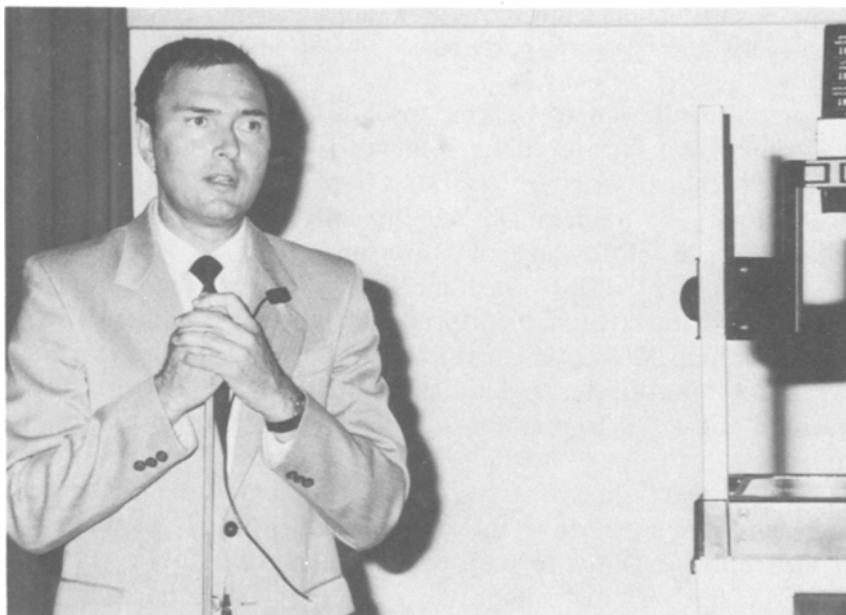


INVESTIGATION OF THERMALLY ACTIVATED OR PHOTOINITIATED POLYMERIZATION BY DSC

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Differential scanning calorimetry is undoubtedly one of the most powerful techniques for investigating the reactions leading to thermoplastic or thermosetting materials. The conditions for the obtaining of reliable experimental results are summarized. A mechanism for the curing of epoxy-amine systems is suggested, which is capable of describing the behaviour of stoichiometric and nonstoichiometric mixtures up to high reaction degrees. The advantage of coupling a DSC instrument with a device for the photochemical activation of polymerizations is demonstrated by some examples.

The absorption or liberation of heat by the reacting substances is the basis for the investigation of thermally or photochemically initiated reactions by DTA or DSC. The assumption of a reaction heat which is independent of the stage of the reaction seems to be valid under nearly all practical conditions. In other words, the difference between the average and the differential molar reaction enthalphy can be neglected to a first approximation. Quantitative

estimation of the extent and rate of the reaction by DTA or DSC is one of the most powerful techniques in polymer chemistry, despite the enormous progress in many structure-sensitive methods in recent years. The following main reasons might be responsible for this situation:

- The sample preparation is fast and very simple, and can in general be performed without special effort.
- The reaction can be started simply by raising the temperature. The sample follows the temperature increase nearly without delay. In the case of isothermal measurements, the time for establishing the temperature equilibrium is very short. A power-compensated DSC instrument needs about 30 seconds.
- The sample is allowed to become insoluble during the reaction. This is a very important fact in polymer chemistry, where the use of structure-sensitive methods, e.g. NMR or GPC, is restricted.
- The sensitivity of modern DSC equipment permits the observation of reactions over the entire range of conversion.
- The evaluation of a DSC experiment supplies the reaction energy and the reaction rate as primary information, both depending on the stage of the reaction. Most other methods provide first an integral and concentration-proportional signal at definite times. The reaction rate, subsequently calculated from these single points, is frequently more or less erroneous.

