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Infrared Spectroscopic Determination of the Kinetic Data of the Polymerization of Aliphatic Bismaleimides

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Synopsis

Bismaleimides polymerize at elevated temperatures, forming highly crosslinked, high temperature-resistant polymers. From the decrease of the ν(H—C=) band at 3100 cm^{-1}, rate constants and activation energies of the polymerization of four homologous aliphatic bismaleimides were determined. Up to a 20–30% conversion, the polymerization is pseudofirst order. An almost linear correlation between the activation energy and the number of methylene groups in the sequence between the maleimide residues was found.

Zusammenfassung

Bismaleinimide polymerisieren spontan bei höheren Temperaturen unter Bildung vernetzter, hochtemperaturbeständiger Polymerer. Aus der Abnahme der Extinktion der ν(H—C=)-Bande bei 3100 cm^{-1} während der Polymerisation wurden Geschwindigkeitskonstante und Aktivierungsenergie der Polymerisation von vier homologen aliphatischen Bismaleinimiden bestimmt. Bis zu einem Umsatz von 20–30% ist die Polymerisation pseudo-erster Ordnung. Zwischen der Aktivierungsenergie und der Zahl der Methylengruppen in der Brücke zwischen den Maleinimideinheiten wurde in dem untersuchten Bereich eine nahezu lineare Abhängigkeit gefunden.

Résumé

Les bis-imides maléiques polymérisent spontanément à hautes températures avec la formation de polymères entrelacés, qui sont résistants à des températures élevées. A l'aide la diminuation de l'extinction de la bande de valence H—C= à 3100 cm^{-1}, la constante de vitesse ainsi que l'énergie d'activation de quatre homologues aliphatiques bis-imides maléiques ont été déterminées pendant la polymerisation. La réaction, pendant laquelle 20 à 30 pour cent des bis-imides maléiques se sont polymérisés, est "pseudo premier ordre." Une rélation à peu près linéaire a été trouvée—dans le domaine ou les mesures ont été effectuées–entre l'energie d'activation et le nombre de groupes méthylène dans le pont entre les unités des imides maléiques.

INTRODUCTION

High temperature-resistant polyimides may be classified into four different groups: linear-thermoplastic,[1–4] linear-nonthermoplastic,[5] cross-

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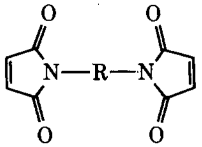
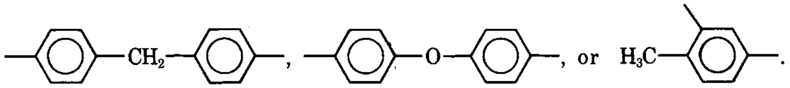
linked-elastomeric,[6] and crosslinked-hard[7–9] (referring only to a few typical patents and publications). The polymerizable monomers leading to the latter group of polymers are formed by the reaction of unsaturated dicarboxylic acids like maleic acid or its derivatives, tetrahydrophthalic acid and citraconic acid, with aliphatic or aromatic diamines. The most important class of monomers of this type are the bismaleimides of the general formula



R typically being $\text{-(}CH_2\text{)-}_n$,



The hydrogen atoms in the maleimide residue are highly activated by the neighboring imide carbonyl groups. Actually, bismaleimides easily polymerize above their melting temperatures without the need of a catalyst, thus forming highly crosslinked polymers with good high-temperature properties. In order to increase the potlife of the monomer melt, an inhibitor such as hydroquinone is added.

In a recent publication,[10] a new technical approach for a processible polyimide binder system based on a close-to-eutectic low melting ternary bismaleimide mixture was described. This system has a melting range of 70° to 125°C, can be processed at 125°C with a melt viscosity of 110 centistokes, and is used, together with glass or carbon fibers, for the production of composites, especially high-performance unidirectional laminates for high-temperature use up to 250°C.

