ELSEVIER

International Journal of Adhesion & Adhesives 20 (2000) 333–340

International Journal of Adhesion & Adhesives

Mechanism of the curing reaction of model epoxy compounds with monuron

H. Brockmann*, M. Haufe, J.O. Schulenburg

Fakultät für Chemie, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld, Germany

Accepted 2 December 1999

Abstract

The ability of monuron (*p*-chlorophenyl-*N*,*N*-dimethylurea) to cure epoxy resins was investigated by means of hardening the mono functional model compound *p*-tolylglycidyl ether. The reaction products were isolated and the possible intermediates were synthesised independently for comparison. Their reactivity was tested. As analytical methods, thermo-FT-IR spectroscopy, DSC and liquid–solid chromatography were applied. The results indicate that during curing monuron reacts without decomposing into free isocyanate and dimethylamine and that the polymer-forming reaction is not terminated by the well-known formation of 2-oxazolidones.

Keywords: Monuron; Epoxides; Hardening; Infrared spectroscopy

1. Introduction

The discovery of amine catalysis in curing of epoxy resins with dicyanodiamide lead to an increasing use of such adhesives in the 1960s. By adding amines it was possible to lower the curing temperature from 190 to 120°C. This was especially important for bonding aluminium because above 150°C a change in the structure of the surface aluminium oxide takes place [1]. The use of latent hardeners such as monuron (*p*-chlorophenyl-*N*,*N*-dimethylurea) instead of secondary amines is state-of-the-art nowadays in the production of heat curing one-part adhesives.

Monuron can be regarded as an isocyanate blocked amine and one would expect that with increasing temperature a thermal decomposition of monuron into amine and isocyanate occurs. In a consecutive reaction step the liberated amine could either enhance the reactivity of dicyanodiamide or react with the epoxy resin itself. The isocyanate may lead to a formation of 2-oxazolidones (see Scheme 1a) in a direct reaction [2,3]. An alternative reaction pathway consists of the reaction of (not thermolysed) monuron with a glycidyl ether which results in the formation of an aminoalcohol. The thereby liberated isocyanate further on can lead to the formation of 2-oxazolidones (see Scheme 1b).

The fact that monuron can be used not only as an accelerator but as curing agent itself and that the polymer forming reaction occurs at temperatures which are significantly lower than the thermal decomposition temperature of monuron was investigated by Holubka et al. [4]. They found no evidence of a thermal decomposition of monuron and suggested a tetra-substituted urea as an important intermediate. It has to be mentioned that they were unable to prove its formation and that such an intermediate is unlikely to be generated. In the present work the monoepoxide *p*-tolylglycidyl ether was used as a model compound to study the polymerisation of glycidyl ethers initiated by monuron. Intermediates and by-products of this reaction were isolated, characterised and compared with samples which were synthesised independently. The reactions were investigated by thermo-FT-IR spectroscopy, DSC and liquid–solid chromatography.

2. Experimental

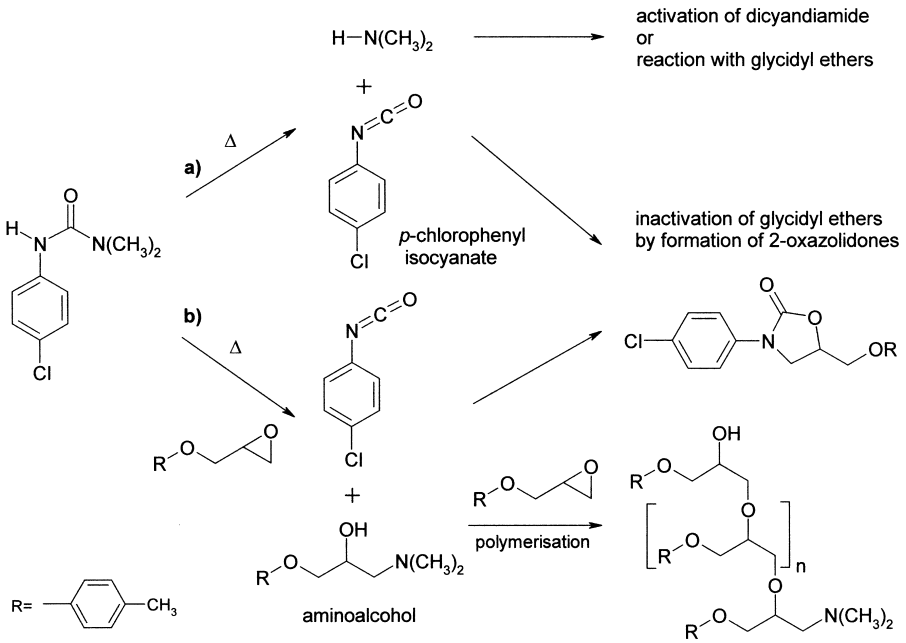
2.1. Syntheses

2.1.1. General consideration

^{1}H NMR spectra were recorded on a Bruker AC 250-P spectrometer by using tetramethyl silane (TMS) as an

* Corresponding author. Tel.: +49-521-106-2071; fax: +49-521-106-6417.

