

Attaching of Flexible Chains to Novolacs on the Basis of Bisphenol A

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SYNOPSIS

Networks containing both flexible segments and rigid structures were synthesized on the basis of bisphenol A novolacs and diglycidylether of butanediol using imidazole as an accelerator. A stoichiometric ratio between epoxy groups and phenolic groups of the novolacs leads to networks with methylene bridges as network junctions. In contrast to this, the same reaction with bisphenol A leads to completely soluble products. The glass transition temperature of this soluble material is considerably lower than the glass transition temperature of the networks. Increasing content of methylene bridges in the novolacs leads to an increase of the glass transition temperature of the networks and to a decrease of the Δc_p value at the glass transition. Furthermore, epoxy excess leads to networks with rubber-like properties. In addition, AM1 calculation were performed to optimize the geometric structure of the bisphenol A novolac used in the reaction with the diglycidylether. It was found that conformations with intramolecular hydrogen bondings exist between phenolic hydroxyl groups, which considerably influence the reactivity of the novolac with the epoxy group. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Phenolic resins are widely used as molding powders, laminating resins, casting resins, binders, impregnants, in surface coatings, and in adhesives. The chemical structure of phenolic resins is a very complex one. Depending on synthetic conditions, thermoplastic novolacs or resols are obtained. Thermal curing is the most important crosslinking process for resols. In contrast to this, novolac resins require the addition of a crosslinking agent. Hexamethylenetetramine, epoxies, and bisisocyanate are used as crosslinking agents. Therefore, the properties of the final product are influenced by a high number of parameters.¹⁻³

In a previous article we described the synthesis and characterization of novolacs on the basis of bisphenol A. It was possible to synthesize novolacs with a different content of methylene bridges by variation

of the ratio of paraformaldehyde to bisphenol A.⁴ The resulting novolacs were crosslinked with a diglycidylether of bisphenol A using imidazole as an accelerator. The structures formed are rigid. Generally, novolacs crosslinked by aromatic glycidylethers are brittle and, therefore, such products are limited in some application possibilities. One possibility to reduce the brittleness of such products is to combine both rigid and flexible structures.

The goal of this work was to synthesize and characterize new polymeric networks containing both flexible segments and rigid structures. Therefore, an aliphatic diglycidylether was used instead of a diglycidylether of bisphenol A to react with bisphenol A novolacs accelerated by imidazole. The resulting networks contain both flexible segments incorporated by an aliphatic diglycidylether and rigid structures of the bisphenol A novolac. Networks with different properties are obtained by variation of the diglycidylether novolac ratio. To discuss reactivity differences between bisphenol A and bisphenol A novolacs in the reaction with the aliphatic diglycidylether, semiempirical quantumchemical calcula-

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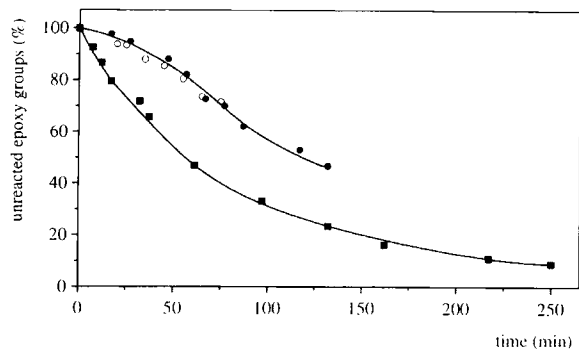


Figure 1 Concentration of unreacted epoxy groups in dependence on the time during the reaction of diglycidylether of butanediol-1.4 with bisphenol A (■) and bisphenol A novolacs [0.38 methylene bridges relative to one bisphenol A structure (●) and 0.85 methylene bridges relative to one bisphenol A structure (○)], respectively, at 100°C using a stoichiometric ratio of epoxy groups to phenolic groups and 0.65 mol % imidazole relative to epoxy groups.

tions were carried out. These semiempirical quantumchemical calculations show the existence of intramolecular hydrogen bondings in the novolacs that strongly influence the reactivity of the bisphenol A novolacs.

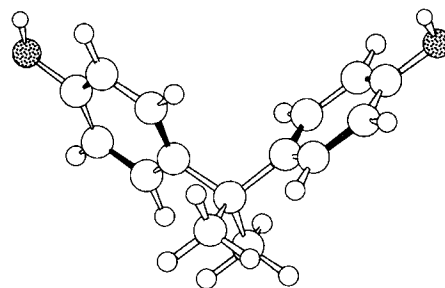
EXPERIMENTAL

The bisphenol A novolacs were synthesized from bisphenol A and paraformaldehyde in a melting process as described in a previous article.⁴ Diglycidylether of butanediol (DGEBD) was purified by distillation; b.p. 1.4 kPa 155–160°C.⁵ Imidazole was recrystallized from a toluene-ethanol mixture with an ethanol content of 1.5 vol %; m.p. 90°C.⁶

The soluble product of bisphenol A and DGEBD was synthesized by the reaction of a stoichiometric ratio of the reactants in the presence of 0.65 mol % imidazole relative to epoxy groups at 120°C.