The quality and validity of reaction experiments are influenced by a number of features, the most important of which are as follows:

- It is absolutely essential to prepare perfect mixtures, even in the case of solids or liquids with high viscosity.
- The mixing and the preserving should be done in such a way that before the DSC measurement the reaction rate is negligible. The temperature range has to be chosen so that undesired secondary reactions do not occur, and substances do not begin to decompose.
- The principal disadvantage of the DTA or DSC technique is that a thermal event is detected, but it is not known in detail what happens. From this, it follows that it is absolutely necessary to combine the results with those from other, preferably structure-sensitive methods. Even the simple question of whether the reaction is complete or not cannot be decided by DTA or DSC alone.

After these points have been taken into consideration, one has to decide the operation mode of the DSC, i.e. whether the normal dynamic or the isothermal technique should be used. Both modes have advantages and disadvantages, and they complement each other. Dynamic measurements are rela-

tively fast and start at temperatures well below that of the beginning of the reaction. They go to completion, if possible, and in principle they provide the kinetic parameters (reaction order, activation energy and frequency factor) from a single curve. However there are some disadvantages too:

- The reactions sometimes go to completion in temperature ranges where secondary reactions, the beginning of decomposition or changes in the reaction mechanism cannot longer be neglected. The upper temperature limit and the highest reasonable heating rate must be determined in careful experiments.
- A strict comparison with the results of other techniques requires similar reaction conditions. The typical reaction conditions used by the preparative organic chemist correspond to the isothermal mode rather than to the dynamic one. However polymers obtained at constant or rising temperature are not necessarily identical, as concluded by Baldini [1] from his theoretical considerations and practical results. To get an unambiguous dynamic baseline, separated from device-typical curvature and changes in the heat capacity and heat conductivity of the reacting mixture, the often made connection of the initial and the final level of specific heat by a straight line seems to be oversimplified. If the curve obtained upon reheating of the reaction product is taken as sample background, a better approximation is obtained than by correcting with the no-sample baseline. The more sophisticated procedure of Bandara [2] uses an iterative algorithm to find a numerical solution for the background correction and accounts for the heat capacity variation of the system during the reaction.
- In the kinetic modelling of unknown, more or less complicated reactions, the risk of misinterpretation increases with the number of factors influencing the rate of reaction. Each reduction of this number, for instance with a constant reaction temperature, would be valuable in such cases.

Experimental

In our laboratory we employ the DSC 2C of Perkin-Elmer with the model 3600 data station. Routine measurements relating to photopolymerization are made on the older DSC 1B, coupled to a self-made data acquisition system. Due to some of the facts mentioned above, we preferably use the isothermal technique. For stabilization of the isothermal baseline the ambient temperature is kept constant at 295 K by Peltier-cooling. The only remaining experimental uncertainty is then the behaviour of the

reacting sample in the first 60 to 90 seconds after the desired reaction temperature is reached. An obvious way to correct this no reaction signal would be to subtract the DSC curve obtained on reheating the reacted sample under the same conditions. [3]. We have found that such a simple subtraction of two runs of the same sample supplies a distinct difference signal in the first minute, caused by the different heat conductivities of the sample in the two runs. If there is no way to reduce this influence appreciably, a simple, easily automated correction of the measuring signal cannot be done. We therefore extrapolate the heat flow after 60 seconds to shorter times. If the decay of the reaction signal obeys an exponential law, this correction could be computed without operator control. An appropriate procedure was suggested by Smith [4], using the Magelsdorf method of analysis. As concerns the range of reaction temperatures, we took into consideration the following demands:

- The temperature should be low enough to avoid side-reactions and to minimize the time lag between the thermal event and the measuring signal, i.e. to avoid the necessity of deconvolution.
- On the other hand, the temperature should be high enough for the reaction to be completed a reasonable time.