The polymerization process is accompanied by a gradual decrease of the concentration of maleic double bonds and by the formation of substituted succinic residues. Necessarily, the cured resin still contains a certain percentage of residual double bonds. It has been the object of this investigation to study the crosslinking process by quantitiative infrared spectroscopic measurements.

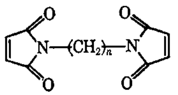
EXPERIMENTAL

Preparation of Bismaleimides

For the infrared measurements, a series of poly(methylene bismaleimides) with an even number of methylene groups was prepared following the method of Searle.[11] 2:1 Molar amounts of maleic anhydride and α,ω-polymethylenediamine were reacted to form a bismaleamic acid. This, in turn, was cyclodehydrated in the presence of acetic acid and sodium acetate thus forming the bismaleimide. Table I shows some data of the bismaleimides used in this investigation.

TABLE I

Some Data on Aliphatic Bismaleimides with General Formula



n	Molecular mass	T_f,[a] °K	Elemental Analysis					
			%C		%H		%N	
			Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
6	276.24	132	60,9	60,2	5,84	5,80	10,15	10,20
8	304.30	123	63,2	62,8	6,62	6,50	9,21	9,30
10	332.35	117	65,1	64,8	7,28	7,20	8,43	8,40
12	360.40	111	66,7	66,9	7,83	7,90	7,77	7,80

[a] DTA peak temperature at a heating rate of 2°C/min, 5-mg sample.

Infrared Spectroscopy

In the spectra of aliphatic bismaleimides, a sharp band is found at 3100 cm^{-1} which has to be assigned to the $\nu(\mathrm{H{-}C{=}})$ vibration of the maleimide ring. This band is useful for quantitative measurements because it shows only little overlapping; during the polymerization process, it shows a gradual decrease in intensity (Fig. 1). The maximum extinction E of this band is supposed to follow Beer's law,

$$\log \frac{I_0}{I} \equiv E = \epsilon c d.$$

When the concentration of the absorbing species is given in $\mathrm{mole/cm^3}$ and the thickness of the cell in cm, the extinction coefficient will be in $\mathrm{cm^2/mole}$.

Determination of Molar Extinction Coefficient of the Maleimide Group

The coefficient ϵ is a physical constant only if a number of conditions is fulfilled. It is, e.g., important that the samples which are measured are in the same physical state and that the molecular neighborhood of the absorbing groups is the same.

Actually, in our own investigations, we had to make two assumptions which were reasonable but could not be proved in a simple way. The extinction coefficient of $\nu(\mathrm{H{-}C{=}})$ of the maleimide group was determined with solutions of bismaleimidododecamethylene in $\mathrm{CDCl_3}$ with concentrations between 0.04 and 0.83 $\mathrm{mole/dm^3}$. Up to a concentration of 0.4 $\mathrm{mole/dm^3}$, the plot of E versus c yielded a straight line (Fig. 2), and only at high concentrations intermolecular interactions caused an increasing deviation leading to low values of E and ϵ. Even at these high concentrations, the deviation was only about 7%. We therefore assumed that the value of ϵ obtained from the linear part of the plot could also be applied to a poly-