0143-7496/00/$ - see front matter
PII: S0143-7496(99)00066-4



Scheme 1.

internal standard. IR and thermo-FT-IR spectra were recorded on a BIO-RAD FTS 175 spectrometer. Epichlorohydrin and 4-chlorophenylisocyanate were purchased from Fluka. The epichlorohydrin was distilled before use.

2.1.2. Preparation of p-tolylglycidyl ether (*monoepoxide*)

89.70 g (0.97 mol) of epichlorohydrin were added slowly with stirring to a solution of 23.35 g (0.58 mol) of 10% aqueous sodium carbonate and 67.08 g (0.62 mol) *p*-cresol. The reaction mixture was stirred 1 h at room temperature and then heated 1 h under reflux. After cooling two layers formed, the organic layer was separated, washed with saturated NaCl solution and neutralised with a NaH_2PO_4/K_2HPO_4 buffer (pH 7). The organic layer was dried over Na_2SO_4 and the crude product was distilled at 74°C / 0.1 mbar yielding 84.39 g (0.51 mol, 83%) of a pale oily liquid. ^{1}H NMR ($CDCl_3$): δ 7.08-6.79 (AA′BB′, 4H, C_6H_4), 4.15 (ABX, 1H, $OCH_AH_BCHCH_2$), 3.91 (ABX, 1H, $OCH_AH_BCHCH_2$), 3.34-3.28 (m, 1H, OCH_2CHCH_2), 2.86 (ABX, 1H, $OCH_2CHCH_AH_B$), 2.72 (ABX, 1H, $OCH_2CHCH_AH_B$), 2.27 (s, 3H, CH_3). IR (NaCl): $\tilde{\nu}$ 3057, 3029, 3001, 2923, 2871, 1614, 1585, 1512, 1453, 1346, 1290, 1242, 1177, 1110, 1038, 915, 863, 842, 818, 772.

2.1.3. Preparation of 1-N,N-dimethylamino-3-(4-methylphenoxy)-2-propanol (*aminoalcohol*)

30 ml of water were added to 50 ml THF saturated with dimethylamine; it contained about 8.00 g of the amine (0.18 mol). During a 1 h period a solution of 4.92 g (30 mmol) of 1,2-epoxy-3-(4-methylphenoxy)propane in 50 ml THF was added dropwise with stirring. After 3 h stirring at 20°C the solvent was removed, the residue dissolved in CH_2Cl_2 and the solution dried over Na_2SO_4. Removing of the solvent and distilling of the crude product afforded an oily colourless liquid, that crystallised after a few days yielding 3.71 g (18 mmol, 60%) of pure 1-*N*,*N*-dimethylamino-3-(4-methylphenoxy)-2 propanol, m.p. 45–46°C. ^{1}H NMR ($CDCl_3$): δ 7.08–6.79 (AA′BB′, 4H, C_6H_4), 4.09-3.99 (m, 1H, OCH_2CHCH_2N), 3.93 (d, 2H, OCH_2CHCH_2N), 3.59 (s, 1H, CHO*H*), 2.53 (ABX, 1H, $OCH_2CHCH_AH_BN$), 2.37 (ABX, 1H, $OCH_2CHCH_AH_BN$), 2.31 (s, 6H, $N(CH_3)_2$), 2.27 (s, 3H, $C_6H_4CH_3$). IR (NaCl): $\tilde{\nu}$ 3412, 3030, 2942, 2862, 2823, 2776, 1613, 1585, 1512, 1461, 1328, 1291, 1244, 1177, 1109, 1042, 934, 880, 817, 753.

2.1.4. Preparation of 1-dimethylamino-3-(4-methylphenoxy)-prop-2-yl-4-chlorophenylcarbamat (*urethane*)

1.25 g (6 mmol) 1-*N*,*N*-Dimethylamino-3-(4-methylphenoxy)-2-propanol were placed in a 50 ml round-bottom flask under nitrogen and heated to 140°C. At this temperature 0.92 g (6 mmol) of 4-chlorophenylisocyanate were added and the mixture was stirred for further 2 h. After cooling, the resulting solid was crystallised from *n*-heptane to yield 0.82 g (2.3 mmol, 38%) of pure colourless urethane, mp 104°C. ^{1}H-NMR ($CDCl_3$): δ 7.74 (s, 1H, N*H*), 7.25–7.15 (AA′BB′, 4H, NC_6H_4Cl), 7.08-6.78 (AA′BB′, 4H, $OC_6H_4CH_3$), 5.37–5.29 (m, 1H, OCH_2CHCH_2N), 4.19 (ABX, 1H, $OCH_AH_BCHCH_2N$), 4.09 (ABX, 1H, $OCH_AH_BCHCH_2N$), 2.98 (ABX, 1H, $OCH_2CHCH_AH_BN$), 2.50 (ABX, 1H, $OCH_2CHCH_AH_BN$), 2.30 (s, 6H, $N(CH_3)_2$), 2.27 (s, 3H, CH_3). IR (KBr):

$\tilde{\nu}$ 3234, 3182, 3109, 3031, 2987, 2949, 2878, 2830, 2781, 1727, 1607, 1549, 1512, 1497, 1463, 1404, 1311, 1291, 1228, 1178, 1118, 1092, 1050, 1029, 1010, 954, 826, 805, 751, 678.