Thermally activated reactions

In recent years we have intensively studied the cold curing of the highly-purified diepoxide DGEBA and a number of highly-purified dissecondary diamines and primary amines. Depending on the structure and on the basic and nucleophilic character of the amines, we found that during solvent-free melt-polymerization soluble high polymers with a linear non-crosslinked structure are formed [5]. The products are suitable as special adhesives for the optical industry. The prediction, optimization and control of the desired properties would be facilitated by a quantitative kinetic model that is valid over the entire range of polymerization.

Figure 1 shows typical isothermal DSC curves for stoichiometric and non-stoichiometric mixtures of DGEBA and aniline. Similar curves are produced by numerous other systems. Diluents and catalysts do not modify the principal behaviour. In Figure 2 the influence of increasing amounts of benzyl alcohol is demonstrated for the system DGEBA/*N,N'*-dibenzyl-4,4'-diaminodiphenyl-methane.

In every case the reaction is typically autocatalytic in nature, due to the increasing number of acidic hydroxyl groups as the reaction proceeds.

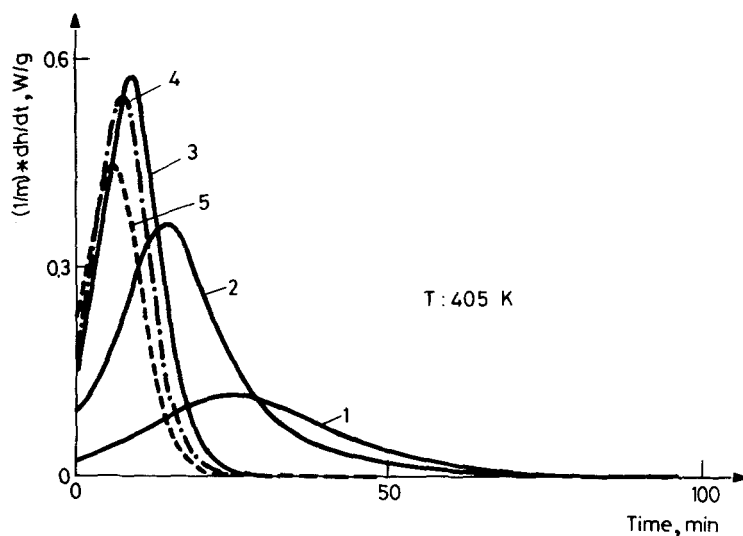


Fig. 1 Isothermal DSC curves for stoichiometric and nonstoichiometric mixture of DGEBA (E) and aniline (A)
 -1.2E/1A, -2.1E/1A, -3.1E/2A, -4.1E/3A, -5.1E/4A

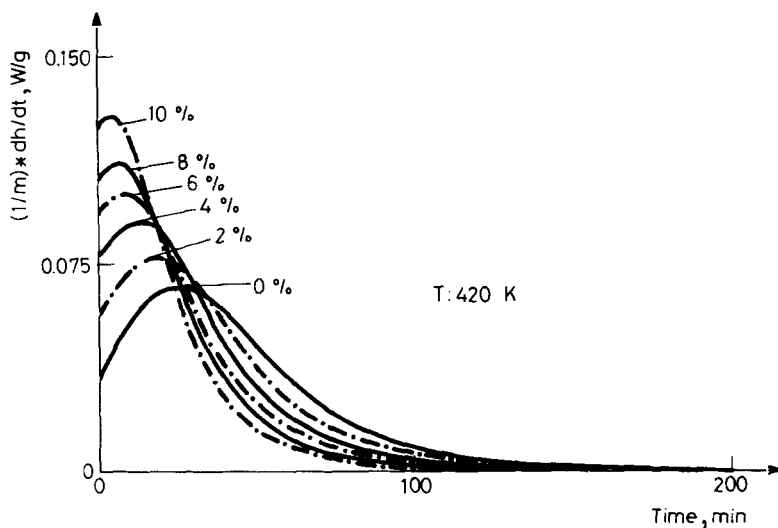


Fig. 2 Influence of increasing amounts of benzyl alcohol on the system DGEBA/N,N-dibenzyl-4,4'-diaminodiphenylmethane

