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INVESTIGATION OF TWO-STEP POLYMERIZATION REACTIONS BY DSC

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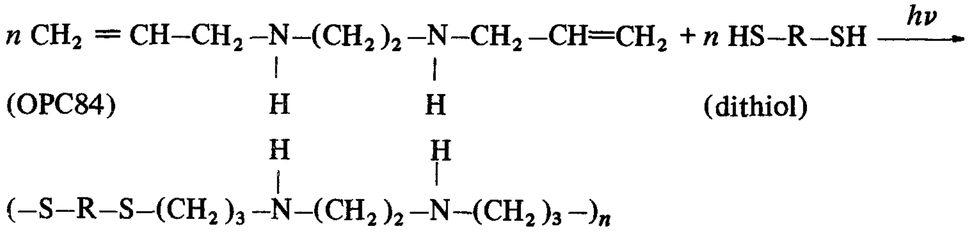
A light-induced thiol-ene addition was combined with a thermally activated amine-epoxide addition. The two-step character of the polymerization in this resin system was proved by DSC measurements. The energies of the light-activated and the thermally activated reactions were determined.

The term "two-step polymerization" is used for resin systems which have already partially reacted, due to light exposure, and which then react once more, in a second and separate step, when heated or further exposed to light. A general method of achieving a step-by-step cure is to use a resin system which contains two different types of reactive groups, one of which is light-sensitive. In our case, the first step of the reaction is the photoaddition of N,N'-diallylethylenediamine (OPC84) with triglycoldithiol (dithiol):



$$n\,CH_2=CH-CH_2-\underset{H}{\underset{|}{N}}-(CH_2)_2-\underset{H}{\underset{|}{N}}-CH_2-CH=CH_2+n\,HS-R-SH\xrightarrow{h\nu}$$

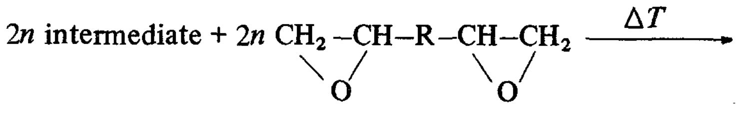
(OPC84) (dithiol)

$$(-S-R-S-(CH_2)_3-\overset{H}{\overset{|}{N}}-(CH_2)_2-\overset{H}{\overset{|}{N}}-(CH_2)_3-)_n$$

(intermediate)

For the production of free radicals, 2,2-dimethylbenzylketal was used as photoinitiator for the rapid initiation of polymerization.

The second step of the reaction is the thermal curing reaction of bisphenol-A diglycidyl ether (DGEBA) with the intermediate:



$$2n\text{ intermediate}+2n\,\underbrace{CH_2-CH}_{O}-R-\underbrace{CH-CH_2}_{O}\xrightarrow{\Delta T}$$

(DGEBA)

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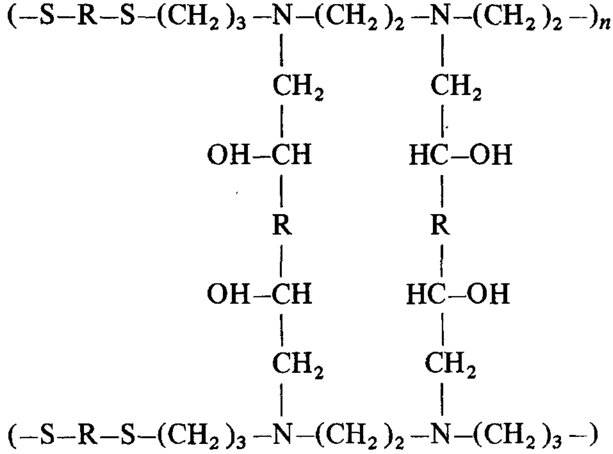

$$\begin{array}{rcccl}
(-S-R-S-(CH_2)_3- & N & -(CH_2)_2- & N & -(CH_2)_2-)_n \\
 & | & & | & \\
 & CH_2 & & CH_2 & \\
 & | & & | & \\
 & OH-CH & & HC-OH & \\
 & | & & | & \\
 & R & & R & \\
 & | & & | & \\
 & OH-CH & & HC-OH & \\
 & | & & | & \\
 & CH_2 & & CH_2 & \\
 & | & & | & \\
(-S-R-S-(CH_2)_3- & N & -(CH_2)_2- & N & -(CH_2)_3-)
\end{array}$$

Experimental

The heat of the light-initiated thiol-ene addition was measured with a modified Perkin-Elmer DSC-1B calorimeter. The heat of the thermally activated amine-epoxide addition was measured under isothermal conditions by using a Perkin-Elmer DSC-2 calorimeter with a data station. The software for isothermal measurements and the experimental details on the monitoring of the thermally [1] and light-activated reactions [2] have already been described.

