Polymer Bulletin 20, 183–188 (1988)

Polymer Bulletin

Crosslinking behaviour of diolmodified epoxies
1. Kinetics and HPLC measurements

W. Tänzer, J. Eisenschmidt, and M. Fedtke*

Technische Hochschule "Carl Schorlemmer" Leuna-Merseburg, Otto-Nuschke-Strasse, DDR-4200 Merseburg, German Democratic Republic

Summary

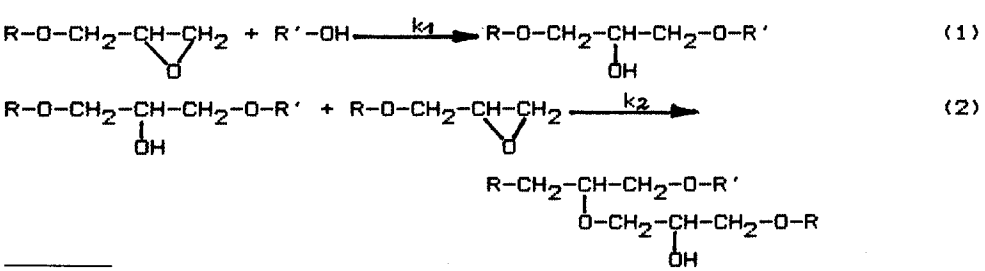
Diglycidyl ether of bisphenol A (BADGE) reacts with aliphatic alcohols to form different products, depending on the type of accelerator. In the presence of magnesium perchlorate the reaction mechanism is nearly independent of the temperature. Using N,N-dimethylbenzylamine (DMBA) as accelerator, different reaction mechanisms can be observed with increasing temperature. These conclusions were drawn by kinetic investigations of the system BADGE/butane-1-ol/accelerator involving HPLC-measurements of reaction products.

Introduction

Diglycidyl ether of bisphenol A (BADGE) only reacts with aliphatic alcohols if suitable accelerators are used. Accelerators that cause a sufficient epoxide consumption below 200°C are acidic or basic compounds. Even under neutral conditions (in the presence of alkali halides or quaternary ammonium compounds), an increasing reaction rate can be observed. In all cases, different reaction mechanisms cause different effects (1-3).

To determine the reaction course and the selectivity of the ring-opening and etherification reaction, $Mg(ClO_4)_2*2H_2O$ was used as an acidic (Lewis-type) and N,N-dimethylbenzylamine (DMBA) as a basic accelerator. The effect of these compounds on the course of the reaction between BADGE and aliphatic alcohols has not been completely elucidated. Nevertheless, the following facts are known to be true (3):

1. Acceleration with magnesium perchlorate in a temperature range between 70 and 110°C leads to the formation of uniform oligohydroxy ethers (Equs. 1,2):



(1)

(2)

* To whom offprint requests should be sent

The ratio of the reaction rates $R=k_1/k_2$ (primary hydroxyl group + epoxide group/ secondary hydroxyl group + epoxide group) is decisive for the real consumption of the alcohol, and with it, for the network formation. Magnesium perchlorate is a latent accelerator, so that the crosslinking reactions take a considerably longer time to proceed than at a decreased reaction temperature (4).

2.DMBA is a more effective accelerator because the reaction rate increases even at lower temperatures (25-40°C). Using HPLC, it was confirmed that different reaction mechanisms take place at different reaction temperatures (3).
At room temperature (25°C) the same reaction mechanism was found for two systems; one accelerated with magnesium perchlorate and the other with DMBA. Using DMBA, at 100°C four different starting steps already take place leading to the formation of oligohydroxy ethers (3). Finally, at 160-180°C, no network formation can be observed, owing to the reduction of the chain length of the oligomers (5).

This different reaction behaviour in both systems was investigated by additional analytical methods. BADGE and butane-1-ol were used as a model system to investigate the selectivity of the accelerators. The reaction products were investigated by means of HPLC.

Experimental

Chemicals: Diglycidyl ether of bisphenol A (BADGE), butane-1-ol, magnesium perchlorate and N,N-dimethylbenzylamine (DMBA) are commercially available products. BADGE was recrystallized from acetone-methanol (m.p.=42°C). 2,2-bis[4-(2-hydroxy-3-butoxy)phenyl]propane (BHBP): 0.3 moles BADGE were melted together with 7.5 moles butane-1-ol in a thermoregulated glass reactor equipped with a mechanical stirrer. After the addition of 0.009 moles DMBA the mixture was stirred at 60-70°C until the epoxide group was completely consumed (determination by titration method). Finally, excess volatile compounds were distilled under reduced pressure (1.32 kPa). The purity of the viscous product was determined by HPLC and small amounts of oligomers were thus found.