The networks were prepared from a bisphenol A novolac and DGEBD in the presence of 0.65 mol % imidazole relative to epoxy groups at 120°C in 5 h. A stoichiometric ratio of epoxy groups to phenolic groups and epoxy excess, respectively, were used for network synthesis.

The concentration of epoxy groups was determined by titration. Therefore, 0.2 g of the sample were dissolved in 10 mL acetone. Then, 25 mL 0.1M sodium acetate solution, 25 mL water, and some gelatin were added. Furthermore, 25 mL 0.1M HBr in acetic acid were added while stirring slowly. Eosin



Scheme 1. Optimized sterical structure of bisphenol A (AM1 calculation, energy minimized conformation; heat of formation -201.3 kJ/mol).

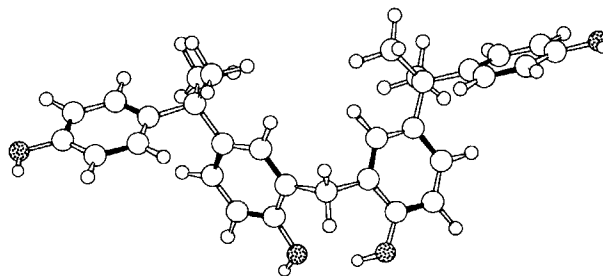
was used as an indicator. It was titrated with a 0.1M AgNO₃ solution in acetic acid.⁷

A type 11.00 Knauer vapor pressure osmometer and dimethylformamide as solvent were used for determining the molecular weight of the soluble product formed by the reaction of bisphenol A and DGEBD.

The glass transition temperatures (T_g) were measured with a Perkin-Elmer DSC in a temperature range of -70 to 200°C, with a scanning rate of 10 K/min. A second run using the same temperature range was started after 30 min isothermal heating at 200°C.

For sol gel analysis, 1 g of the rasped sample was extracted with 170 mL acetone on a soxhlet extraction for 16 h. The mass of the soluble part of the sample was determined after evaporation of acetone and drying in vacuum. Furthermore, the insoluble part was measured after drying.

Quantumchemical calculations were carried out with the program AMPAC 5.0 (Semicem Inc.). The integrated AM1 method with the corresponding parameters was applied for energy minimizations. The gradients obtained after calculations were used as a quality parameter about the calculations performed.

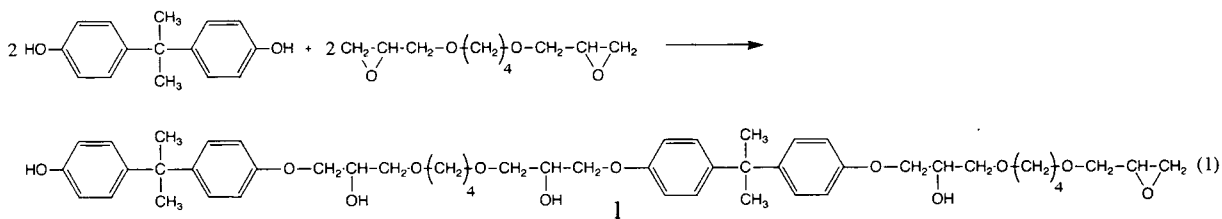


Scheme 2. Sterical structure of methylene-linked bisphenol A structures calculated using AM1 (energy minimized conformation; heat of formation -412.4 kJ/mol).

RESULTS AND DISCUSSION

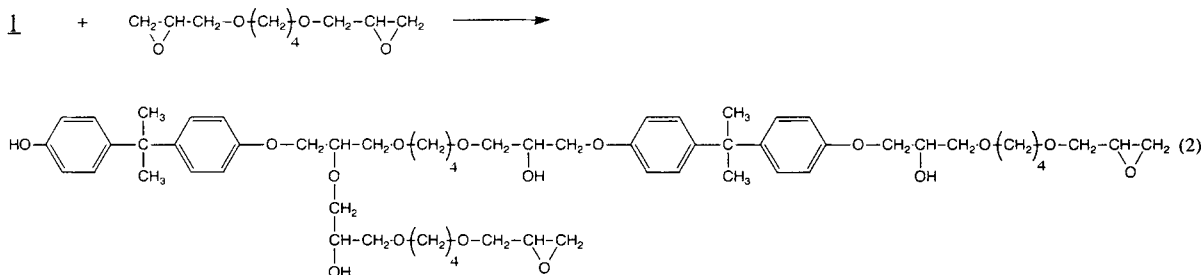
In this work, a novolac on the basis of bisphenol A was crosslinked with an aliphatic diglycidylether accelerated by imidazole. First, the chemical reactions are considered because the material properties of the final product are also influenced by the chemical processes occurring during crosslinking. Many studies