Numerous attempts have been made in the literature [6–9] to describe the kinetic behaviour of the amine-epoxy reaction. The simplest way is to assume normal n -th order kinetics, as very frequently done for technical systems. Technical systems in general contain large amounts of catalytic impurities and/or catalysts. Sample mixtures with less catalytic groups yield a similar picture to the stoichiometric DGEBA / aniline sample. This means that the situation with high concentrations of catalysts corresponds to a limiting case, which must be included in a more detailed model. Since the fundamental studies of Smith [6], the most frequently used kinetic equation is:

$$dx/dt = (k_1 c + k_2 x) \cdot (e-x) \cdot (a-x)$$

where e , a and x are the concentrations of epoxy, amine, and reacted groups, respectively. The original equation was used for DSC data evaluation by Horie *et al.* [10] and by Surour and Kamal [7]. If this equation is rewritten for a stoichiometric mixture by introducing the reaction degree α , one obtains:

$$d\alpha/dt = (k_1' + k_2 \alpha)^m (1-\alpha)^n$$

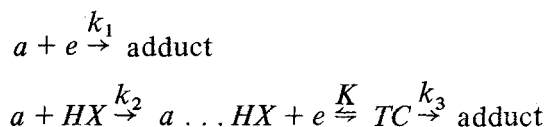
The mechanism proposed by Smith yields $m = 1$ and $n = 2$. However all the investigated systems follow this equation only up to $\alpha \approx 0.6$. There have been numerous attempts to extend the range of validity of this equation, most frequently by fitting of n and m [9, 11, 12], but these modifications are chemically not defined. Diffusion-controlled kinetics is sometimes introduced [13, 14]. This assumption is physically often meaningless. Recently, Mita and Horie [15] discussed the influence of increasing viscosity on reaction kinetics. To summarize their results, it can be concluded that the viscosity of the system, and therefore the competition situation between chemical and diffusion control of the reaction rate, must be considered in at least two cases:

1. Reaction progress occurs by means of the reaction of macromolecules or macroradicals.
2. The reaction temperature is below the glass transition temperature of the system.

The first case is for a polyaddition reaction much less important than for polymerizations. The second one is excluded by us by setting the reaction

temperature at least 30 deg above the final T_g of the system: We have further substituted DGEBA by the monofunctional phenyl glycidyl ether. In such systems, the reaction products are normal low-molecular compounds with very low viscosity, but the principal behaviour remains unchanged compared to that of DGEBA. Further, the reaction curves of nonstoichiometric mixtures are strongly dependent on the nature of the excess component, and not on the total or the changing viscosity. Therefore, models with additional diffusion control are valid and physically reasonable only in some special cases.

We can describe the whole reaction of stoichiometric and nonstoichiometric mixtures by the following mechanism:



where HX = acid catalytic groups from catalysts or from the product, and TC = ternary transition state. Instead of the term $k_1 c$ of the original Smith equation, we formulate a noncatalytic competition reaction with the rate constant k_1 , because the relatively high initial rates of the highly-purified components vary strongly with the nature of the amine and cannot be correlated with catalytic impurities. Further, the reaction curves of stoichiometric and nonstoichiometric samples can only be simulated by model calculations if we assume a hydrogen-bonded complex between amine and hydroxyl groups. This was proposed by Tanaka [16], while Smith [6] discussed an activation of epoxide by hydrogen-bonding. The recent careful spectroscopic results of Bellenger *et al.* [17] show that the strength of the hydrogen-bonding decreases in the sequence hydroxyl groups/nitrogen of amino groups, hydroxyl groups/hydroxyl groups and hydroxyl groups/oxirane oxygen. This is consistent with our mechanism. The model calculations have shown that the slowest rate-determining step is the formation of the amine-hydrogen complex. The conventional equilibrium constant K of the ternary complex is small and somewhat dependent on the stage of the system.