2.1.5. Reaction of urethane with monoepoxide

0.91 g (2.5 mmol) 1-Dimethylamino-3-(4-methylphenoxy)-prop-2-yl-4-chlorophenylcarbamat were heated to 140°C and 0.41 g (2.5 mmol) monoepoxide were added. The reaction was stirred for 1 h at this temperature and the crude reaction product was purified then by crystallisation from toluene, yielding 0.19 g (0.6 mmol, 24%) of colourless crystals, m.p. 215°C. ^{1}H-NMR ($CDCl_3$): δ 7.54–7.33 (AA′BB′, 4H, NC_6H_4Cl), 7.10–6.78 (AA′BB′, 4H, $OC_6H_4CH_3$), 4.99–4.91 (m, 1H, NCH_2CHCH_2O), 4.20–4.00 (m, 4H, NCH_2CHCH_2O), 2.29 (s, 3H, CH_3). IR (KBr): $\tilde{\nu}$ 3106, 3067, 2960, 2879, 1738, 1702, 1602, 1582, 1509, 1446, 1339, 1251, 1147, 1097, 1043, 991,898, 817, 753. The isolated compound showed identical analytical data as an authentic sample of the 2-oxazolidone, which was synthesised by a method described by Braun et al. [5].

2.2. Curing of the monuron/monoepoxide system and purification of the products

1.98 g (10.0 mmol) of monuron and 1.64 g (10.0 mmol) of monoepoxide were placed in a 50 ml round-bottom flask and heated for 1 h at 140°C with stirring. After cooling the reaction mixture was suspended in 15 ml of CH_2Cl_2/acetone (10 : 1) and filtered. The insoluble part was crystallised from ethanol while the evaporation residue of the filtrate was purified by column chromatography using silica gel 60 H (Merck) and CH_2Cl_2/acetone (10 : 1) as eluent.

2.2.1. Products

N,*N*′-Di-(4-chlorophenyl)urea was obtained as a colourless solid, mp 269°C. ^{1}H-NMR (DMSO): δ 8.82 (s, 1H, N*H*), 7.51-7.29 (AA′BB′, 4H, NC_6H_4Cl). IR (KBr): $\tilde{\nu}$ 3295, 3168, 3077, 2979, 1631, 1591, 1563, 1556, 1492, 1396, 1298, 1281, 1238, 1100, 1065, 1013, 857, 822, 776, 753, 640. Monuron was obtained as a colourless solid, mp 172°C. ^{1}H-NMR ($CDCl_3$): δ 7.35–7.19 (AA′BB′, 4H, NC_6H_4Cl), 6.37 (s, 1H, N*H*), 3.01 (s, 6H, $N(CH_3)_2$). IR (KBr): $\tilde{\nu}$ 3298, 3098, 2937, 1643, 1591, 1510, 1402, 1376, 1189, 1087, 1066, 898,829, 651. 3-(4-Methylphenyl)-5-(4-methylphenoxymethyl)-2-oxazolidone was obtained as colourless crystals, m.p. 215°C. It showed identical analytical data as the product obtained in the reaction of urethane and monoepoxide. In addition, a fraction containing various polyethers was extracted. Due to their chemical similarity, these oligomers could not be further purified by means of column chromatography.

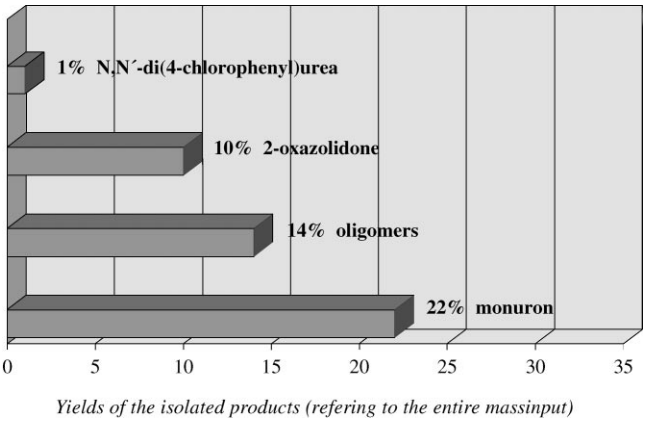


Fig. 1. Column chromatography of monoepoxide + monuron (1 : 1 / 140°C).