Analysis: Samples of the reaction mixture were analyzed using epoxide titration and HPLC. Determination of the epoxide content was carried out by a direct titration method with tetraethylammoniumbromide and perchloric acid at room temperature (6).
Analytical HPLC-separations were obtained using Knauer HPLC-equipment (Wissenschaftliche Geräte KG, FRG), column: 250*4 mm LiChrosorb RP-18 (5µm). Detection wavelength was 255 nm. Two mixed solvents were used in a gradient mode (glass distilled acetonitrile and distilled water). Other pertinent conditions are listed with the chromatograms.

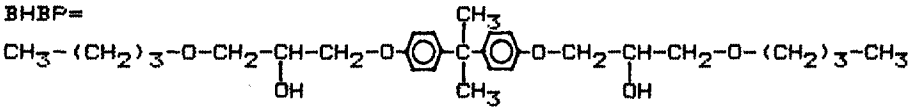
Results and Discussion

The following reactions were used to determine the selectivity of magnesium perchlorate and DMBA dependent on the reaction temperature (Equs. 3,4).

BADGE + 2 $CH_3-(CH_2)_2-CH_2-OH \xrightarrow{k_1}$ BHBP (3)

BADGE + BHBP $\xrightarrow{k_2}$ oligomers (4)

BHBP=



2,2-bis[4-(2-hydroxy-3-butoxy)phenyl]propane

The extent of linear chain propagating reactions and branching reactions in bifunctional systems is determined approximately by the ratio of the rate constants R (R= k_1/k_2). Some of these values for R are known for the reaction of BADGE with bisphenol A (7). They vary from 17 for LiOH as accelerator to 1100 for tri-n-butyl amine. We found that such high ratios cannot be achieved in the presence of aliphatic alcohols as chain lengthening agents.

For magnesium perchlorate the rate constants k_1 and k_2 were measured at 90, 100 and 110°C. The evaluation of the epoxy contents against the reaction time gave the best fit into a kinetic equation of pseudo-first order (Equ. 5).

$$-d[EP]/dt = k[Ac][EP] = k'[EP] \quad (5)$$

[EP] = concentration of epoxide group
[Ac] = concentration of accelerator

The rate constants are summarized in Tab. 1.

T	BADGE:n-BuOH:$Mg(ClO_4)_2*2H_2O$ 1 : 2 : 0.03	BADGE:BHBP:$Mg(ClO_4)_2*2H_2O$ 1 : 1 : 0.03	R
(°C)	k_1 (s^{-1})	k_2 (s^{-1})	
90	0.0000566	0.0000067	8.5
100	0.0001183	0.0000133	8.9
110	0.0002416	0.0000283	8.5

Table 1. Rate constants k_1 (Equ.3), k_2 (Equ.4) and their ratio R between 90 and 110°C (accelerator: magnesium perchlorate)

It is evident that the ratio of linear chain growth to branching reaction in the system considered is 8.5-8.9 at temperatures between 90 and 110°C. This ratio does not even deviate significantly from 8.5-8.9 at temperature ranges below 90°C (70-90°C) or above 110°C (110-160°C). Consequently, the selectivity of the perchlorate-induced reaction cannot be influenced by changing the reaction temperature.

The rate constants k_1 and k_2 were also measured for the DMBA-accelerated system. The results are summarized in Tab. 2.

T	BADGE:n-BuOH:DMBA 1 : 2 :0.03	BADGE:BHBP:DMBA 1 : 1 :0.03	R
°C	k_1	k_2	
60	0.00015 s^{-1}	0.00002 s^{-1}	7.4
80	0.01666 $mol^{-1}*s-1$	0.005 $mol^{-1}*s^{-1}$	3.3
100	0.01833 $mol^{-1}*s^{-1}$	0.00533 $mol^{-1}*s^{-1}$	3.4

Table 2.Rate constants k_1 (Equ. 1), k_2 (Equ. 4) and their ratio R between 60 and 100°C (accelerator: DMBA)

These results are different from those of the first system mentioned. The following conclusions can be drawn:
1.The evaluation of the epoxy contents against the reaction time gave the best fit into a kinetic equation of pseudo-second order at a temperature range between 80 and 100°C.
2.At a reaction temperature of 60°C a kinetic law of pseudo-first order was found which deviates from known results (8-10).