The influence of lower-molecular hydroxyl groups can be described by the same set of equations as that for the higher-molecular ones. Whereas the rate constant k_2 for the interaction of the low-molecular hydroxyls with the amine is in general somewhat larger than that for the high-molecular ones, the equilibrium constant and the rate constant k_3 possess the same values.

Photochemically activated reactions

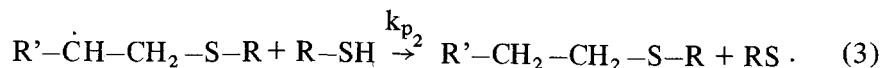
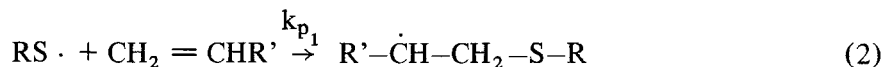
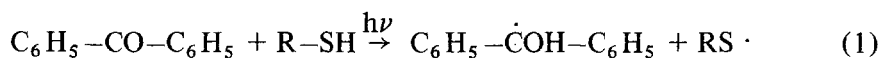
Photocured systems have the great advantage of unlimited stability in the dark, combined with very short reaction times at room temperature or at slightly elevated temperatures. A simple modification of a standard DSC instrument adding a device for UV irradiation of the sample allows the progress of the reaction of the photocurable material to be followed. UV light from a mercury high-pressure lamp arrives at the polymerizing substance after separation of the desired wavelength and definite weakening of the radiation flux. The sample pans, covered with thin quartz windows, are our own developments. The exact light intensity on the surface of the sample is simply measured by the calorimeter itself, which reproducibly changes almost 95% of the radiation energy into heat. Similar devices have already been described [18]. A merely qualitative investigation allows the solution of a large number of questions of importance for industrial research as concerns the optimization of the systems. There are correlations between the reaction rate and the reaction stage and such parameters as the type of monomer, the type and concentration of the photoinitiator, the light intensity, the wavelength of the lights, the thickness of the sample, the presence of inhibitors, etc.

Some examples of such qualitative measurements are to be discussed. The phenomena investigated are simultaneous or successive radical and cationic polymerization, highly desirable from the application side. Methyl methacrylate (MMA) and phenyl glycidyl ether (PGE) were chosen as monomers. The former easily polymerizes in the presence of radical formers, e.g. benzoin methyl ether or benzophenone during illumination with UV light. Arylonium salts can initiate the cationic and/or radical polymerization, as shown by Crivello and Lam [19]. The selectivity of the radical and cationic reaction is determined by the nucleophilic character of the anions MX_n^- of the aryonium salts. In general, both components of a mixture of MMA and PGE react nearly simultaneously. However conditions may be found [20] at which the reactions of both monomers take place slightly separated. These conditions are, for instance, a high fraction of MMA, a very low light intensity, and the addition of inert compounds with high viscosity. Under these circumstances, the separation of the two reactions is much better with BF_4^- than with PF_6^- or SbF_6^- . First MMA reacts, then PGE.

Vice versa, in the presence of radical formers, the radicals of which cannot be oxidized, a successive reaction of both monomers should be possible to a greater extent. This postulate was verified by substituting benzoin methyl ether by di-tertiary-butyl peroxide, which initiates the thermal polymer-

ization of MMA. Under these combined activations, the separation of the two effects is the better, the higher the light intensity and the lower the temperature. First PGE is photochemically activated, then MMA is thermally started. Meanwhile, we have found systems and conditions, under which the competing reactions proceed apparently one after another. For instance, a combined system of acrylates (capable of radical reaction) and of epoxyamine systems (which undergo the normal stepwise addition polymerization) can be handled for some months if stored in a refrigerator. The photofixing of this mixture takes about 30 seconds, and the following thermally activated epoxy-amine reaction can be accomplished at room temperature in several hours to days or much faster at increased temperatures. The reactivity of the amine-epoxy system and hence the stability in darkness can be strongly influenced by the amount of OH groups in the acrylates. At certain concentration ratios, dependent on the type of acrylate and on the epoxy-amine system, the sequence of the reaction steps (photochemically, thermally, or thermally photochemically) does not influence the properties of the reaction products. The only effect of precurcuring the amine-epoxy system is a rate increase of acrylate hardening caused by the increasingly higher viscosity at the beginning of the photoreaction.