Results and discussion

The following discussion relates to the pure partial systems for the light- and thermally initiated reactions (Figs 1–5). Table 2 contains the corresponding values for the same systems in the complete two-step reacting mixture. System II contains an additional amine (IPD) and more DGEBA for the thermally activated step than in system I. The measured heats are referred to 1 g of the complete mixture. The corrected reaction energies take into consideration the dilution by those components not involved in the first polymerization step, and by the photoinitiator. From this, it follows that only the molar reaction energies should be compared.

Figure 1 shows typical DSC curves obtained upon isothermal light-initiated polymerization at 318 K. The average reaction heat ($\Delta_R H$) of the UV light-initiated thiol-ene addition is -60.7 ± 2.5 kJ/mol.

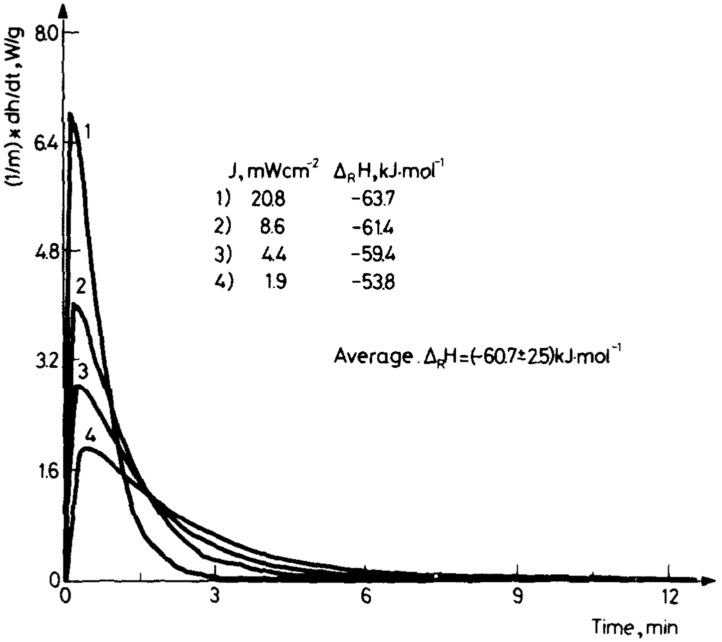

Fig. 1 Isothermal DSC plot of 1:1 molar mixtures of OPC84 and dithiol irradiated by UV light at various light intensities at 318 K

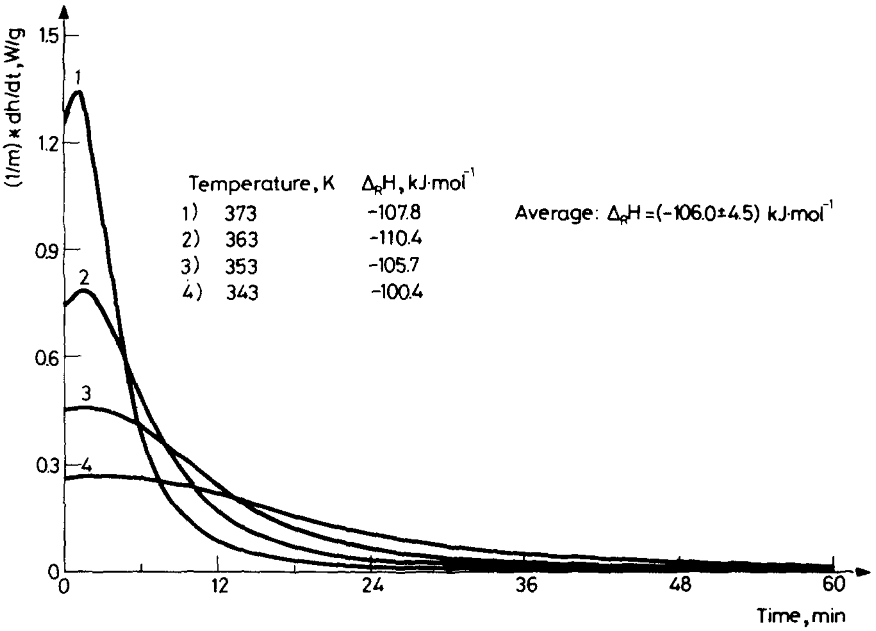

Fig. 2 Isothermal DSC plot of 1:1 molar mixtures of OPC84 and DGEBA at various temperatures

Figure 2 shows DSC exotherm curves of an equimolar mixture of OPC84 and DGEBA at various temperatures. The reaction is always autocatalytic. The average heat of the thermally activated amine-epoxide addition is −106.0±4.5 kJ/mol.