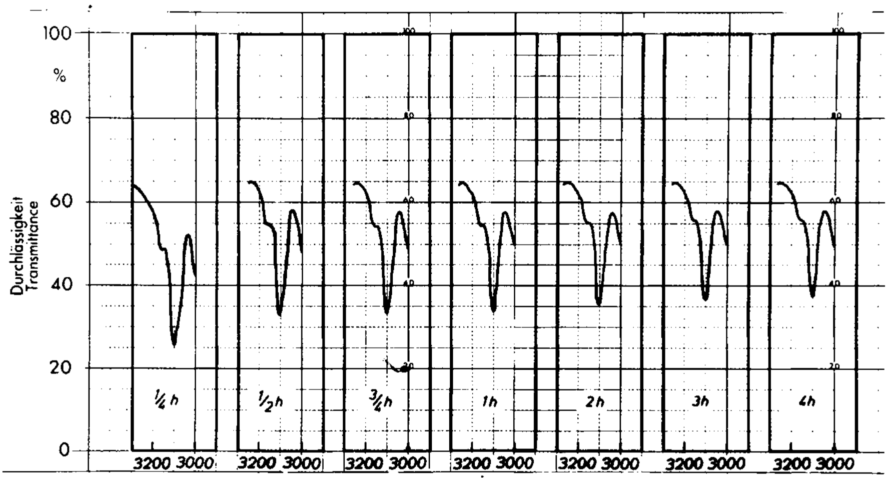


Fig. 1. Polymerization of 1,10-bismaleimidodecamethylene at 453°K; decrease of intensity of the analytical band $\nu(\mathrm{H{-}C{=}})$, at 3100 cm^{-1}.

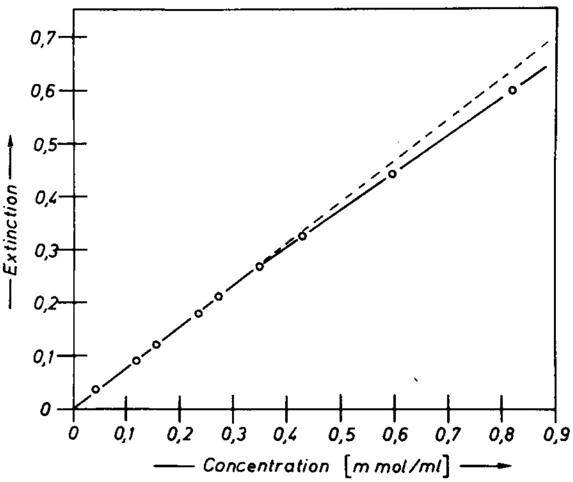


Fig. 2. Determination of extinction coefficient of ν(H—C=) of 1,12-bismaleimidododecamethylene at 3100 cm^{-1}; solvent, $CDCl_3$.

merizing system in the absence of a solvent. The value for $\epsilon[\nu(\text{H—C=})]$ determined in this way was (7.87×10^4) cm^2 per mole 1,12-bismaleimidododecane, or (3.93×10^4) cm^2 per mole maleimide unit.

In addition, we assumed that the coefficient ϵ during polymerization remained approximately constant despite the fact that the chemical nature of the system, and therefore the chemical neighborhood of the remaining maleic imide groups, gradually changes during the reaction.

Determination of Reaction Rates for Polymerization of Aliphatic Bismaleimides

In order to obtain films with defined thickness, aluminum spacers with a thickness of 50 μm were used. Upon a KBr crystal plate which was preheated on a heating plate about 10° above the melting temperature of the sample, first the spacer and then approximately 9 mg of the bismaleimide were placed. Immediately after, a second KBr plate of the same temperature was put upon the arrangement in a way that a liquid melt filled the space within the sandwich without air bubbles. Without delay, the sandwich was screwed tight in a cell and put in the spectrometer. In this way, a spectrum of the amorphous sample could be obtained also at the beginning of the polymerization. This was important because the spectrum of the crystalline bismaleimides differed considerably from the spectrum of the amorphous ones. Thus, the ν(H—C=) band of crystalline samples was split into a doublet whereas, in amorphous samples, it is a singlet.

After measurement of the monomer melt, the sandwich was put into an oven which was preheated to the exact polymerization temperature. At certain time intervals, the cell with the sample was cooled quickly to room temperature, and the spectrum was measured in the analytical range. It was made sure that the samples remained amorphous during this treatment. After each measurement, the sample was again heated in the oven to the polymerization temperature. In order to avoid possible errors due to the emission of the hot arrangement, the sample beam was chopped twice with a 90° chopper phase.