have been published concerning the mechanism of the epoxy phenol reaction, the crosslinking process, and the network structure of epoxy crosslinked novolacs.⁸⁻¹⁹ Model reactions give a clear picture about the chemical reactions occurring.¹⁸ The primary reaction is that of a phenolic group with an epoxy group forming a secondary hydroxyl group [eq. (1)]. A linear non-branched product results from this reaction.



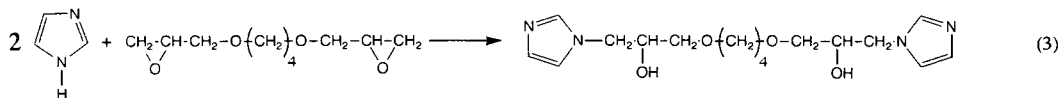
The secondary hydroxyl group formed can also react with an epoxy group [eq. (2)]. The result of

this secondary reaction is a branched and a cross-linked product, respectively.



The reactions described above are more effectively in the presence of an accelerator. Lewis bases, tertiary amines, and imidazole derivatives are used to accelerate the reaction between epoxies and phenolic compounds. The accelerator concentration strongly influences the selectivity.¹⁸ If a low imidazole concentration is used for acceleration of the

stoichiometric epoxy phenol reaction, only the epoxy phenol reaction [eq. (1)] occurs. In the case of epoxy excess, the reaction of the secondary hydroxyl group formed with epoxy groups is also accelerated by imidazole.¹⁸ On the other hand, imidazole reacts very fast with an epoxy group forming a 1 : 1 adduct [eq. (3)], which is also an effective accelerator.^{20,21}



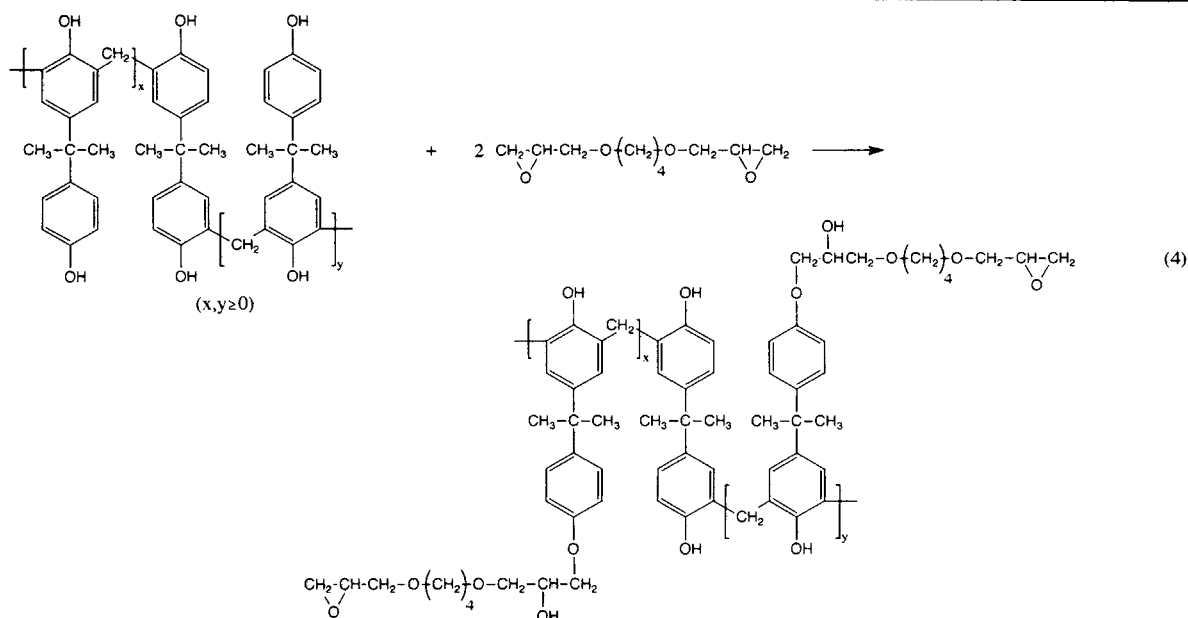
¹³C-NMR studies support the hypothesis that imidazole reacts with an epoxy group forming a 1 : 1 adduct also in an epoxy phenol reaction system.¹⁸ Therefore, both imidazole and the 1 : 1 adduct formed are accelerators in an epoxy phenol reaction system.