Mixing of the very reactive amine OPC84 with a less reactive amine, e.g. dicyclohexylisophoronediamine (IPD), allows control of the reaction rate of the amine-epoxide addition (Fig. 3). The glass transition temperature of a polymerizate obtained with both amines is between the corresponding values of the systems which only contain one amine component (Table 1).

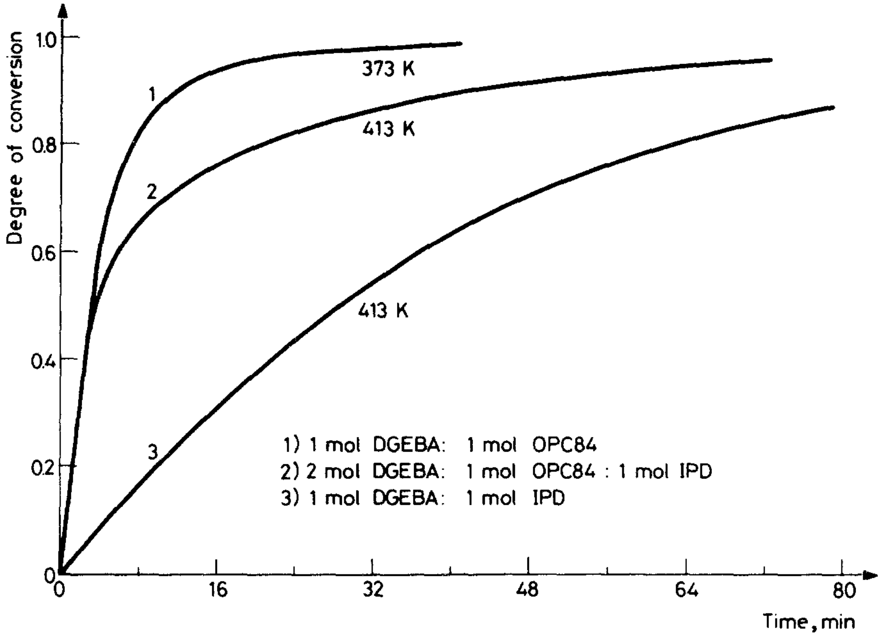

Fig. 3 Conversion degree *vs.* time for several DGEBA/amine mixtures

Table 1 Glass transition temperatures of several amine-epoxide polymerizates

System	T_g, K
1 mol OPC84:1 mol DGEBA	294± 3.5
1 mol OPC84:1 mol IPD:2 mol DGEBA	324± 1.5
1 mol IPD:1 mol DGEBA	355± 2.0

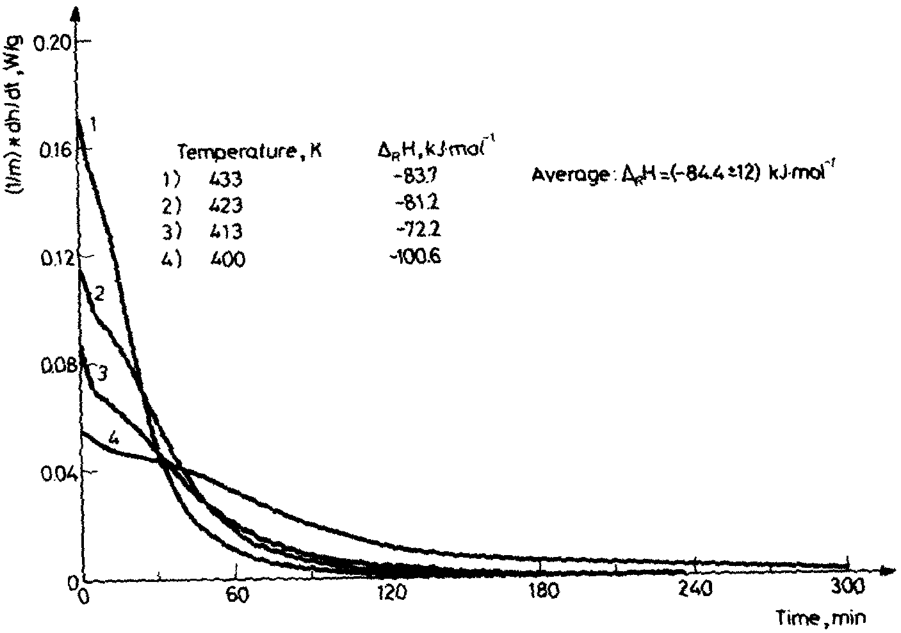

Fig. 4 Isothermal DSC plot of 1:1 molar mixtures of IPD and DGEBA at various temperatures

