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The step growth polymerization of dithiols and diisocyanates.
Part 1. DSC and spectroscopic investigations regarding the mechanism [1]

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Abstract

The polyaddition reaction of diisocyanates and dithiols was investigated by isothermal DSC measurements and by the spectroscopic methods IRS, UVS and NMR. Using multivariate, non-linear regression, a reaction mechanism is suggested, which is capable of explaining all the experimental results.

INTRODUCTION

The reaction between diols and diisocyanates has been investigated intensively over the last forty years because of the great technical importance of the polyurethanes formed. The mechanism of the polyaddition is very well-known, although minor inconsistencies in detail remain. Replacing the diols by dithiols, polythiocarbamates, the sulfur-containing counterparts of the polyurethanes, are formed. For the kinetics and mechanism, the results of a few investigations have been published for reactions in solvents alone. The results [1, 2] are inconsistent in many respects (above all in the role of the autocatalysis), but they clearly indicate distinct differences in comparison with those obtained with the addition of alcohols. The solvent-free reaction between diisocyanates and dithiols in the presence of nitrogen-containing bases yields linear, soluble, high-molecular products for special industrial applications. The linear structure has been confirmed by determinations of molecular weights, and by NMR and IR spectroscopies [3].

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The objective of this paper is to develop a reaction model which is capable of explaining all the experimental results. Due to their chemical structures, numerous intermolecular interactions are possible between the catalyst and both reactants [4–7]. A simple reaction mechanism is thus very unlikely.

The experimental heat flow curve of a DSC apparatus is caused by the total heat production of all the single reaction steps. If more than simple curve fitting to the experimental curve is intended, both additional structural investigations (NMR, UV, IR) and the results or reasonable assumptions regarding the heats of formation of possible intermediates are needed. Only in this way can the calculated concentration–time curves for a certain reaction model be transformed into the measured total heat flow curves.

EXPERIMENTAL

The diisocyanate (TMDI) was a mixture of 2,2,4-trimethylhexamethylene diisocyanate and 2,4,4-trimethylhexamethylene diisocyanate. The SH component was either octane-1,8-dithiol (ODT) or 3,6-dioxaoctane-1,8-dithiol (TGDT). The preparation and purification procedures are described elsewhere [3]. We used distilled and dried pyridine, 2-picoline, 4-picoline, 3,5-lutidine, 2,4-lutidine, 2,6-lutidine and 2,4,6-collidine as catalysts (all from SIGMA Chemie-GmbH).

Reaction mixtures were prepared by rapid mixing of the liquid components. After adding accurately weighed amounts of catalysts, the mixtures were immediately transferred to pans for volatile samples. Care was taken to avoid introducing humidity while mixing. Until the DSC measurements, the samples were kept in liquid nitrogen.

All measurements were recorded using the power-compensated Perkin-Elmer DSC 2C and DSC7 calorimeters. The temperature calibration and the heat calibration were controlled weekly in the usual manner.

The first measurements immediately indicated that the overall activation energy is low (15–25 kJ mol^{-1}). Therefore, the reaction rate at room temperature cannot be neglected and the sample preparation must be as rapid as possible; the error in the experimental conversion–time curve has to be corrected if necessary. Moreover, the increase in reaction rate with increasing temperature is expected to be small. In spite of the low scan rate (≤ 1 K min^{-1}), the dynamic DSC experiments reach temperatures (>200°C) at which the reaction is still proceeding; nor can undesired side reactions be excluded.

Therefore, in general, isothermal reaction conditions are preferred. The shortest time for establishing the temperature equilibrium of the calorimeter is needed if the drop-in technique is used. The heat flow during the first 40 s, when the apparatus is out of control, was obtained by extrapolation of the data measured at longer times. The scans at five temperatures, separated by 10–15 K, were repeated until nearly identical curves were obtained at the same temperature. Typical reaction times were 30–500 min. The longest times require a baseline stability of the order of the isothermal short-time noise (4–6 μW). This condition was accomplished by stabilizing the room temperature (±0.1 K) and by adding a controlled Peltier cooling device (−5°C, fluctuations ±0.01 K) to the sample holder. After setting up a new isothermal reaction temperature, it takes about 5 min before absolutely constant heat exchange conditions permit the start of a new reaction.

Using spectroscopic methods (NMR, UV, IR), the existence of the intermediates of the assumed reaction mechanism could be confirmed.