Stoichiometric Ratio between Phenolic Groups and Epoxy Groups

In contrast to soluble monofunctional model systems, the reaction of a bisphenol with an epoxy

compound containing two functional groups gives soluble products only in case of a stoichiometric ratio of epoxy groups to phenolic groups. In case of epoxy excess, networks are formed. The products of the reaction of bisphenol A with diglycidylether of butanediol (DGEBD) catalyzed by imidazole using a stoichiometric ratio of epoxy groups to phenolic groups were soluble over the whole reaction time. Therefore, it was possible to follow the content of epoxy groups in this reaction mixture by titration until a limited conversion is reached (Fig. 1).

Furthermore, Figure 1 demonstrates the concentration of unreacted epoxy groups during the imidazole catalyzed reaction of bisphenol A novolacs with DGEBD. The same ratio of epoxy groups to phenolic groups was used for these investigations. This reaction can be followed by titration only just before gelation occurs because of insoluble product formation. The reaction of a bisphenol A novolac with DGEBD gives products containing methylene bridges [eq. (4)]. These methylene bridges cause the formation of insoluble products and they are network junctions formed in a further reaction.



higher molecular weight products are steric hindered for the reaction with epoxy groups. An optimized structure of a simple novolac molecule is plotted in Scheme 2.

The methylene bridges in the ortho position to the hydroxyl groups in the bisphenol A structure of the novolacs are responsible for stronger hydrogen bondings in comparison to bisphenol A, which was also experimentally detected by FT-IR spectroscopy⁴ in a previous work. For a better theoretical

In addition, the reaction of epoxy groups with bisphenol A is faster in comparison to the reaction of epoxy groups with bisphenol A novolacs. Several influence factors may be responsible for this effect. First, bisphenol A is better soluble in DGEBD in comparison to bisphenol A novolacs. Moreover, there is no steric hindrance of the phenolic groups in bisphenol A (Scheme 1).

A distance of about 9.3 Å between both the OH groups exists according to the AM1 calculation for this compound. Under these circumstances, the reactivity of this compound is mainly caused by the acidity of the phenolic hydroxyl group in the epoxy system investigated. The existence of strong intermolecular hydrogen bondings can be excluded because there is no induction period (Fig. 1).

On the other hand, bisphenol A novolacs affect an induction period in the reaction with DGEBD accelerated by imidazole (Fig. 1). The bisphenol A novolacs are a mixture of higher molecular products with different molecular weight also containing bisphenol A.⁴ In contrast to the more reactive phenolic groups of bisphenol A, some phenolic groups of the

understanding of this phenomenon, AM1 calculations were performed in this work. A distance of about 2.1 Å between both the OH groups in the ortho position to the methylene bridge exists after geometry optimization. This distance is short enough for the formation of intramolecular hydrogen bonding aggregates, which occurs usually at distances lower than about 2.9 Å.²² It will be shown later in this work that a dependence exists between the torsion angle of the phenyl-C(CH₃) group and the en-

ergy of the optimized structure. Furthermore, the reactivity of bisphenol A novolacs with DGEBD is lower in comparison to bisphenol A at the beginning of the reaction because of existing intramolecular hydrogen aggregates in the novolacs used. Therefore, the reaction becomes faster after breaking the hydrogen aggregates. These hydrogen aggregates and their breaking during the reaction with the diglycidylether are responsible for the induction period in the bisphenol A novolac DGEBD imidazole reaction system (Fig. 1). The results of the theoretical calculations are reasonable, and they are a key to understand the reactivity differences of the novolacs used in this work in comparison to bisphenol A.

In addition, it was shown that intramolecular hydrogen bondings exist in novolacs on the basis of bisphenol A, which considerably influence the reactivity of the phenolic groups. Figure 2 demonstrates that these intramolecular forces lead, in fact, to stable structures that exist in the novolacs. Therefore, these intramolecular hydrogen bondings may also influence the structure of the networks.

For the geometry optimizations, the Ph—C(CH₃)₂ single bond was rotated in 10° steps. It can be seen in Figure 2 that a minimum for a theadre angle exists at about 250°. On the other hand, a maximum exists in the energy potential curves at an angle of about 0°, which is mainly affected by the sterical hindrance of the phenyl groups. A further local minimum exists at about 100°. The phenyl groups have a low sterical hindrance at this geometry but the largest distance for the H...O bonding exists at this point. Further rotation leads to a decrease of the energy because both sterical hindrance and H...O bonding distance reach a minimum. Stable intramolecular hydrogen intermediates are existent in this region. It can be seen in this figure that an energy stabilization of about 10–15 kJ/mol exists for conformations at an angle of about 250° where the lowest H...O distance was calculated. It is known from the literature that stable H...O aggregates exists up to distances of about 3–4 Å.²² As a result, the existence of such hydrogen bonding aggregates explains the existence of the induction period in the epoxide–novolac reaction. Therefore, an additional amount of energy is necessary because the O...H bonding has to be broken before the OH–epoxide reaction can start. Furthermore, there are not only differences in the reactivity between bisphenol A and bisphenol A novolacs, there also exist differences between the products of the reaction of bisphenol A and bisphenol A novolacs, respectively, with DGEBD.