Consequently, a change in the reaction mechanism takes place if different reaction temperatures are used. Elevated temperatures lead to a lower selectivity in the reaction system. This reaction behaviour was previously proved for the monofunctional system phenyl glycidyl ether/butane-1-ol/DMBA (3). It succeeded in confirming the change of the product structure in bifunctional systems using HPLC (Figs.1,2).

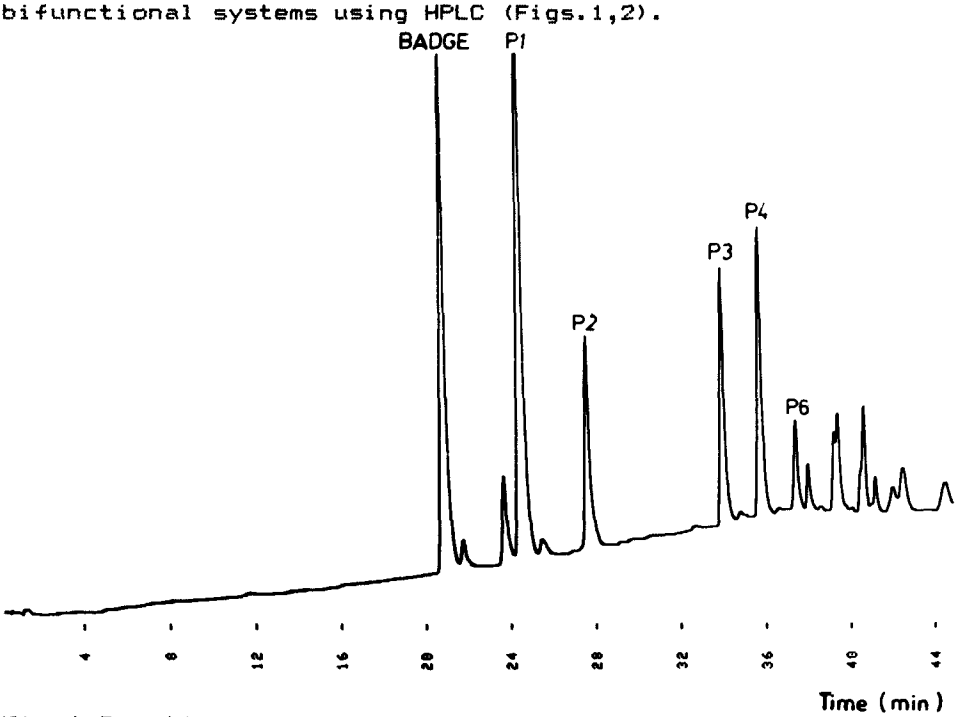


Fig.1.Reaction products of the system BADGE:n-BuOH:DMBA=1:2:0.03 T=60°C. Conversion of epoxide:53%. Products as listed in Tab. 3 HPLC: $CH_3CN:H_2O$=30:70 to 100:0 in 40 min, solvent flow=1.8 $ml*min^{-1}$, sample concentration=5 wt-%, sample volume=10 µl.