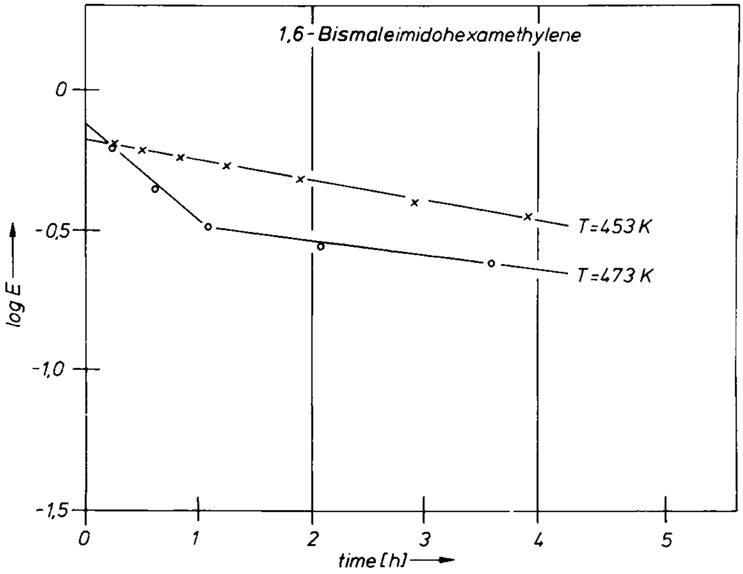


Fig. 3. Polymerization of 1,6-bismaleimidohexamethylene at 453°K and 473°K; determination of rate constants.

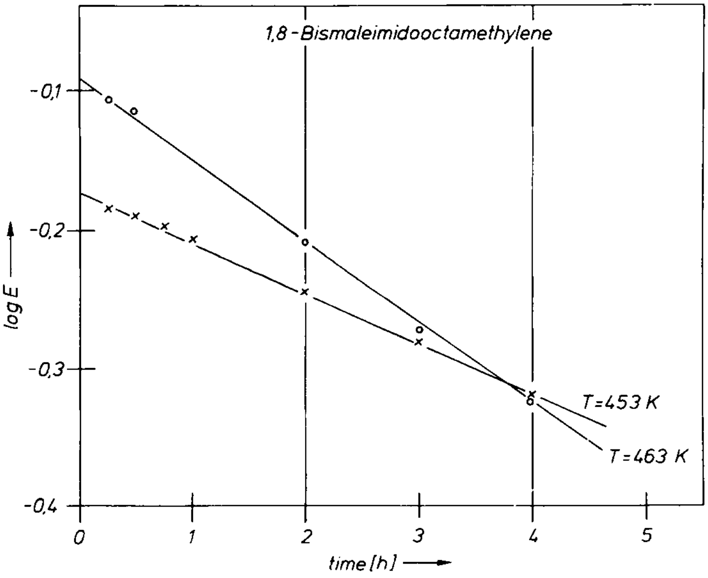


Fig. 4. Polymerization of 1,8-bismaleimidooctane at 453°K and 463°K; determination of rate constants.

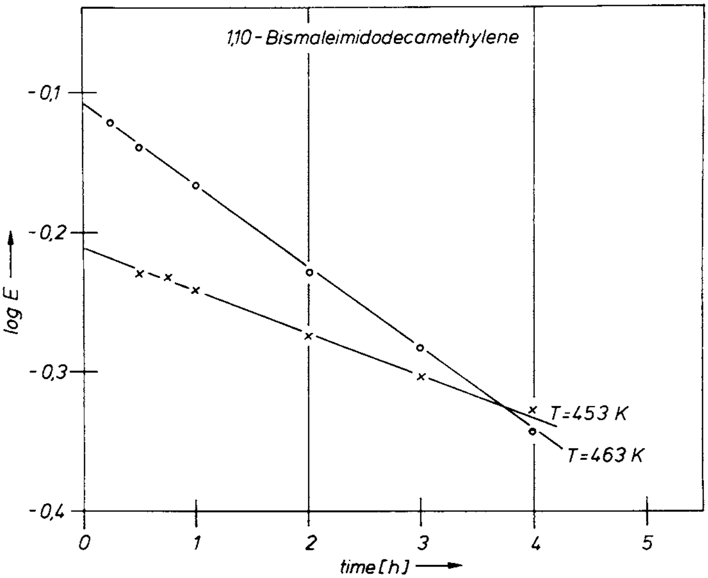


Fig. 5. Polymerization of 1,10-bismaleimidodecamethylene at 453°K and 463°K; determination of rate constants.