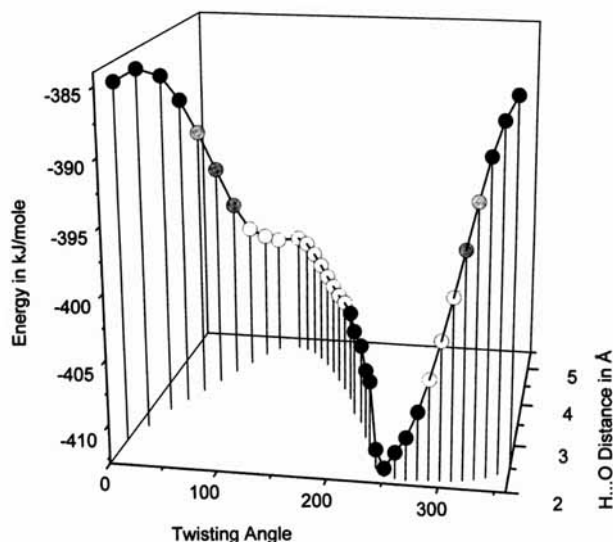
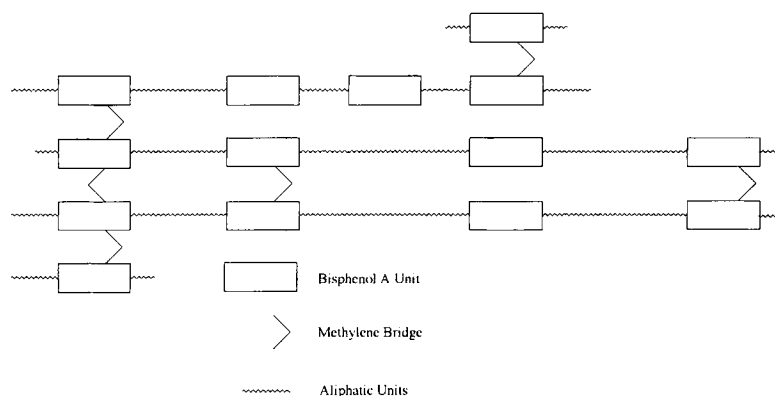


Figure 2 Energy calculated by the AM1 method by varying the theadre angle between the phenyl group and the C(CH₃)₂ group in the methylene linked bisphenol A demonstrated in Scheme 2; the distance of the neighbored OH groups was calculated for each geometry optimization at the corresponding theadre angle.

The DGEBD bisphenol A reaction at 100°C results an oligomer with an average molecular weight of 1280 g/mol determined by vapor pressure osmometry. In contrast to this, networks are formed during reaction of bisphenol A novolacs with DGEBD. These networks contain methylene bridges as network junctions, which are demonstrated in Scheme 3.

Other points of interest are the thermal properties of these new materials (e.g., glass transition temperature) because of their importance for many applications. The first step was to prepare specimens by using a stoichiometric ratio of epoxy groups to phenolic groups. Specimens prepared by reaction of a stoichiometric ratio of DGEBD and bisphenol A using imidazole as accelerator at 120°C are fully soluble. In contrast to this, a similar reaction of bisphenol A novolacs with DGEBD leads to networks with a content of soluble products between 3% and 10%. These soluble products are contributed to the content of bisphenol A in the novolacs on one side. On the other side, unreacted epoxy groups remain in the networks, which was measured by FTIR spectroscopy. DSC measurements support these results. A small postreaction was observed in the DSC curves during the first run. Therefore, the samples were allowed to react at 200°C for 30 min before a second measurement was started under the same conditions



Scheme 3. Structures in networks synthesized from bisphenol A novolac and diglycidylether of butanediol-1.4 using a stoichiometric ratio of epoxy groups to phenolic groups.

like the first run. These second DSC measurements are demonstrated in Figure 3.