2.3. Thermo-FT-IR-spectroscopy

The fragmentation of thermally unstable compounds, induced by heating, can usually be detected by thermo-FT-IR-spectroscopy. Using this technique a small sample of the compound under investigation is heated up continually to 190°C while IR-spectra are measured in defined periods of time. The recorded spectra are displayed in a waterfall plot and show the possible structural changes by changing spectra.

In case of blocked isocyanates the formation of free isocyanate by thermal decomposition is indicated by a characteristic absorption in the range of 2200 – 2250 cm^{-1}. The deblocking temperature is the temperature where the isocyanate absorption begins to occur.

2.4. Differential scanning calorimetry (DSC)

The DSC measurements were carried out with a Thermal Analyst 3100 of TA Instruments using a DSC 2920 analyse cell. The spectra were recorded according to DIN 53765 and observance of DIN EN ISO 11357-1. About 5 mg of the freshly prepared mixture of the reactants were applied on the analyse cell and during heating (10°C/min) the sample was flushed with nitrogen.

3. Results

3.1. Column chromatography

The products and their quantities are given in Fig. 1.

3.2. Thermo FT-IR

The thermo FT-IR spectra of monuron and of the urethane are given in Figs. 2 and 3.

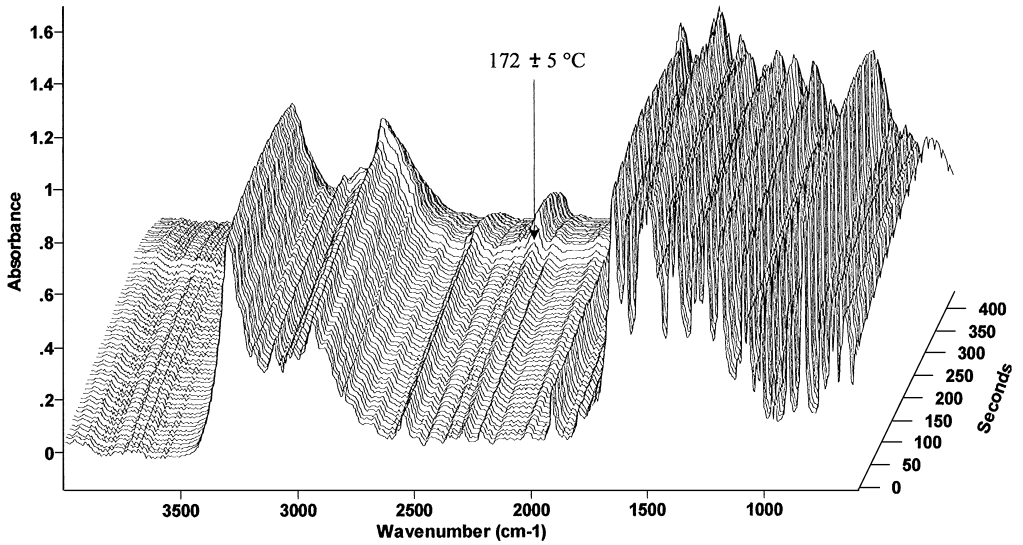


Fig. 2. Thermo FT-IR spectrum of monuron.

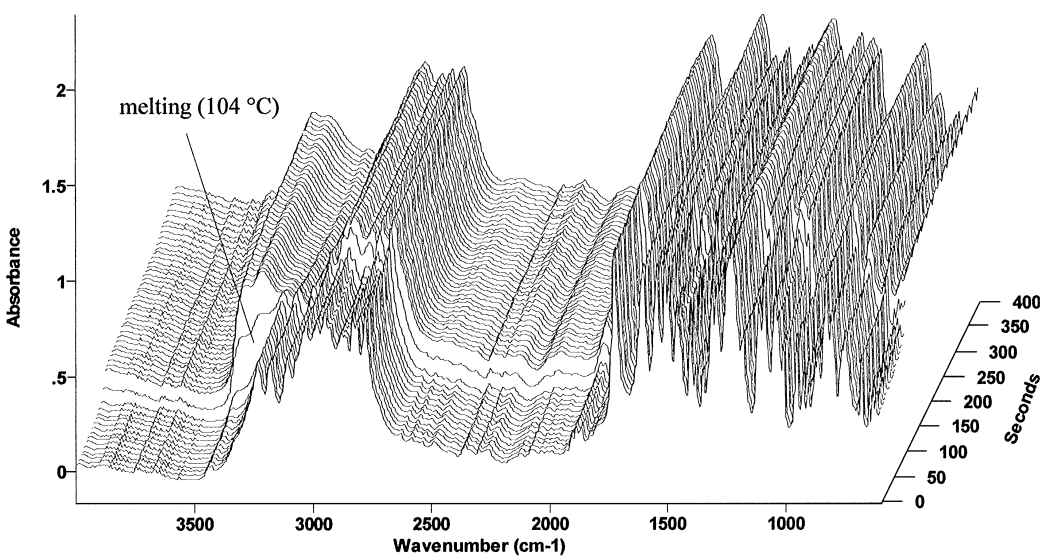


Fig. 3. Thermo FT-IR spectrum of urethane.