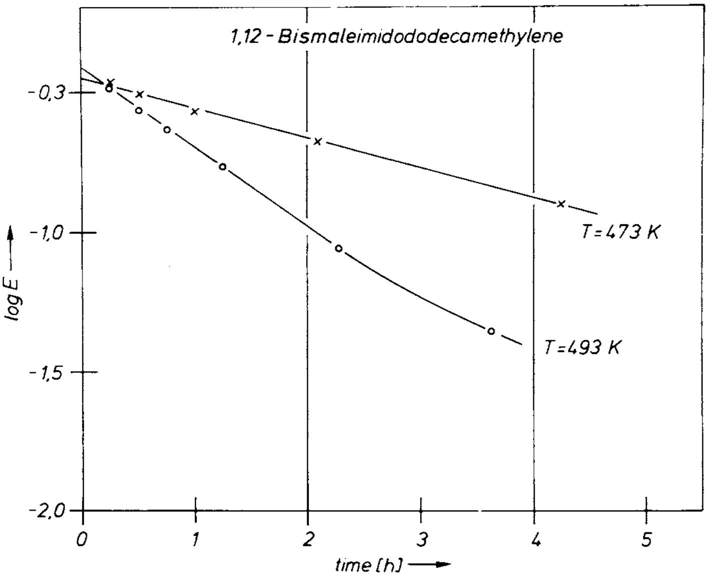


Fig. 6. Polymerization of 1,12-bismaleimidododecamethylene at 473°K and 493°K; determination of rate constants.

Another problem was the possible shrinkage of the polymerizing film. Measurements of the films after curing showed that the shrinkage was minor and well below the other errors of the method.

The analytical band was evaluated by the baseline method. Figures 3 to 6 show the results for the polymerization of the four investigated bismaleimides, each for two different polymerization temperatures.

Determination of Activation Energies for the Polymerization of Aliphatic Bismaleimides

From the infrared data, both the reaction rates for the polymerization of the different monomers at different temperatures and the related activation energies have been determined. Up to a conversion of 20–30%, the reaction was pseudofirst order. This can be seen from the almost linear decrease of log $E[\nu(\mathrm{H{-}C{=}})]$ with time during the first hours of the reaction. Bismaleimidohexamethylene at 473°K (Fig. 3) behaved unusually. After a conversion of about 30%, the curve made a rather sharp bend, from there being rather flat and nonlinear. The reason for this behavior seems to be the rather short methylene sequence of this monomer which is responsible for a rapid increase of viscosity already at low conversions. This, in turn, is a consequence of the small size of the meshes in the three-dimensional network.

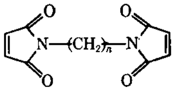
RESULTS AND DISCUSSION

Table II shows the kinetic data obtained by the described method. From the reaction rates determined for two different temperatures, the activation energies can be calculated using the following Arrhenius equation:

$$E_a = \frac{R \ln \frac{k_2}{k_1} T_1 T_2}{T_1 - T_2}.$$

Figure 7 gives the values of the different molar activation energies as a function of the number of methylene groups between the imide rings. The results agree quite well with the ones obtained by an independent DTA method.[12] Apparently, in this intermediate range of methylene sequence lengths, there is a linear relationship between the activation energy of the polymerization and the length of the methylene sequence. A plausible explanation for this result would be the following.