Figure 3 shows that the glass transition temperatures of the networks are considerably higher than the glass transition temperature of the soluble product synthesized by reaction of the bisphenol A with DGEBD accelerated by imidazole. Furthermore, a shifting of the glass transition temperature to higher values was observed with increasing content of methylene bridges. The glass transition temperatures of the samples are plotted in dependence of the content of methylene bridges relative to bisphenol A structures (Fig. 4). The significant increase of the glass transition temperature of the networks in comparison to the soluble DGEBD bis-

phenol A product is caused in a reduction of the degree of rotation freedom by network formation.^{23,24} The glass transition temperature of the networks increases with increasing content of methylene bridges in the novolacs used for network synthesis. Bisphenol A novolac DGEBD networks contain methylene bridges as network junctions. Therefore, an increasing content of methylene bridges in the novolacs causes an increasing concentration of network junctions and a reduction of the degree of rotation freedom in the networks.

In general, the tendency of the glass transition temperatures of the samples determined before and after isothermal heating at 200°C are plotted is similar. Furthermore, it can be seen that the glass transition temperature is lower before isothermal heating

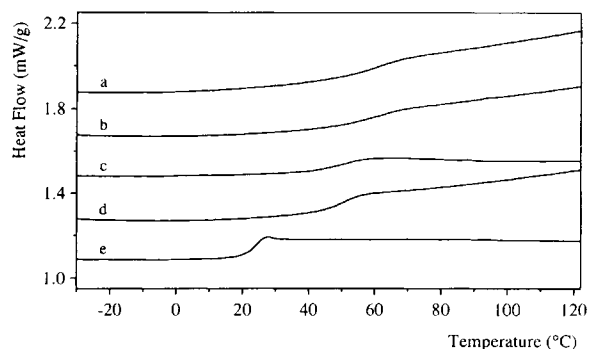


Figure 3 DSC curves of samples synthesized of diglycidylether of butanediol-1.4 and bisphenol A (e) or bisphenol A novolacs (methylene bridges relative to one bisphenol A structure in the novolacs: 0.38 (d); 0.6 (c); 0.75 (b); 0.85 (a) using a stoichiometric ratio of epoxy groups to phenolic groups and 0.65 mol % imidazole relative to epoxy groups at 120°C (reaction time 5 h) after isothermal heating at 200°C for 30 min; DSC curves were measured with a heating rate of 10 K/min.

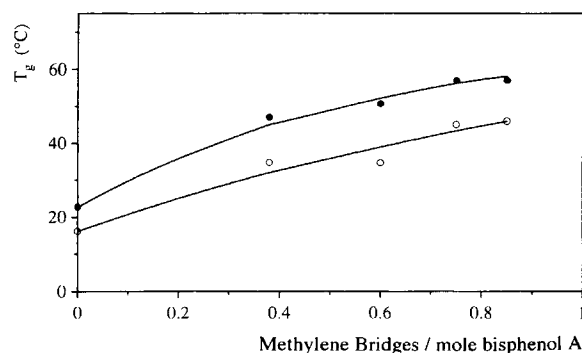


Figure 4 Glass transition temperatures of samples synthesized of diglycidylether of butanediol-1.4 and bisphenol A or bisphenol A novolacs using a stoichiometric ratio of epoxy groups to phenolic groups and 0.65 mol % imidazole relative to epoxy groups at 120°C in dependence of the ratio of methylene bridges to one bisphenol A structure; 1. DSC measurement (○) and 2. DSC measurement after isothermal heating at 200°C for 30 min (●).

at 200°C in case of all samples. Isothermal heating after the first DSC run increases the glass transition temperature of all samples because of a conversion of unreacted epoxy groups remain in the networks at 200°C. However, the difference of the glass transition temperatures between the first and the second DSC run is higher in case of the networks in comparison to the soluble product of bisphenol A and DGEBD. The reason for this effect can be seen in the reactivity difference of bisphenol A and bisphenol A novolacs, which is demonstrated in Figure 1. Because of a higher reactivity of bisphenol A during the reaction with DGEBD in comparison with bisphenol A novolacs, a lower content of unreacted epoxy groups remain in the DGEBD bisphenol A product. An increase of the reaction temperature results in a faster break of hydrogen bondings of the novolacs and a faster reaction of epoxy groups, which remain in the networks.

In addition, the difference between the specific heat above and below the glass transition temperature (Δc_p) was determined from the second DSC measurement. It was found that this Δc_p value is also a function of the content of methylene bridges (Fig. 5).