3.3. DSC

The collected DSC data are given in Figs. 4–7.

4. Discussion

The fact that *p*-tolylglycidyl ether (monoepoxide) reacts with monuron at about 130°C demonstrates that a curing is possible even in the absence of dicyanodiamide. By analysing the different products of the polymerisation (Fig. 1) it can be stated that in comparison with the reaction of monuron with monoepoxide the proceeding polymersation is favoured. Therefore, about 40% of the monuron were left unreacted or either undergo a thermal decomposition. Moreover, only one defined 2-oxazolidone (3-(4-methylphenyl)-5-(4-methylphenoxymethyl)-2-oxazolidone) was isolated, which will become quite obvious by the following discussion of the reaction mechanism. The formation of di-*p*-chlorophenyl urea seems to be rather unimportant but it proves the existence of *p*-chlorophenylisocyanate as an intermediate. This is due to the fact that isocyanates react with traces of water to form ureas. The isolated polymer

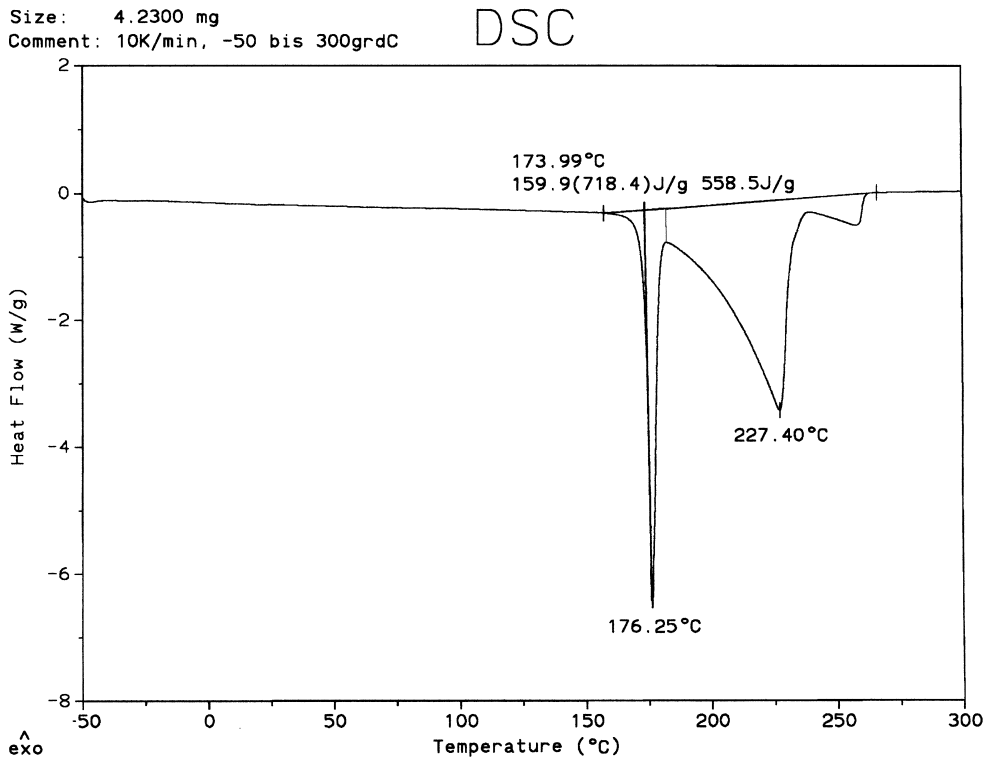


Fig. 4. DSC-data of monuron.

consists of polyethers. Their formation and structure had been already investigated by Barwich et al. [3].

4.1. Thermal properties of monuron

In order to understand the curing mechanism, the thermal behaviour of monuron was investigated. Since monuron can be regarded as an isocyanate blocked amine, its thermal decomposition into dimethylamine and *p*-chlorophenylisocyanate can be detected by thermo-FT-IR spectroscopy (Fig. 2). The initial liberation of isocyanate takes place at 172 ± 5°C and roughly correlates to the DSC data of monuron (Fig. 4). The melting, respectively thermal decomposition, starts at 159.9°C and reaches its endothermic maximum at 176.3°C. At higher temperatures the evaporation of *p*-chlorophenyl isocyanate occurs (endothermic maximum at 227°C). In contrast to this, the DSC data of the reaction of monuron with *p*-tolylglycidyl ether exhibit an endothermic reaction which starts at 80°C and reaches its maximum at 143.4°C (Fig. 5). Thus the conclusion can be drawn that monuron does not undergo a thermal splitting at temperatures at which it already initiates the polymerisation of glycidyl ethers (see pathway b in Scheme 1). Nevertheless, at higher temperatures a thermal decomposition of unreacted monuron is also documented by the weak endothermic peak at 166.4°C.

