and co-workers.[2]   Several degradation schemes especially related to the glycidyl ether side chain were proposed, based on the principles of the cleavage of simple ethers and the products obtained from the pyrolysis study.

This part of the study was carried out to confirm our previous findings and understand the degradation schemes especially related to the phenolic segments of uncured epoxy resins.   An epoxylated novolac resin, D.E.N.

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438 resin, and an epoxylated bisphenol-A resin, D.E.R. 331 resin, were used as models. The degradation schemes for these two types of epoxy resins are proposed to account for the phenolic compounds obtained from the pyrolysis.

It is important to note that, in practice, it is not easy to isolate the pure thermal degradation from the oxidative degradation. As mentioned previously, the curing of epoxy resins is generally carried out in the presence of air. Oxidation could have taken place easily prior to the thermal degradation. Therefore, it is difficult to discuss the thermal degradation without mentioning the oxidative degradation.

The oxidation of the methylene bridges in the phenolic resins was studied by Ouchi and Honda,[3] Levine,[4] and Conley.[5] In novolac resins and in the epoxylated novolac resins, such as D.E.N. 438 resin, the oxidation of methylene bridges should follow the same pattern. The oxidative degradation of bisphenol-A epoxy resin was reported by Park and Blount[6] and Conley.[7] In this study, we intend to limit our discussion predominantly to the mechanisms of thermal degradation under idealized conditions.

EXPERIMENTAL

Materials

D.E.R. 331 resin is a liquid resin with an epoxide equivalent between 186 and 192 (total chlorine 0.35%). D.E.N. 438 resin is a viscous semisolid with an epoxide equivalent between 175 and 182 (total chlorine 0.30%). The n value for the phenolic unit was found to have an average value of 3.5 (or 1.5 for the center unit). A novolac resin of higher n value also prepared in the presence of an acid catalyst was used as reference for the degradation study.

Mass Spectrometric Analysis of the Pyrolyzed Products

The pyrolysis tube consisted of an 8-in. glass tube sealed at one end. There was a 90° bend 5 in. from the sealed end. This tube was connected to a vacuum pump. The polymer was pyrolyzed at 475°C. under vacuum for 3 hr. The U-tube was immersed in liquid nitrogen during pyrolysis. After the pyrolysis, the contents of the various portions of the tubes and the residue in the pyrolysis tube were washed several times with acetone. After the acetone evaporated from the extract, the wet residue was then extracted with methylene chloride to separate the organic materials from water.

For these uncured epoxy resins, a major difficulty during the pyrolysis was the distillation of the resins with the pyrolyzed volatile products. The unpyrolyzed resin remained as a part of the high-boiling volatiles which could not be detected in the mass spectrum. Therefore it was difficult to carry out a quantitative study.

However, a semiquantitative study was carried out to show the relative abundance of phenolic compounds: The epoxylated novolac resin, D.E.N. 438 resin (1.70 g.) was pyrolyzed in the above-described apparatus. The tarry residue weighed 0.69 g. (40.6%). The soluble fraction weighed 0.81 g. (53.6%). A portion of the latter fraction (0.021 g.) was analyzed with a 90° sector magnetic scanning mass spectrometer. The low molecular weight phenolic compounds were found to be phenol (3%) cresols (6%), C_2H_5 phenols (0.3%), $C_6H_5OC_3H_3$ or $C_6H_4OC_3H_4$ (0.2%), C_3H_5 phenols (0.08%), and C_3H_7 phenols (0.1%). Other compounds found in small quantities are shown in Table I. The relative abundance of the low molecular weight phenolic compounds is shown in Table II.

