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The Polyaddition, Chain, and Polycondensation Mechanisms of Formation of Networks Based on Bismaleimides

Boris A. Rozenberg[1*], Emma A. Dzhavadyan[1], Roger J .Morgan[2] and Eugene E. Shin[2]

[1]Institute of Problems of Chemical Physics Russian Academy of Sciences
Chernogolovka, Moscow region, 142432, Russia
[2]Advanced Materials Engineering Experiment Station,
Michigan State University, 2203 Eastman Avenue, Midland, MI 48640, USA

SUMMARY: The kinetics and mechanisms of polymerization of equifunctional 4,4′–(N,N′–bismaleimide)–diphenylmethane/2,2′–diallyl–bisphenol A (BMDM /DABPA) and model (phenylmaleimide/2-allylphenol) (PMI/AP) systems have been studied in the temperature range 140 – 400 °C using IR-, ^{1}H and ^{13}C NMR spectroscopy, GC/MS, DSC, and isothermal calorimetry. It was established that the cure mechanism consisted of a unique combination of step-wise and chain polymerization as well as polycondensation reactions: the polyaddition "ene" addition of the allyl group to the maleimide and the consecutive and parallel chain polymerization of maleimide and propenyl groups generated by the first reaction. The last reaction was the main branching reaction. The second source of branching was the dehydration reaction of phenol groups (polycondensation reaction) that proceeds with the participation of the 1:1 "ene" adduct as one of the component. Homopolymerization of maleimide groups proceeded autocatalytically, initiated by free radicals generated by thermal decomposition of the maleimide-propenyl group's donor-acceptor pairs. The steric hindrance in 2,2′–diallyl–bisphenol A prevented the reversible Diels-Alder reaction, but the reaction proceeded in model systems. Some thermodynamic and kinetics parameters of the reactions have been determined.

Introduction

The reactivity of bismaleimides is determined by the ability of maleimide double bonds to add to substances containing active hydrogen atoms and to act as dienophiles in Diels-Alder reactions, as well as to participate in radical and anionic homo- and copolymerization reactions with other unsaturated and cyclic monomers.[1,2)] The reactions proceed, as a rule, at elevated temperature and hence restrict the processability of the resins.

Ciba-Geigy Co. has proposed the use of 2,2′–diallylbisphenol A as a comonomer.[3)] The processability of an equifunctional 4,4′-(N,N′-bismaleimide)-diphenylmethane/2,2′-diallyl-

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bisphenol A (BMDM/DABPA) system turned out to be excellent. The brittleness has been substantially reduced with the preservation of high thermostability. Despite the high interest of researchers in this system,[4-9] which is supposed to be applicable as one of the most promising high-temperature matrices for composites for aeronautics and high-speed aircraft, there is an obvious lack of understanding of the kinetics and mechanism of the cure process.

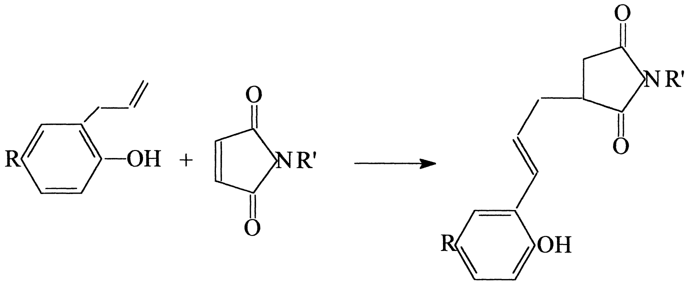
The aim of this paper is to reduce the gap in understanding the cure mechanism. Monofunctional models of the components, namely phenyl maleimide (PMI) and 2-allyl phenol (AP) have also been used in this study. The equimolar BMDM/DABPA system is usually cured in the polyaddition cure schedule in the range 180 – 250 °C. In this study, we have expanded the temperature range and molar ratio of the reagents in order to obtain more detailed kinetics information.