4.2. Formation and consecutive reactions of aminoalcohol

Though it is interesting to know that a thermal decomposion of monuron is not necessary to induce the polymerisation of glycidyl ethers, it is more important to understand why a polymerisation is possible in spite of the liberation of isocyanate. Remarkably the curing proceeds also at high ratios of monuron/monoepoxide (1:3 or even 1:1).

The favoured reaction pathway 1b (Scheme 1) includes the formation of aminoalcohol and isocyanate which in a consecutive step forms 2-oxazolidones. One would assume that the isocyanate reacts promptly with aminoalcohol to form an urethane. It should be kept in mind, however, that the isocyanate can also react with the terminal OH-group of an (growing) oligomer formed by the polyaddition of aminoalcohol and glycidyl ethers (but for simplification we only refer to the aminoalcohol in the following). One could suppose that the formation of urethane would terminate the polymerisation. In fact the urethane appears to be only an intermediate in the formation of the 2-oxazolidone which can be generated in two different pathways. (a) The 2-oxazolidone is formed by direct cyclisation of the urethane under elimination of dimethylamine or it is (b) formed in an alternative step which consists

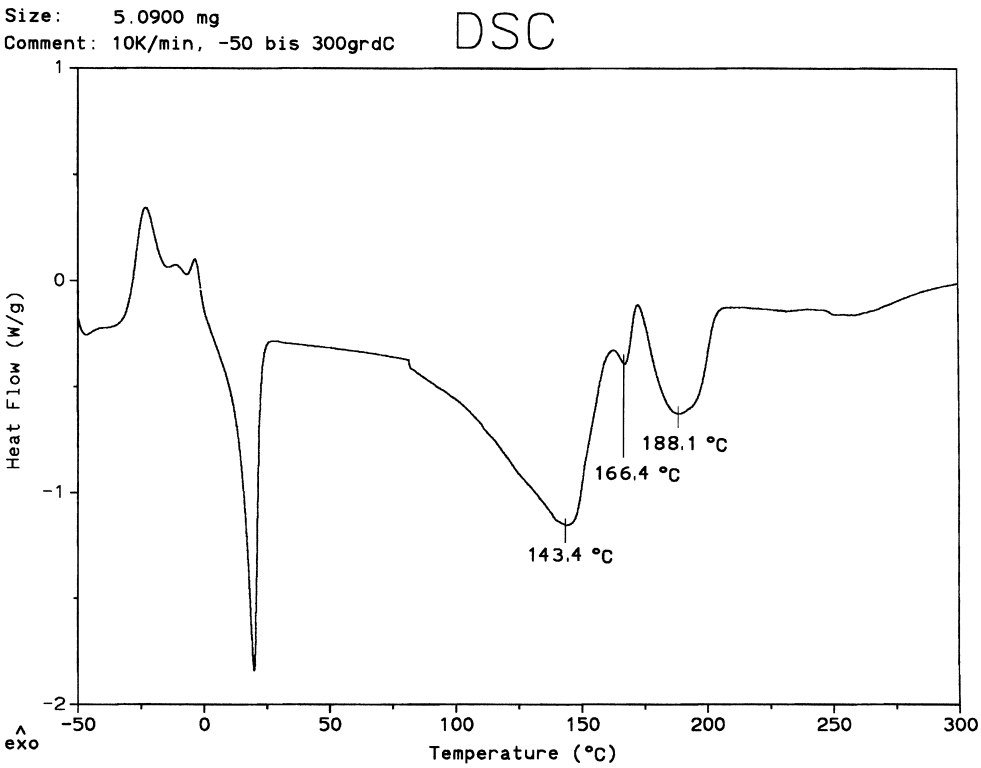
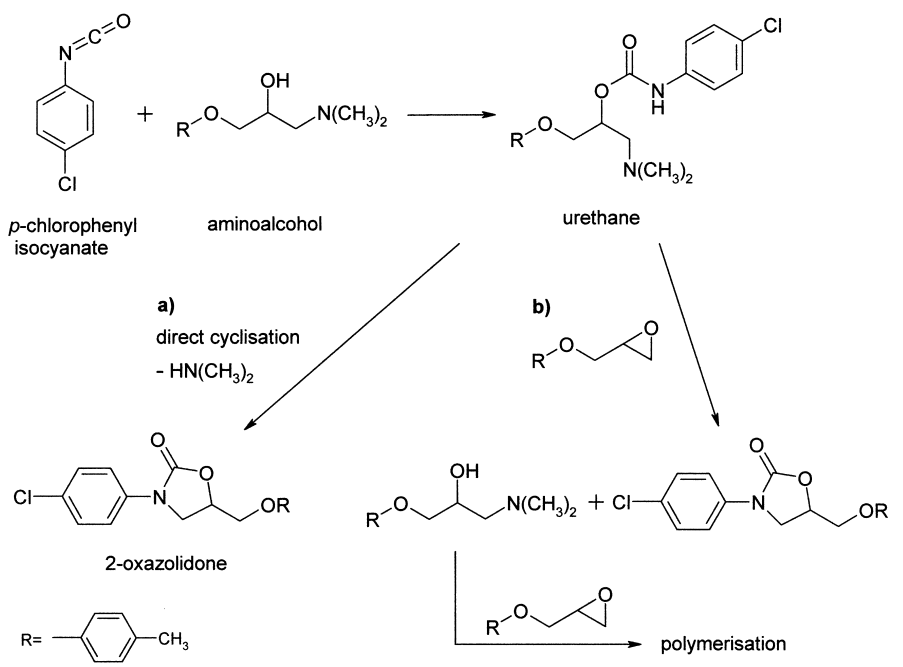