TABLE I
High-Boiling Products from Pyrolysis of Uncured Resins
(470°C. under Vacuum)

Compounds	m/e	Novolac resin (acid-catalyzed)	D.E.N. 438 (epoxy eq. 175–182)	D.E.R. 331 (epoxy eq. 186–192)
Cresols	108	Largest	Largest	Major
Phenol	94	Major	Major	Largest
$(HOC_6H_4)_2CH_2$	200	Major	Major	—
C_2H_5 phenols	122	Minor	Minor	Major
$(HOC_6H_4)_2(CH_2)_2$	214	Minor	Minor	—
$C_6H_4OC_2H_4$	132	—	Minor	Major
C_3H_5 phenols	134	—	Trace	Major
C_3H_7 phenols	136	—	Trace	Major
Bisphenol—A	228	—	—	Minor
Compounds in trace quantities	—	100, 128, 152, 178, 180, 182, 190, 196, 208	120, 152, 164, 181, 196, 197, 256	146, 150, 160, 174, 211, 213, 264, 278, 292

TABLE II
Relative Abundance of Low Molecular Weight Phenolic Compounds in
the Pyrolysis Products of the Uncured Epoxy Resins
(470°C. under Vacuum)

Compounds	D.E.N. 438 (epoxy eq. 175–182), %	D.E.R. 331 (epoxy eq. 186–192), %
Phenol	30.9	40.0
Cresols	61.8	12.0
C_2H_5 phenols	3.1	8.0
$C_6H_4OC_3H_4$	2.1	8.0
C_3H_5 phenols	0.8	12.0
C_3H_7 phenols	1.0	20.0

The epoxylated bisphenol-A resin, D.E.R. 331 resin, was pyrolyzed in a similar manner. The residue weighed 0.02 g. The soluble fraction weighed 2.30 g. (97.4%). This fraction contained most of the unpyrolyzed resin. A portion of this fraction (0.022 g.) was analyzed with the mass spectrometer. The low molecular weight phenolic compounds were found to be phenol (1%), cresols (0.3%), C_2H_5 phenols (0.2%), $C_6H_5OC_3H_3$ or $C_6H_4OC_3H_4$ (0.2%), C_3H_5 phenols (0.3%), and C_3H_7 phenols (0.5%). The remaining portion was chiefly the unpyrolyzed resin. The relative abundance of the phenolic compounds is shown in Table II.

DISCUSSION

Degradation Schemes of Epoxide

In Part II,[1] the degradation schemes of the epoxide group on the side chain were discussed. According to Anderson,[7] the epoxide may isomerize into an aldehyde group to account for the exothermic reaction observed for most epoxy resins during the thermal degradation. This scheme is equivalent to scheme I described in Part II. For the epoxylated novolac resin, most of the *ortho* positions were blocked. It seems likely that the isomerization may be one of the major degradation schemes.

The epoxide may undergo etherification or polymerization to form 1,3-diethers. The ethers may cleave according to any one of three different schemes depending upon the type of group attached to the ether oxygens as discussed in scheme II. Two types of Claisen rearrangement could take place to give rise to vinylphenols or allylphenols (or isopropenylphenols) to account for the formation of the polymeric residue and the gaseous compounds, such as allene. For the well-cured epoxy resin, 1,2,3-triether should be the predominant linkage; the cleavage of this type of linkage would give acetaldehyde, acrolein, formaldehyde and other gaseous compounds (scheme III). The last scheme in the previous study described the cleavage involving the oxidized linkage to yield carbon dioxide, vinylphenol and/or an unsaturated acid.

In general, according to the experimental results, phenolic compounds were the major decomposition products. The presence of various phenolic compounds is sufficient to support the main theme of the degradation mechanisms proposed by us involving the cleavage of phenoxy oxygen. Therefore, the cleavage should take place between the phenoxy oxygen and the carbon on the glycidyl ether side chain under normal conditions. In the following sections, the identification of various phenols should further confirm the overall degradation mechanisms proposed in the previous paper.