TABLE II
Kinetic Data for Polymerization of Aliphatic Bismaleimides with General Formula



	k, s^{-1}				
n	453°K	463°K	473°K	493°K	E_a, kJ/mole
6	4.8×10^{-5}	—	2.34×10^{-4}	—	140.2
8	2.2×10^{-5}	4.45×10^{-5}	—	—	121.4
10	1.67×10^{-5}	3.20×10^{-5}	—	—	114.3
12	—	—	7.00×10^{-5}	1.87×10^{-5}	94.2

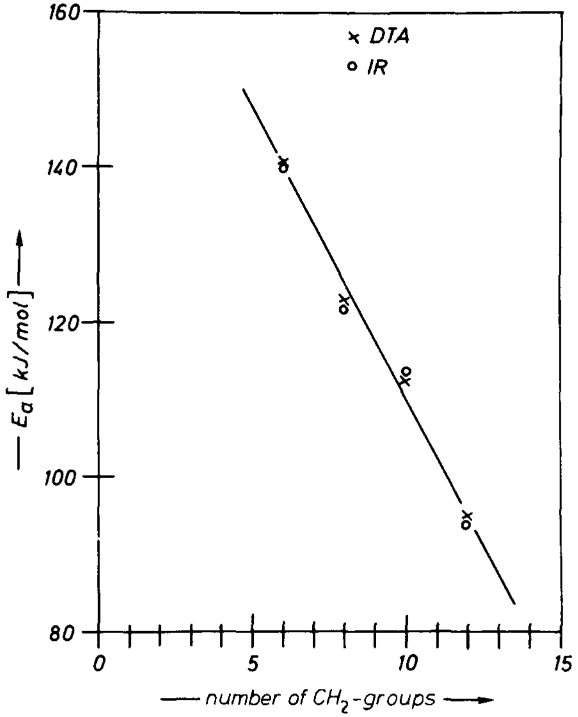


Fig. 7. Activation energy E_a of thermal polymerization of aliphatic bismaleimides as a function of the number of methylene groups between the imide rings.

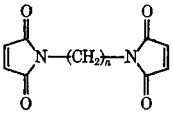
The overall reaction rate of the polymerization is determined by (1) the reactivity of the maleic double bond and (2) by the mobility of the reactive sites in the system. The reactivity of the maleimide unit will certainly not, or only to a small degree, depend on the length of the methylene sequences. These reactive units are sufficiently "insulated" even by a small number of methylene units, and will therefore show the same electron distribution.

The mobility of the reactive sites in the system is highly influenced by the viscosity of the medium and, finally, by the degree of crosslinking. The viscosity of the system with long methylene sequences is at the beginning of the reaction lower than that of the ones with short sequences; it increases also more slowly during polymerization. Bisimides with short methylene sequences crosslink much faster; the viscosity of the system increases rapidly.[10] With crosslinked systems, finally, in the ones being formed by bisimides with long methylene sequences and thus exhibiting larger mesh sizes, the mobility of the reactive groups should be higher than the one in the systems with short sequences.

Not only the steep slope of the curve of the activation energies but also the high value at least for the bismaleimides with short methylene sequences need an explanation. For hexamethylenebismaleimide, an overall activation energy of 140 kJ/mole was found, and this is unusually high for a

TABLE III

Conversions of Different Aliphatic Bismaleimides After Curing Time of 3 Hours



	Conversion, %			
n	453°K	463°K	473°K	493°K
6	21	—	38	—
8	22	37	—	—
10	18	30	—	—
12	—	—	27	44

radical polymerization with a highly active monomer. Very likely, this is due to the part of the activation energy of diffusion. At the beginning of the polymerization, the viscosity is low, and the activation energy is predominately determined by the reactivity of the maleic double bond. With increasing conversions, the viscosity of the system increases rapidly, and the mobility of the reactive sites in the polymer and finally also the mobility of the monomer molecules will be hindered. Thus, the rate of the process might be controlled by the small mobility of the reactants. This view is supported by the bend in the log E versus t diagram (Fig. 3) for hexamethylenebismaleimide at 473°K.

For industrial application, bismaleimide mixtures are cured at 200–250°C during 5–3 hr. Evaluation of our infrared results (Table III) shows that the conversions after 3 hr are generally lower for the bismaleimides with long methylene sequences.

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