Fig. 5. DSC-data of monuron + monoepoxide (1:3)



Scheme 2.

of the reaction of the urethane with an other molecule of glycidyl ether. Iwakura and Izawa [6] reported that urethanes and glycidyl ethers can form 2-oxazolidones under the catalysing effect of tertiary amines. In our case the urethane would be not only the reactant but, due to its dimethylamino group, also the catalyst itself. Both reaction pathways are presented in Scheme 2.

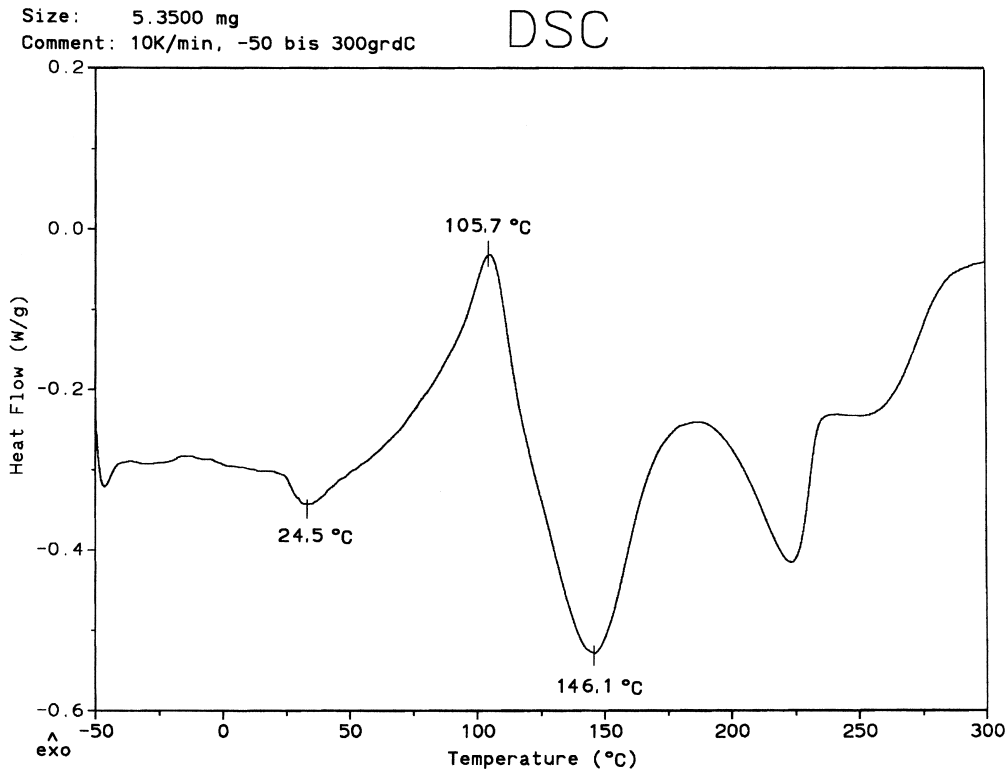


Fig. 6. DSC-data of aminoalcohol + monoepoxide (1:3)