RESULTS AND DISCUSSION

An important advantage of isothermal scans is that certain qualitative characteristics of the reaction are clearly apparent. This is very helpful during the search for the most probable mechanism. Figure 1 shows the scans of the system 1 TGDT/1 TMDI/pyridine for varying catalyst concentrations at the same temperature. The apex of the curves results from autocatalytic steps and/or consecutive reactions. Unusually, the increase in the reaction rate on the leading edge of the reaction peak increases in proportion to the concentration of the catalyst. This can only be explained if one assumes a direct coupling of catalysis and autocatalysis. Unlike in the case of the formation reaction of urethanes, the non-catalytic reaction between isocyanate and thiol can be neglected; this is clearly demonstrated by the lack of a reaction in catalyst-free systems. The

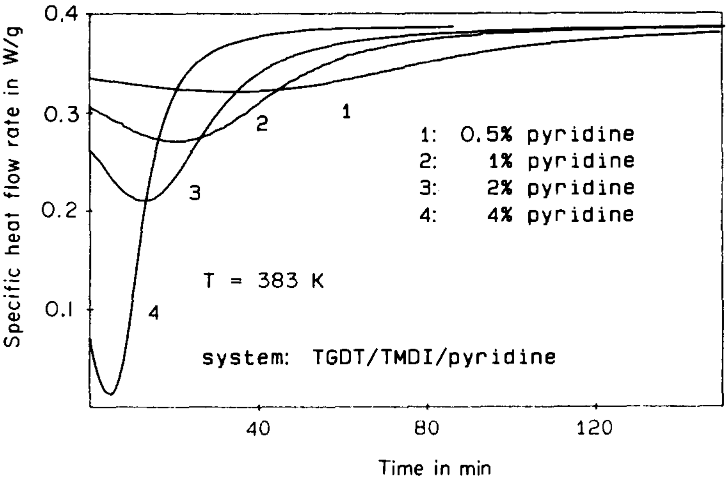

Fig. 1. The influence of increasing amounts of catalysts.

spectroscopic measurements confirm the existence of diisocyanate–catalyst and dithiol–catalyst complexes.

The most probable mechanism that agrees with all experimental findings is

$$S + K \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SK \tag{1}$$

$$I + K \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} IK \tag{2}$$

$$IK + S \xrightarrow{k_3} P + K \tag{3}$$

$$IK + P \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} PIK \tag{4}$$

$$PIK + S \xrightarrow{k_5} 2P + K \tag{5}$$

where S is dithiol, I is diisocyanate, K is catalyst and P is product.

Contrary to the former conclusions of Iwakura and Okada [2], Burkus [6], and Smith and Friedrich [5], the SK complex is not a reactive component. But its existence diminishes the S and K concentrations. Step (3) is the catalytic reaction, caused by the IK complex. The complimentary relationship between catalysis and autocatalysis mentioned above is due to the formation of a PIK intermediate, according to eqn. (4). The existence of the hydrogen-bonded molecule associates, IP and PIK, can be concluded from the IR spectra in the region between 3200 and 3500 cm^{-1}. Because of the probably very small equilibrium constants and the same spectral region, differentiation of both of these intermediates is difficult, and quantitative evaluation is not possible at present.

The unknown equilibrium constant of PIK is probably smaller than 0.1. Therefore, it is impossible to calculate significant kinetic parameters for the coupled reactions (4) and (5). So we have replaced steps (4) and (5) by the overall reaction

$$IK + P + S \xrightarrow{k_6} 2P + K \tag{6}$$

This does not influence the quality of the model adjustment (correlation coefficients are generally higher than 0.998), but the overall kinetic constant k_6 ($k_6 = k_4 k_5 / k_{-4}$) can now be calculated significantly. The limits of the present methods are reached here.

The reaction scheme shows clearly that isocyanate and thiol are involved in a different manner. Therefore the most significant information regarding alternative models should be obtained from reaction mixtures with

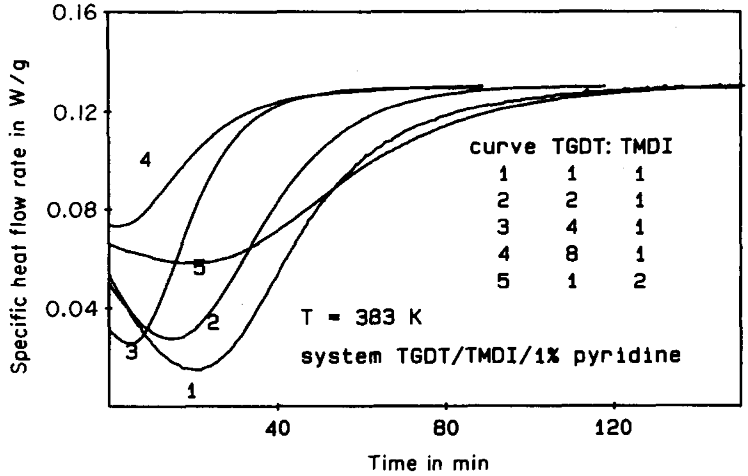

Fig. 2. The influence of different stoichiometries.

different stoichiometries. This is demonstrated in Fig. 2 for the system TMDI/TGDT/pyridine, with constant temperature and catalyst concentration.