With increasing content of methylene bridges Δc_p decreases because of a decrease of the degree of rotation freedom in the networks in comparison to the uncrosslinked product. Furthermore, an increasing content of methylene bridges as network junctions affects a further decreasing of the degree of rotation freedom. A similar result was obtained investigating the crosslinking process of an other epoxy system.¹² During the crosslinking process the glass transition temperature of the reaction system increases; however, the change of c_p at the glass transition state (Δc_p) decreases.¹²

Epoxy Excess

In contrast to the systems investigated using a stoichiometric ratio of epoxy groups to phenolic groups, etherification reactions of secondary hydroxyl groups formed are of importance in epoxy excess systems [eq. (2)]. Therefore, bisphenol A reacts with epoxy excess forming networks with different properties depending on the excess of epoxy groups.¹¹ In case of the reaction of novolacs with an excess of epoxy groups relative to hydroxyl groups, etherification reactions are the cause for the formation of two different network junctions. Methylene bridges between phenyl rings of the novolacs result as network junctions because of the reaction of phenolic groups, and methine groups are formed as network junctions by etherification of the

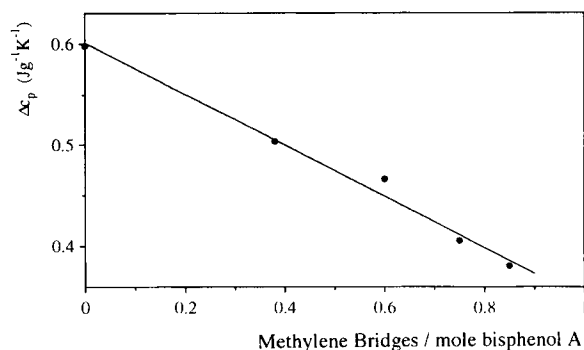
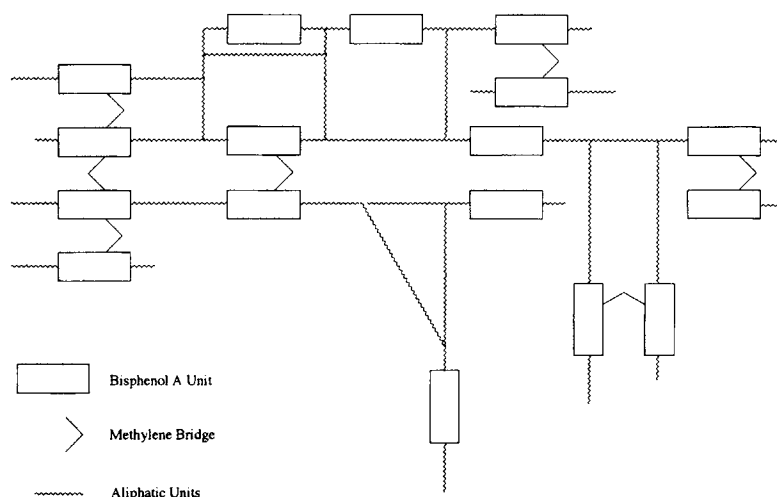


Figure 5 Change of c_p at the glass transition state (Δc_p) of samples synthesized of diglycidylether of butanediol-1.4 and bisphenol A or bisphenol A novolacs using a stoichiometric ratio of epoxy groups to phenolic groups and 0.65 mol % imidazole relative to epoxy groups at 120°C for 5 h and isothermal heating at 200°C for 30 min in dependence of the ratio of methylene bridges to one bisphenol A structure.

secondary aliphatic group formed. Structures of networks synthesized using epoxy excess are demonstrated in Scheme 4.

Bisphenol A structures linked by methylene bridges are rigid parts in the networks. In contrast to this, the aliphatic chains and the methine network junctions are flexible structure units. Furthermore, the networks contain also longer segments between the network junctions resulting from the DGEBD bisphenol A reaction. The formation of methine network junctions can be increased using higher epoxy excess. To investigate the influence of epoxy excess on the glass transition temperature in detail, networks were synthesized of one novolac and different amounts of DGEBD. The imidazole concentration relative to epoxy groups was the same for all networks synthesized. The soluble content of the resulting networks varied between 5 and 11%. Comparing the soluble content of all networks synthesized, it was found that there is no significant difference between networks synthesized using a stoichiometric ratio of epoxy groups to phenolic groups and epoxy excess, respectively. Furthermore, DSC measurements were carried out using the same conditions called above. One example for the first DSC run of a network synthesized by using DGEBD excess is given in Figure 6. The heat flow as well as the temperature are plotted as a function of the time. After the glass transition state, an exothermal process can be detected. This postreaction is more intensive in case of an epoxy excess in comparison to the stoichiometric ratio, which is contributed to a higher content of unreacted epoxy groups remaining in the networks.