Phenolic Cleavage during the Thermal Degradation of Novolac Resin

In the absence of oxygen, the cleavage of the methylene bridges in the novolac resin followed a chain-scission path. The predominant reaction was therefore a homolytic cleavage. Subsequently, the radicals so formed
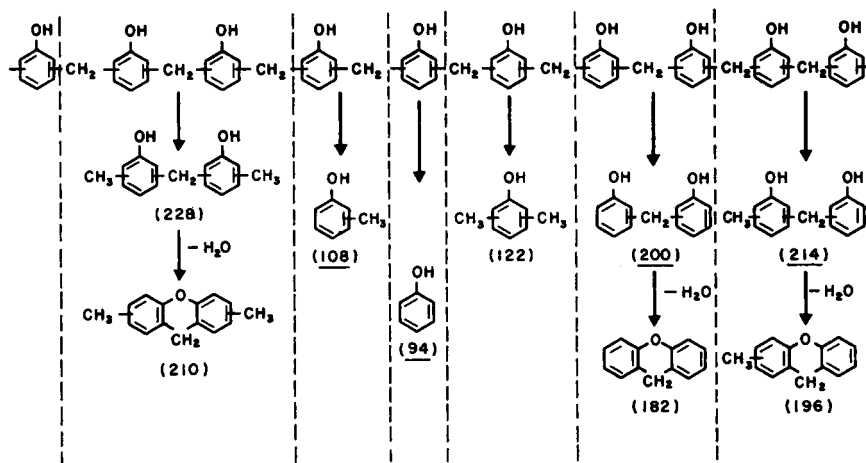
Fig. 1. Proposed scheme for the thermal degradation of novolac resin.

underwent a hydrogen abstraction. This could account for the two major types of phenolic compounds, cresols and phenol, obtained from the pyrolysis (Table I). A small amount of dehydration could account for the formation of xanthene or the substituted xanthenes. A degradation scheme such as that shown in Figure 1 is proposed.

Phenolic Cleavage during the Thermal Degradation of Epoxylated Novolac Resin

The novolac resin was used as the model for the epoxylated novolac resin. In fact, the degradation schemes of these two resins are similar.
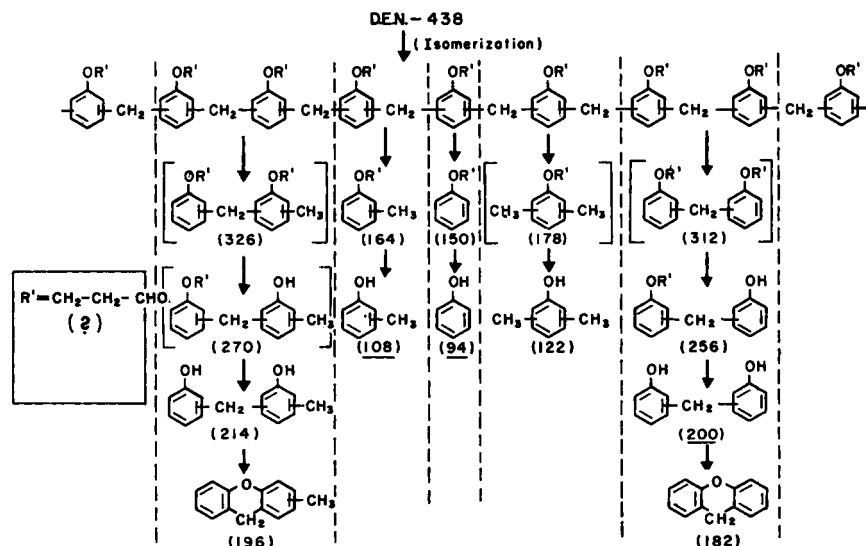
Fig. 2. Proposed scheme for the thermal degradation of epoxylated novolac resin.

A difference was found in the cleavage of the glycidyl side chain. From the compounds listed in Table I, a slight difference is found in the trace impurities but not in the major compounds.