If, for a certain mechanism, all heat-exchanging steps are known, adjustment of the measured heat flow curves to the calculated concentration–time curves is possible using multivariate, non-linear regression [8]. With very low concentrations of catalysts, the total reaction heat (72 ± 6 kJ mol^{-1}) should correspond, to a good approximation, with the nearly equal heat production of steps (3) and (4). The energies of formation of the SK complexes (7.5–12 kJ mol^{-1}) were taken from the literature [9], from the observed IR spectroscopic shift of the SH absorption according to the Badger–Bauer rule [10], and from the temperature dependence of the equilibrium constants, using IR spectroscopy. Finally, corresponding values were obtained from the model calculations. These calculations are at present the only way of obtaining the energies of formation of the IK complexes (15–35 kJ mol^{-1}, depending strongly on the steric hindrance of the catalyst).

To avoid misinterpretation and to reach the highest possible degree of model significance, we have included several reaction curves with simultaneous variation of stoichiometry, temperature and concentration of catalyst in the non-linear regression (at most, 16 simultaneous data sets). An impression of the quality of the adjustment is given in Fig. 3, which compares measured and calculated isotherms for the system DMDI/ODT/3,5-lutidine. The concentrations of all components are listed in Table 1. The calculated activation parameters are $E_A = (43.5 \pm 2)$ kJ mol^{-1} and $\ln(A/s^{-1}) = 8.27 \pm 0.25$ for step (3), and $E_A = (44.7 \pm 3)$ kJ mol^{-1} and $\ln(A/s^{-1}) = 7.94 \pm 0.45$ for step (4). The energies and entropies of formation are $\Delta H = (-32 \pm 3)$ kJ mol^{-1} and $\Delta S = (-94 \pm 11)$ J K^{-1} mol^{-1} for IK, and $\Delta H = (-10.5 \pm 1)$ kJ mol^{-1} and $\Delta S = (-35 \pm 3)$ J K^{-1} mol^{-1} for SK. A very good agreement was achieved between literature data for

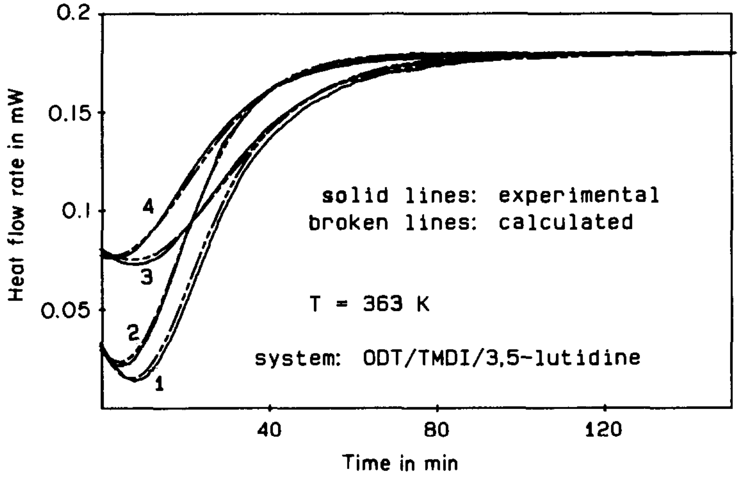

Fig. 3. Comparison between experimental and calculated reaction isotherms.

TABLE 1

Stoich. comp. ODT:TMDI	Curve number in Fig. 3	Conc./mol l^{-1}		
		ODT	TMDI	3,5-Lutidine
≈1:1	1	4.881	4.870	0.477
≈1:2	2	3.142	6.359	0.561
≈2:1	3	6.834	3.225	0.361
≈3:1	4	7.709	2.343	0.439

Composition of the investigated ODT/TMDI/3,5-lutidine mixtures.

these complexes and the energies of formation calculated from the temperature dependence of the equilibrium constants.

As mentioned above, the apparent activation energy of the whole reaction is very small. This is because of the coupling of the exothermic formation of IK during a reversible reaction (step (2)) with the consecutive reactions of steps (3) and (5), which have normal activation energies.

CONCLUSIONS

Three intermolecular complexes are important for the course of the polyaddition reaction between diisocyanates and dithiols. The isocyanate–catalyst complex is responsible for the catalysis, and the unusual coupling of catalysis and autocatalysis is caused by the ternary isocyanate–catalyst–adduct complex. In addition, the thiol and the catalyst form a non-reactive complex. The non-catalytic reaction between the reactants may be neglected. Contrary to the apparent very low activation energy of the whole reaction (15–25 kJ mol^{-1}), the activation energies of the single steps are of the normal order of magnitude (about 45 kJ mol^{-1}).

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