The glass transition temperatures of the networks



Scheme 4. Structures in networks synthesized from bisphenol A novolac and an excess of diglycidylether of butanediol-1.4.

were determined from the second DSC run. The results are demonstrated in Figure 7. It can be seen that the glass transition temperature is significant dependent from the ratio of epoxy groups to phenolic groups. The glass transition temperature continuously decreases from about 50°C in case of a stoichiometric ratio of epoxy groups to phenolic groups to about 6°C if a ratio of epoxy groups to phenolic groups of two was used for network synthesis. An increasing DGEBD content for network formation leads to an increase of the content of flexible aliphatic structures in the networks formed. Therefore, the glass transition temperature of the networks is reduced. However, these networks contain also soluble products. To eliminate the influence of soluble products on the glass transition temperature of the networks, all samples were extracted

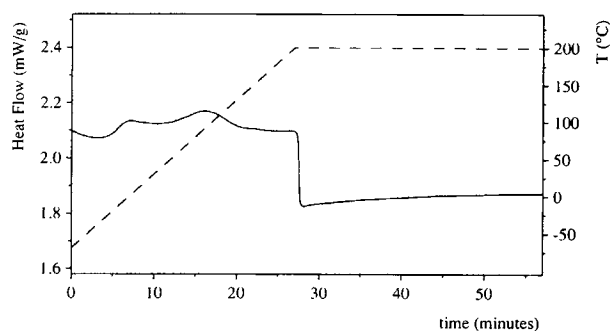


Figure 6 Heat flow and temperature as a function of the time during DSC measurement of a network synthesized of diglycidylether of butanediol-1.4 and a bisphenol A novolac containing 0.6 methylene bridges to one bisphenol A structure using a ratio of epoxy groups to phenolic groups of 2 : 1 and 0.65 mol % imidazole relative to epoxy groups at 120°C for 5 h.

as described in the experimental part above. The glass transition temperature of the extracted samples was determined after drying. The results are demonstrated in Figure 7.

The dependence of the glass transition temperature of these extracted networks on the ratio of epoxy groups to phenolic groups is similar to those obtained for networks before the extraction procedure was performed. However, extracted networks show a remarkable higher glass transition temperature in the second DSC run than networks before extraction. This difference is contributed to the influence of the soluble products remaining in the networks after network synthesis. The soluble products cause a plastification of the networks. In addition, the extracted networks

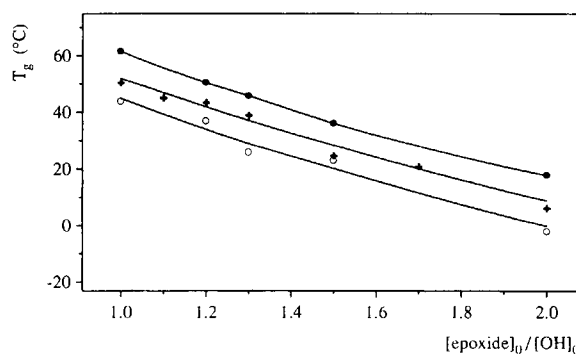


Figure 7 Glass transition temperatures of samples synthesized by reaction of different amounts of diglycidylether of butanediol-1.4 and bisphenol A novolac containing 0.6 methylene bridges to one bisphenol A structure using 0.65 mol % imidazole relative to epoxy groups at 120°C for 5 h in dependence of the ratio of epoxy groups to phenolic groups. DSC measurement of the sample 2. run (+); of the extracted sample 1. run (○) and 2. run (●).

show also a difference in the glass transition temperature between the first and the second DSC run. This effect indicates that unreacted epoxy groups exist as free chain ends in the networks, which is contributed to the relatively low reactivity of the aliphatic diglycidylether and to sterical effects.

CONCLUSIONS

New crosslinked materials based on butanedioldiglycidylether and bisphenol A novolacs containing a different content of methylene bridges and using imidazole as accelerator were synthesized. The properties of these new materials are influenced by the functionality of the novolac and the ratio of epoxy groups to phenolic groups in the reaction mixture.

The networks contain methylene bridges as network junctions if a stoichiometric ratio of epoxy groups to phenolic groups is used for network synthesis. In case of epoxy excess, etherification reactions also occur. Therefore, network junctions are methylene bridges and methine groups resulting from etherification reactions. Variation of the content of methylene bridges in the novolacs as well as of the ratio of epoxy groups to phenolic groups are responsible for different network structures and different thermal properties of the networks. In this way, the glass transition temperature of the networks can be varied. On the other hand, networks synthesized from bisphenol A novolacs and DGEED are more flexible in comparison to networks prepared of bisphenol A novolacs and bisphenol A diglycidylether, which contributed to the content of aliphatic structures. The specific properties of bisphenol A novolacs crosslinked with aliphatic epoxies may open new applications for novolac crosslinked epoxies. This result can get a gained importance concerning the substitution of complicate flexibilized epoxy systems.

In addition, the semiempirical quantum chemical calculations show that conformations exist where the existence of intramolecular hydrogen bonding leads to an energy stabilization. As a consequence for the novolac-epoxide reaction, those structures have to be broken before the reaction of the epoxide and the novolac can start effectively. Therefore, this theoretical treatment is a reasonable approach to explain some phenomenons in this work.

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