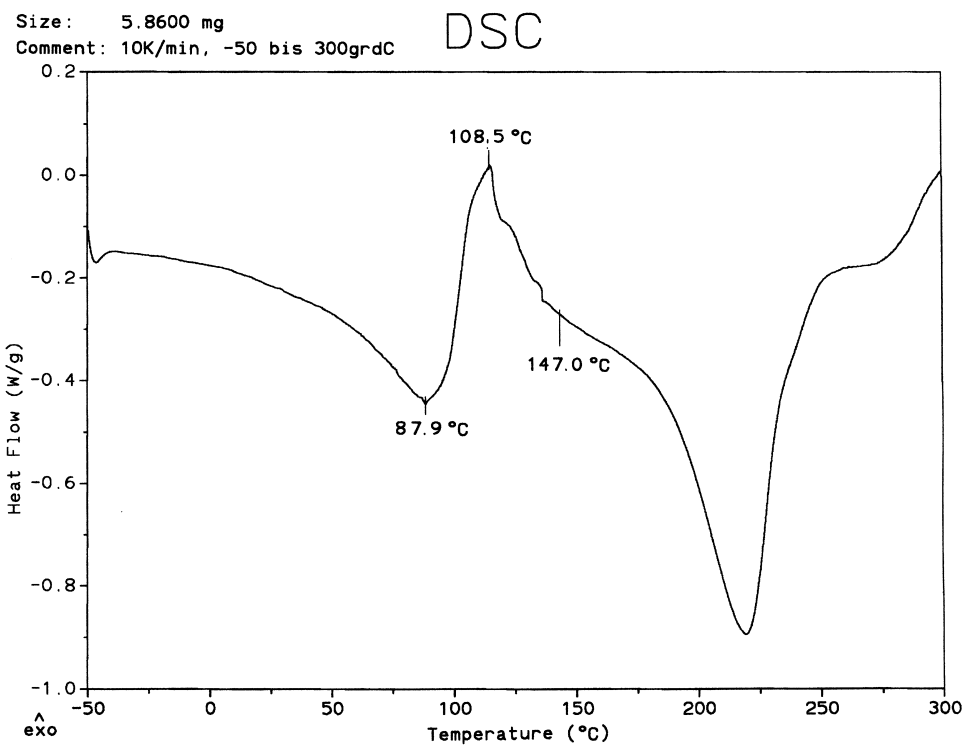


Fig. 7. DSC-data of urethane + monoepoxide (1:1).

4.3. Release of the growing oligomer chain

The displayed pathways are essentially different. Whereas pathway 2a leads to the release of dimethylamine, pathway 2b includes the liberation of the aminoalcohol. Based on pathway 2a, aminoalcohol could be consecutively formed by dimethylamine and glycidyl ether. Thus, the pathways 2a and b appear to be equivalent but this is not true. The important difference is that in the case of pathway 2b the aminoalcohol or a previously formed oligomer would be released, so that the chain growth proceeds. Which of the reactions takes place can be proved by comparing the thermal properties of the aminoalcohol and the urethane. The DSC diagram of the aminoalcohol/monoepoxide (1:3) (Fig. 6) exhibits a strong exothermic signal which has its maximum at 106°C and is followed by an intensive endothermic reaction with its maximum at 146°C. The first signal relates to the exothermic addition of the aminoalcohol at the monoepoxide whereas the second can be interpreted as the ongoing polymerisation. By comparison of the DSC diagram of urethane/monoepoxide (1:1) (Fig. 7) with Fig. 6 it can be seen, that both show the same exothermic signal with a maximum at approx. 106°C. Since this has to be interpreted as the exothermic addition of aminoalcohol to monoepoxide, a liberation of aminoalcohol had taken place during the reaction of the urethane with monoepoxide. Its formation is expressed by the first endothermic signal (start 43°C, maximum 88°C). That even at a ratio of 1:1 of urethane/monoepoxide not only the addition of the aminoalcohol but also a polymerisation (shoulder at 147°C) can be observed proves that the polymer forming reaction is highly favoured. This might be due to the catalytic effect of the basic dimethylamino group of the aminoalcohol. Besides the thermal analyses the synthesis of 3-(4-methylphenyl)-5-(4-methylphenoxymethyl)-2-oxazolidone, by reacting monoepoxide with urethane, also confirms the reaction pathway 2b. Although a polymerisation of the monoepoxide with the urethane can also be explained by a direct cyclisation (2a), the thermo-FT-IR spectrum (Fig. 3) of the urethane indicates clearly that it is stable up to 190°C.

5. Conclusions

The latent hardener monuron (*p*-chlorophenyl-*N*,*N*-dimethylurea) does not only accelerate the curing of epoxy resins with dicyanodiamide but can also be used as a curing agent itself. Even if it can be regarded as an isocyanate blocked amine, the curing already starts far below the temperature of its thermal decomposition. By the reaction of monuron with an epoxy resin isocyanate is liberated. This consecutively reacts with the aminoalcohol (generated as an intermediate) or it reacts with oligomers resulting from its reaction with further glycidyl ethers. The urethanes thus formed do not cyclise directly under elimination of dimethylamine but react with a further molecule of glycidyl ether to form 2-oxazolidones instead. By this reaction the aminoalcohol or any relating oligomer is released. Hence, the polymerisation proceeds and due to the catalytic effect of the basic dimethylamino group of the aminoalcohol (or oligomer) it is highly favoured.

Acknowledgements

The authors wish to thank the Fraunhofer Institut für Angewandte Materialforschung Bremen for carrying out the DSC measurements.

References

[1] Brockmann W, Hennemann OD, Kollek H, Matz C. Adhäsion 1986;30(8):3.
[2] Smith DA. Nature 1963;197:286.
[3] Barwich J, Guse D, Brockmann H. Adhäsion 1989;33(5):27.
[4] Holubka JW, Carduner KR. J. Adhesion 1992;37:239.
[5] Braun D, Weinert J. Liebigs Ann. Chem. 1979;1:210.
[6] Iwakura Y, Izawa S. J. Org. Chem. 1964;29:379.