FTIR, ^1H and ^{13}C NMR spectroscopy, GC/MS, DSC and isothermal calorimetric techniques were used. For detailed description of experiments, IR–spectra assignments of analytical bonds and chemical shifts in the ^1H and ^{13}C NMR spectra the reader should refer to the data published elsewhere.[8,9]

Results and Discussion

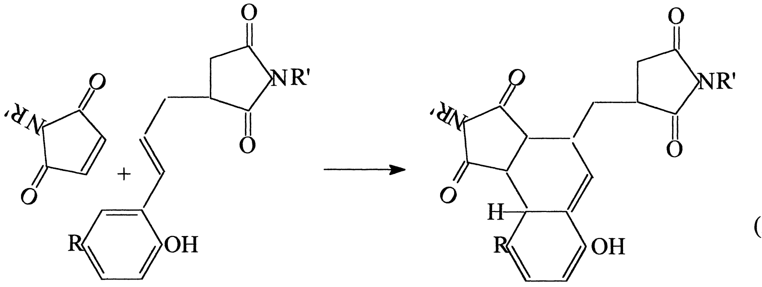
Polyaddition

The inventors formulated first ideas about the cure mechanism of the BMDM/DABPA system.[3] The allyl group addition to maleimide, the so-called "ene" reaction was suggested to occur initially (Scheme 1):



(1)

Here R and R′ are the rest of the corresponding monomers. Studies by FTIR and NMR spectroscopy[8] confirmed the correctness of this mechanism. Additionally, it was found that the hypothesis[3] that the adduct further reacted with another maleimide group by a Diels-Alder reaction with subsequent rearomatization of a phenol ring (scheme 2) was wrong. It could not occur due to steric hindrance of the isopropylidene group in the BADPA molecule.[7,8)]



(2)

However, the monofunctional AP reacts readily and reversibly with maleimide groups to yield a Diels-Alder 2:1 adduct (Fig. 1a) which decomposes at high temperatures (retro Diels-Alder reaction) and forms an 1:1 "ene" adduct as in the network system (Fig. 1b).

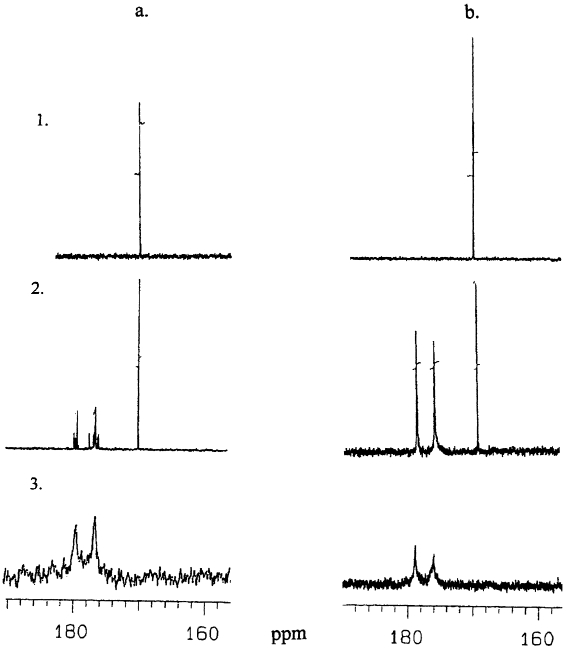


Fig. 1: ^{13}C NMR-spectra in $CDCl_3$ in area of carbonyl carbons of PMI/AP (1:1) (a) and PMI/DABPA (2:1) (b). 1 – initial systems; 2 – after heating at 140 °C (21 hr); 3 – after heating at 200 °C (21 hr).

The FTIR kinetics data on consumption of maleimide and allyl groups and accumulation of generated succinimide groups are presented in Figs. 2 and 3. One can see in Fig. 2 that 1:1 ratio in consumption of maleimide to allyl groups is observed. Each maleimide group consumed generates one succinimide group (Fig. 3). The data in Fig. 2 have been interpreted[4)] as evidence that curing proceeds through an alternating copolymerization of maleimide and allyl groups. However, spectral data (^{1}H and ^{13}C NMR and FTIR) on the formation and consumption of propenyl groups unambiguously testify that, on curing a BMDM/DABPA (1:1) system at low temperatures (<200 °C), the "ene" reaction is practically the only one involving unsaturated groups. Within experimental accuracy, there are no other reactions of the maleimide and allyl functional groups (homo- and copolymerization, or reactions with the participation of phenolic groups). The propenyl group concentration, generated by the "ene" reaction, grows initially, passes through a maximum, and then decreases due to radical polymerization.[5,7] Particularly strong decrease is observed at high temperature (> 250 °C). The kinetics parameters of the "ene" reaction based on the initial rates of reaction are presented for all systems in Table 1.