Cresols and phenol were shown to be the two largest components (Table II). A small amount of $C_6H_5OC_3H_3$ or $C_6H_4OC_3H_4$ could indicate that there could be some cyclization taking place as described in the later section regarding bisphenol-A epoxy resin. This compound was not found in the pyrolysis products of the novolac resin discussed in the preceding section. A degradation scheme is proposed as in Figure 2. In this scheme, the sequence of the cleavage of the glycidyl ether side chain and that of the phenolic unit is immaterial. We have not established the exact sequence which actually takes place. However, from the bond energy data, one might expect that the C—O bond (85 kcal./mole) is slightly stronger than the benzylic C—C bond (<82.6 kcal./mole).

Phenolic Cleavage during the Thermal Degradation of Bisphenol-A Epoxy Resin

Phenol instead of cresols was found to be the largest component in the pyrolysis products of the uncured D.E.R. 331 resin (Table I). Based on the relative abundance of other low molecular weight phenolic compounds
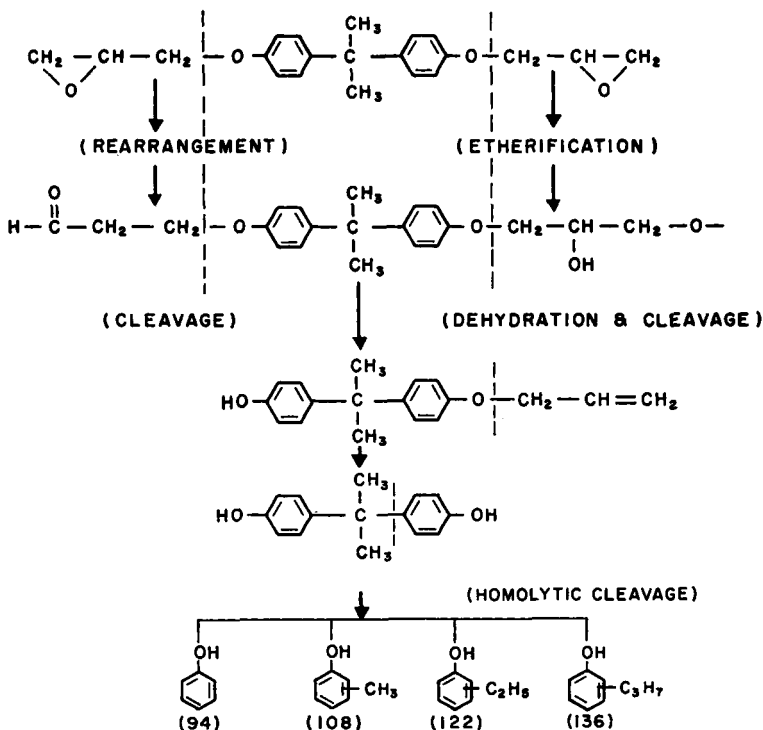

Fig. 3. Proposed scheme for the thermal degradation of bisphenol-A epoxy resin. Phenolic cleavage I.

(Table II), one could establish two major and one minor degradation mechanisms. The first mechanism regarding the phenolic cleavage appears to be the homolytic breakdown to yield isopropylphenol, C_2H_5 phenols, cresols, and phenol as shown in Figure 3. The second mechanism