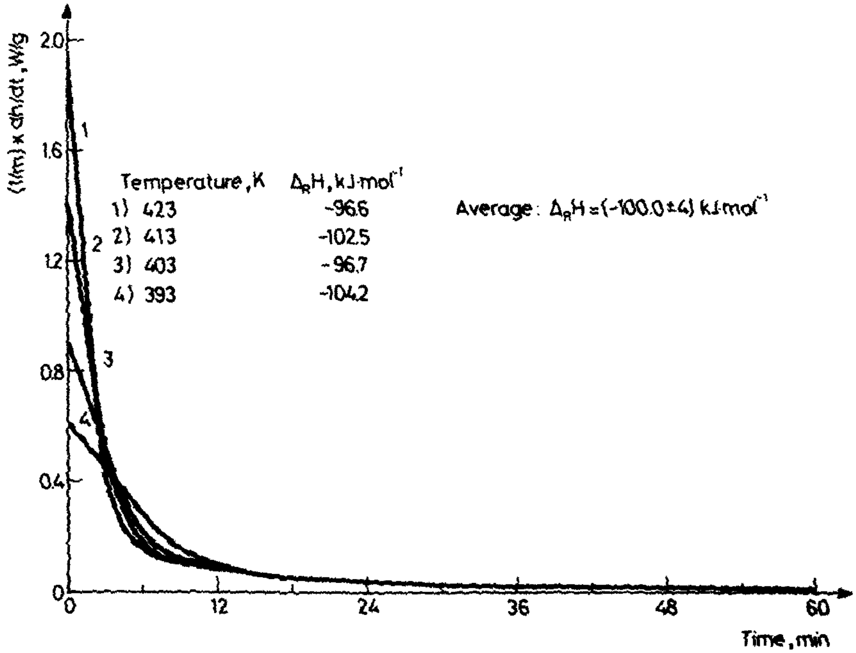

Fig. 5 Isothermal DSC plot of 1:1:2 molar mixtures of OPC84/IPD/DGEBA at various temperatures

The isothermal DSC curves of the curing reaction of DGEBA with IPD are shown in Fig. 4. For an equimolar mixture of IPD are shown in Fig. 4. For an equimolar mixture of IPD and DGEBA, the average heat of reaction is −84.4±12 kJ/mol.

The average reaction heat of a system in which both amines (1 mol OPD84:1 mol IPD:2 mol DGEBA) are present (Fig. 5) is −100.0±4 KJ/mol. The initial reaction rate of this mixture is relatively high. This can be explained by catalytically active impurities in the substances.

As shown in Table 2, the corrected molar reaction energies for the partial systems approximately correspond to those for the single systems. The value for the first photoinitiated step is slightly larger, whereas the corresponding one for the thermally activated step is a little smaller. This is caused by the not really complete separation of the two reactions.

Table 2 Heats of reaction of the two-step polymerization

	First reaction step, thiol-ene photoaddition	Second reaction step, amine-epoxide addition
System I	1 mol dithiol* 1 mol OPC84* 1 mass % ketal 1 mol DGEBA	1 mol intermediate* 1 mol DGEBA*
excitation	light/365 nm $I \triangleq 20.8$ mW cm^{-2}	thermal/80 °C
ΔR^H meas.	−212.8 J g^{-1}	−259.4 J g^{-1}
ΔR^H corr.	−442.1 J g^{-1}= −71.5±2.6 kJ mol^{-1}	−262.6 J g^{-1}= −86.1 kJ mol^{-1}
System II	1 mol dithiol* 1 mol OPC84 * 1 mass % ketal 2 mol DGEBA 1 mol IPD	1 mol intermediate* 2 mol DGEBA* 1 mol IPD*
excitation	light/365 nm $I = 20.8$ mW cm^{-1}	thermal/150 °C
ΔR^H meas.	−112.8 J g^{-1}	−268.4 J g^{-1}
ΔR^H corr.	−467.4 J g^{-1}= −75.6±3.5 kJ mol^{-1}	−271.4 J g^{-1}= −89.9 kJ mol^{-1}

* Components involved in the reaction in the particular step

References

1 H.–J. Flammersheim, Wissenschaftliche Beiträge der FSU Jena "Thermische Analysenverfahren in Industrie und Forschung" (1983) 152.

2 H.–J. Flammersheim, Wissenschaftliche Beiträge der FSU Jena "Thermische Analysenverfahren in Industrie und Forschung" (1981) 160.

Zusammenfassung – Die lichtinduzierte Thiol-en-Addition wurde mit der thermisch aktivierten Amin-Epoxid-Addition kombiniert. Der zweistufige Ablauf der Polymerisation in einem derartigen Harzsystem wurde mittels DSC nachgewiesen. Die Energien beider Teilschritte, der lichtinduzierten und der thermisch aktivierten Reaktion, wurden bestimmt.

РЕЗЮМЕ — Инициированная светом тиол — тиоленовая реакция присоединения была связана с термически активированным амино-эпоксид присоединением. Методом ДСК доказан двухступенчатый характер полимеризации этой смолы. Определены энергии активаций обоих реакций как инициированной светом, так и термически активированной.