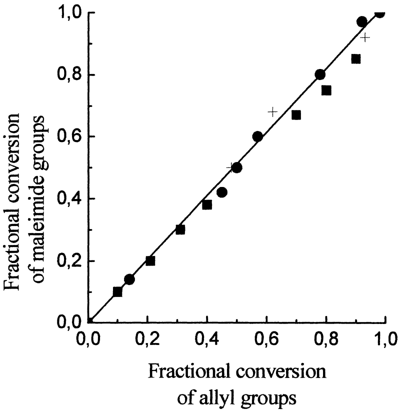


Fig. 2: Comparison of maleimide and allyl groups' consumption in BMDM/DABPA (1:1) curing at different temperatures. Data from ref.[4] (●), ref.[5] (■) and ref.[6](+).

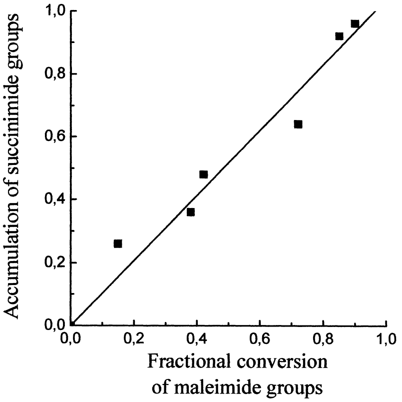


Fig. 3: Accumulation of succinimide vs. consumption of maleimide groups in the curing BMDM/DABPA (1:1) system[6].

Within limits of experimental error, the values of rate constants do not depend on the ratio of components at temperatures below 200°C. They show an obvious tendency to grow for all investigated systems at 200°C thus testifying an increasing role of thermal homopolymerization of maleimide groups with temperature increase (see below). It is reflected also in some increase of the activation energy with increasing excess of the maleimide component. Hence, the activation energy for PMI/AP system grows by 4 kcal/mol with the change of component ratio by 3 times.

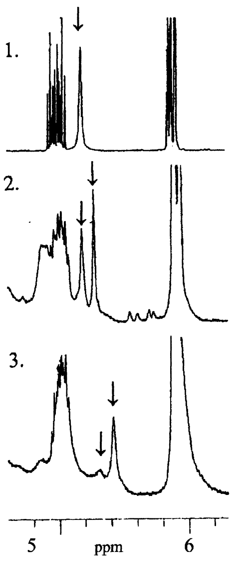
As expected, the reactivity weakly depends on the structure of reagents. The reactivity of BMDM only slightly exceeds that of its monofunctional analogue.

Table 1: Kinetic parameters of BMDM/DABPA cure and of model reactions.[9)]

System	Concentrations of components / mol l^{-1} / mol l^{-1}	$10^4 k_1$ / l mol^{-1}s^{-1} at temperatures /°C				E_1 /kcal mol^{-1}
		140	160	180	200	
PMI/AP	3.77/3.77	0.076	0.25	0.81	1.68	20.0±1.0
	5.02/2.51	0.055	0.18	0.86	1.96	22.5±2.0
	5.63/1.88	0.041	0.18	0.89	1.99	24.0.±1.5
BMDM/AP	3.78/3.78	0.072	0.30	0.96	2.03	21.6±1.4
	5.02/2.51	0.056	0.38	1.22	2.58	23.8±2.6
	5.65/1.88	0.074	0.47	1.50	3.00	24.0±2.0
PMI/DABPA	3.61/3.61	0.080	0.27	0.80	1.35	18.5±1.0
	4.88/2.44	0.100	0.27	0.70	1.93	19.6±1.0
	5.52/1.84	0.110	0.34	0.77	2.30	19.8±1.2
BMDM/ DABPA	3.62/3.62	0.108	0.30	0.74	1.44	19.0±1.0
	4.90/2.44	–	–	–	1.90	
	5.57/1.81	–	–	–	2.27	

Polycondensation

The consumption of hydroxyl groups during cure can clearly be seen in the model PMI/DABPA system by using ^{1}H NMR (Fig. 4). Two types of phenol groups are formed in the first product of the addition of PMI to DABPA. Accordingly, two types of signals can be seen. In subsequent reactions, one of them is consumed much faster than the second. This fact once again confirms that the dehydration reaction proceeds essentially with the phenol group of the 1:1 adduct. With conversion, both signals ascentially undergo a shift towards a lower field within phenol group area. The same occurs at higher reaction temperatures.