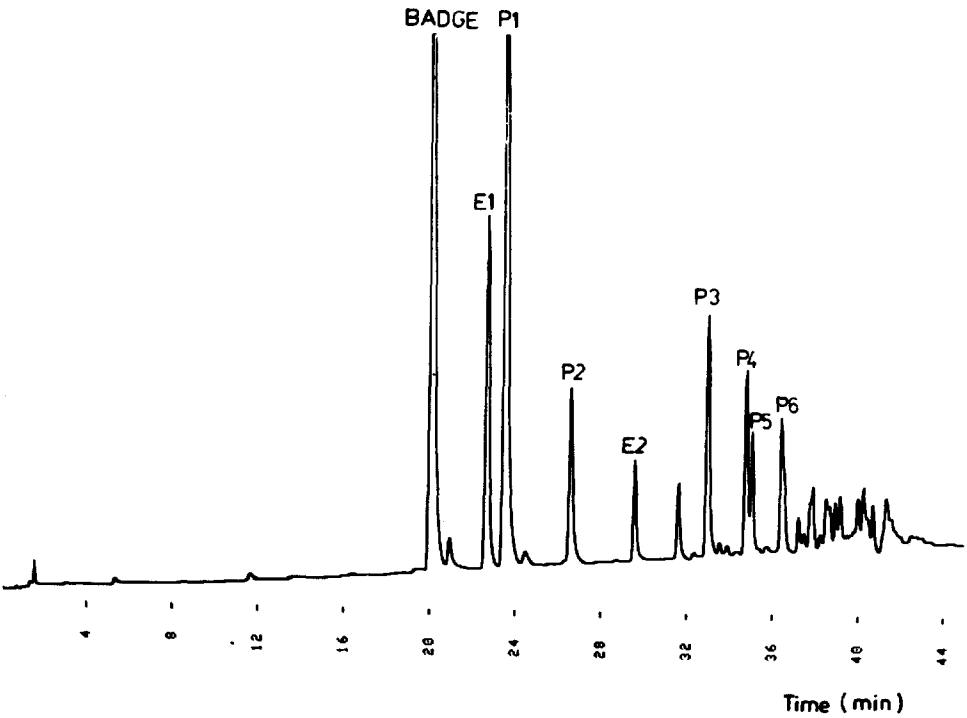


Fig.2.Reaction products of the system BADGE:n-BuOH:DMBA=1:2:0.03 T=100°C. Conversion of epoxide: 51%. Products as listed in Tab.3 HPLC: Conditions as listed under Fig.1.

At 60°C, mainly the addition products from BADGE and butane-1-ol are formed. At 100°C, additional compounds can be observed in the chromatogram. These compounds are products of the oligomerization of BADGE alone (Figs. 1,2). The structures were assigned by preparative synthesis of selected compounds in excess reactions (1-3).

The structure of E1 and E2 were not identified, but they can be detected as main products in the system BADGE:DMBA=1:0.03 (T=100°C). Hence, it can be assumed that these products are oligohydroxy ethers with terminal double bonds (5).

These differences in the reaction mechanism of acidic and basic accelerated systems can be proved even for the bifunctional system BADGE/butane-1,4-diol/accelerator, although crosslinking takes place at lower epoxide conversions (3).

compound	primary OH	secondary OH	epoxide	ratio BADGE	ratio BuOH	M (calc.) g*mol^{-1}
P1	-	1	1	1	1	414
P2	-	2	-	1	2	488
P3	-	1	2	2	1	754
P4*	-	2	1	2	2	828
P5*	-	2	1	2	2	828
P6	-	3	-	2	3	902

Table 3.Products according to Figs.1,2. * P4 and P5 are isomers.

Conclusions

In the reaction of diglycidyl ether of bisphenol A (DGEBA) with butane-1-ol, $Mg(ClO_4)_2*2H_2O$ proved to be a more selective accelerator in comparison with N,N-dimethylbenzylamine (DMBA). In the first case, mainly one single type of starting reaction proceeds independently of the reaction temperature. Using DMBA as accelerator, the number of starting steps increases as the reaction temperature rises. Furthermore, the ratio of the reactivity of primary and secondary hydroxyl groups in the amine-accelerated system changes and leads to superimposed reaction orders.

References

1. W.Tänzer, M.Fedtke: Acta Polym. 37 (1986) 1, 24
2. W.Tänzer, H.Fiedler, M.Fedtke: Acta Polym. 37 (1986) 2, 70
3. W.Tänzer, M.Fedtke: Acta Polym. (in press)
4. DD 240904 (1985), inv.: W.Tänzer, M.Fedtke, J.Schillgalies, E.Born
5. M.Fedtke, E.Domaratius (paper in preparation)
6. R.R.Jay: Anal. Chem. 36 (1964) 667
7. F.B.Alvey: J. Appl. Polym. Sci. 13 (1969) 1473
8. L.Shechter, J.Wynstra, R.P.Kurkjy: Ind. Eng. Chem. 48 (1956) 86
9. L.Shechter, J.Wynstra, R.P.Kurkjy: Ind. Eng. Chem. 49 (1957) 1107
10. G.Gee, W.C.E.Higginson, P.Levesley, K.T.Taylor: J. Chem. Soc. (1959) 1338

Accepted June 6, 1988 C