BISPHENOL CLEAVAGE
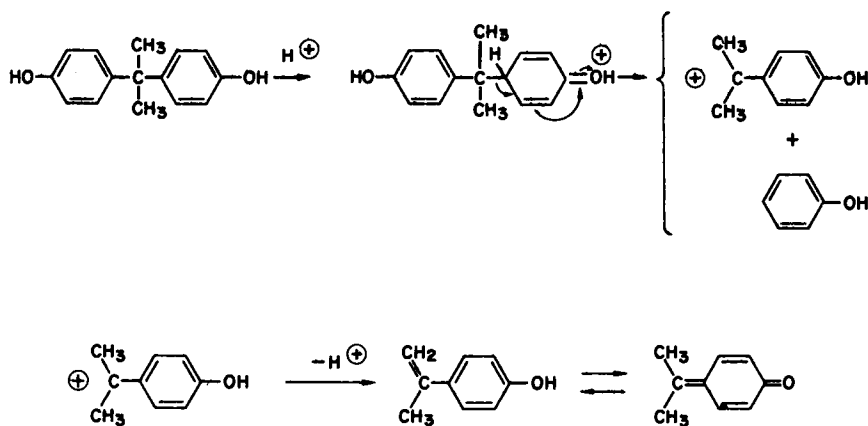**(HETEROLYTIC)**

Fig. 4. Proposed scheme for the thermal degradation of bisphenol-A epoxy resin. Phenolic cleavage II.
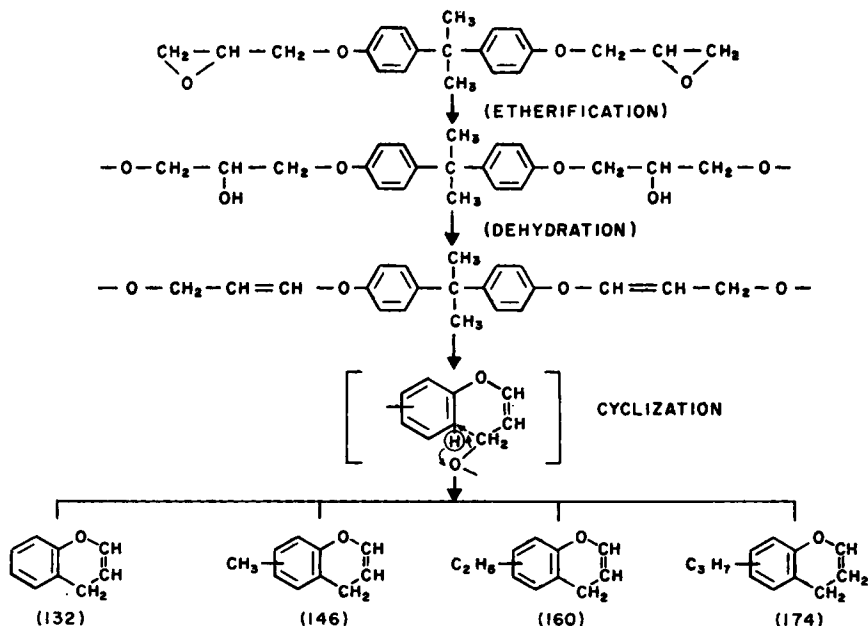

Fig. 5. Proposed scheme for the thermal degradation of bisphenol-A epoxy resin. Phenolic cleavage III.

appears to be the heterolytic cleavage of the bisphenol-A unit to yield
isopropenylphenol and phenol (Fig. 4). As discussed in Part I[8] of this
series, isopropenylphenol could easily isomerize into a dienone (Fig. 5)
which is usually stabilized by a further substitution, e.g., the attack by
oxygen. We also found that this unsaturated isopropenylphenol de-,
composed readily in the presence of ultraviolet radiation. Therefore
from both the color and the light stabilities, this heterolytic cleavage is
highly detrimental.

The third minor mechanism has not yet been established. It is pos-
tulated that a cyclization may take place to form a benzopyran structure
as shown in Figure 5. This type of compound can be used to account for
the unidentified product $C_6H_5OC_3H_3$ or $C_6H_4OC_3H_4$ and the homologs
detected by the mass spectrometer.

CONCLUSIONS

The thermal degradation schemes for epoxy resins proposed in the pre-
vious paper were confirmed by the identification of various phenolic com-
pounds in the pyrolysis products. The phenolic cleavage of the uncured
epoxy resins was further substantiated by the semiquantitative study. In
general, the phenolic cleavage (at 475°C.) of the epoxylated novolac resin,
D.E.N. 438 resin, was found to be similar to that of the unepoxylated
novolac resin. Cresols and phenol were the major products. The homo-
lytic cleavage took place at the methylene bridge. The radicals so formed
underwent a hydrogen abstraction. A small amount of dehydration could
account for the formation of xanthene or the substituted xanthenes. A
small amount of $C_6H_5OC_3H_3$ or $C_6H_4OC_3H_4$ could indicate that there could
be some cyclization of the glycidyl ether side chain of the epoxylated
novolac resin.