Another example is the photocuring of a mixture of dithiols (e.g. 1,8-dithio-3,6-dioxaoctane) and diallylic compounds (e.g. phthalic acid bisallyl ester) [21]. The probable chain mechanism without termination reactions is shown for a monofunctional model compound by the following scheme:



The irradiation of dithiols in the presence of benzophenone (1) yields the thiyl radical, which then starts the chain reaction. The rate-determining slowest step is the formation of carbon radicals (Eq. 2). We conclude this from the following results. When the light is turned off during polymerization, the reaction falls nearly instantaneously to zero. Upon reillumination the reaction starts with a rate which corresponds exactly to that before the interruption. This means that chain carriers must exist in the reaction mixture, which do not recombine very quickly and are otherwise reactive enough only in the presence of light. Careful investigations of monofunctional model compounds have shown that reaction product from the

recombination of the various radicals present in the system are not formed to a larger extent. ESR investigations have shown that carbon radicals must exist in the mixture, the concentration of which follows nearly instantaneously the light-on/light-off conditions. The final experimental proof would be the finding of two different sulfur radicals, a reactive one in the presence of light and a less reactive one in the dark after illumination. However, the latter type of radicals should have a distinctly longer lifetime than the first type. Further investigations on this subject are in progress. One final note should be made. The quantitative estimation of rate constants for chain propagation and chain termination is not possible with the usual DSC technique, even if all experimental and theoretical difficulties are neglected as to quantum yield, changing light absorption in the sample, etc. The combined evaluation of light and dark periods [18] in principle provides the possibility of calculating these rate constants, but the evaluation of the dark period is restricted to systems with a distinct dark reaction and it is purposeful only after deconvolution of the original curve. A simple possible way out of this difficulty is the use of the rotating sector technique [22] coupled with a DSC instrument [23]. Under certain circumstances this combination permits a simple estimation of the average lifetime of the chain carriers. Knowing a certain ratio of rate constants for chain propagation and chain termination from the normal mode of operation, one can easily calculate absolute values of both constants. The limits and the difficulties of this technique cannot be discussed here.

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Zusammenfassung – Die Differential-Scanning-Kalorimetrie (DSC) gehört ohne Zweifel zu den leistungsfähigsten Methoden der Untersuchung von Bildungsreaktionen thermoplastischer und thermisch härtbarer Substanzen. Die Bedingungen zur Gewinnung zuverlässiger experimenteller Ergebnisse werden zusammengestellt. Für die Härtung von Epoxid-Amin-Systemen wird ein Mechanismus vorgeschlagen, der das Verhalten stöchiometrischer und nichtstöchiometrischer Mischungen bis zu hohen Umsätzen beschreiben kann. Die Vorzüge der Kopplung eines DSC-Instruments mit einer Einrichtung für die photochemische Aktivierung von Polymerisationen wird an einigen Beispielen demonstriert.

РЕЗЮМЕ – Дифференциальная сканирующая калориметрия несомненно является одним из самых мощных методов исследования реакций получения термопластических и термореактивных материалов. Обобщены условия для получения приемлемых экспериментальных результатов. Предложен механизм отверждения эпокси-амино систем, описывающий поведение стехиометрических и нестехиометрических смесей до высоких степеней их превращения. На нескольких примерах показано преимущество соединения ДСК аппаратуры с устройством для фотохимической активации реакций полимеризации.