The phenolic cleavage of the epoxylated bisphenol-A resin, D.E.R. 331
resin, was found to follow two major and one minor scheme. The first
scheme was the homolytic cleavage of the bisphenol-A unit to yield iso-
propylphenol, C_2H_5 phenols, cresols, and phenol. The second scheme was
the heterolytic cleavage of the bisphenol-A unit to yield isopropenylphenol
and phenol. The third scheme was postulated to be the cyclization of the
glycidyl ether side chain to yield $C_6H_5OC_3H_3$ or $C_6H_4OC_3H_4$.

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Résumé

La scission phénolique des résines époxy non-recuites a été également prouvée par l'étude semi-quantitative au moyen de l'analyse par spectrographie de masse. En général, la scission phénolique (à 475°C) de la résine 'novolaque' époxylée, résine D.E.N. 438, est semblable à celui de la résine 'novolaque' non-époxylée. Dans les deux cas, les crésols et le phénol sont les produits principaux de la rupture homolytique et de l'arrachement subséquent d'hydrogène. En même temps, une petite quantité de xanthène ou de xanthènes substitués apparaît dans le mélange, ce qui est probablement dû à la déshydratation des composés phénoliques. Une petite quantité de $C_6H_5OC_3H_3$ ou de $C_6H_4OC_3H_4$ pourrait indiquer qu'il y a une certaine cyclisation des chaînes latérales d'éther glycidylique de la résine 'novolaque' époxylée. Pour la résine époxylée bisphénol-A, résine D.E.R. 331, la scission phénolique à température élevée semble suivre deux schémas principaux et un schéma secondaire. Le premier type de scission est indubitablement homolytique et fournit de l'isopropylphénol, des phénols C_2H_5, des crésols et du phénol. Le second type de scission n'a pas été trouvé dans les deux résines ci-dessus et est de nature hétérolytique. Cette rupture conduit à la formation d'isopropénylphénol et de phénol. A cause de la présence de $C_6H_5OC_2H_3$ ou de $C_6H_4OC_3H_4$, on postule que la cyclisation de la chaîne latérale d'éther glycidylique peut également avoid lieu.

Zusammenfassung

Die Phenolspaltung ungehärteter Epoxharze wird durch eine halbquantitative Untersuchung mit Massenspektrometeranalyse bewiesen. Im allgemeinen erwies sich die Phenolspaltung (bei 475°C) des epoxylierten Novolakharzes, Harz D.E.N. 438, als derjenigen des nicht epoxylierten Novolakharzes ähnlich. In beiden Fälen waren Cresole und Phenol die Hauptprodukte als Ergebnis einer homolytischen Spaltung und darauffolgender Wasserstoffabstraktion. Gleichzeitig trat offenbar durch Dehydratation verwandter phenolischer Verbindungen eine kleine Menge von Xanthen oder von substituierten Xanthenen in der Mischung auf. Eine kleine Menge von $C_6H_5OC_3H_3$ oder $C_6H_5OC_2H_4$ könnte auf eine gewisse Zyklisierung der Glycidylätherseitenkette der epoxylierten Novolakharze hinweisen. Bei dem epoxyliertem Bisphenol-A-Harz D.E.R. 331 scheint die Phenolspaltung bei hoher Temperatur zwei Hauptwegen und einem Nebenweg zu folgen. Der erste Spaltungstype ist unzweifelhaft homolytisch und liefert Isopropylphenol, C_2H_5-Phenole, Cresole und Phenol. Der zweite Spaltungstyp konnte bei den obigen zwei Harzen nicht festgestellt werden; er verläuft heterolytisch. Diese Spaltung führte zur Bildung von Isopropenylphenol und Phenol. Wegen der Anwesenheit von $C_6H_5OC_3H_3$ oder $C_6H_4OC_3H_4$ wird angenommen, dass auch eine Zyklisierung der Glycidylätherseitenkette stattfinden kann.