← Fig. 4: ^{1}H NMR-spectra in the area of phenol group shifts (marked by arrows) in the model PMI/DABPA (2:1) system in $CDCl_3$. 1– initial system; 2 – after heating at 140°C (21 hr); 3 –after heating at 200 °C (21 hr).

Direct observation of water formation in the reacting system was made by GC/MS. The quantitative analysis of water has shown, that 17 % and ≈ 50 % of the theoretical amount of water are evolved during 2 hours at 140°C and 180°C, respectively. These results are reasonably consistent with the data obtained by IR-spectroscopy[4)] (10 and 38 %, respectively). The consumption of phenol groups in the PMI/DABPA system, as revealed by ^1H NMR-spectroscopy, after reaction had been carried out at 140 and 200 °C for 21 hours, was 62 and 86 %, respectively.[8)]

In the real system, the dehydration reaction serves as a rather powerful source of additional crosslinks in the curing system and leads to the formation of internal stresses and microcracks and negative consequences for the physico-mechanical properties of a network.

Chain Polymerization

As already mentioned, the high-temperature polymerization of propenyl groups (generated by the "ene" reaction) proceeds by a radical chain-growth mechanism. It is well known that maleimide and allyl groups also undergo a high-temperature radical polymerization. It was found in our study[9)] that the maximal rates of thermal homopolymerization of BMDM, PMI and DABPA, recorded by DSC at the scanning rate 5 $K\,min^{-1}$ are observed at the temperatures 212, 304, and 341 °C, respectively. Hence, the reactivity of maleimide groups in the radical polymerization is quite high. It was interesting to assess its competitiveness with the "ene" reaction. A kinetics study of the systems with an excess of maleimide components was undertaken by isothermal calorimetry. The results are presented in Fig. 5.

Fig. 5 shows that at all investigated temperatures the thermally induced polymerization of maleimide groups occurs, whereas maleimide groups do not polymerize alone at temperatures lower than 180°C. Note, that the addition of radical initiators makes polymerization of maleimide derivatives feasible in the melt or in solution, even at rather low temperatures.[10,11)] These facts indicate that the rate-limiting step of the thermally induced polymerization of maleimides is the initiation reaction. On the other hand, these facts shows that the presence of allyl components in maleimide systems, or the presence of the product of their reaction, makes the thermal initiation easier.

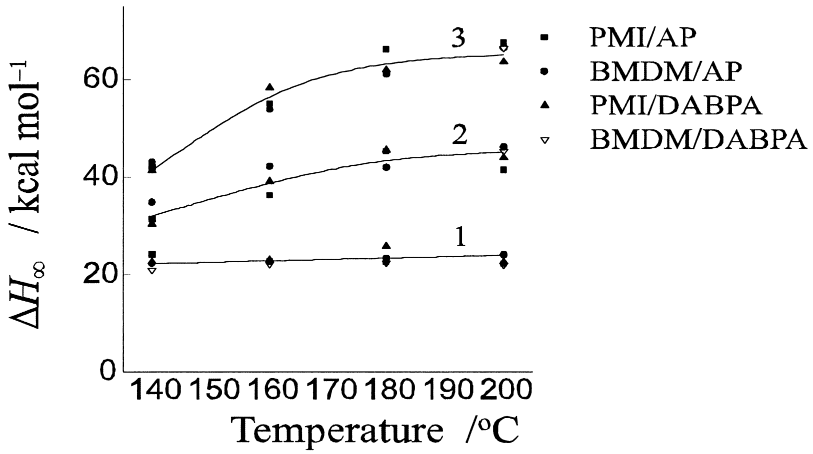


Fig. 5: ΔH_∞ vs. temperature for investigated systems at maleimide/allyl groups ratios equal to 1 (1), 2 (2), 3 (3).

Fig. 5 also shows that the ultimate heat of reaction for all investigated systems is proportional to the concentration of maleimide groups. It can therefore be deduced, that the heat of opening the maleimide double bond in both the reactions taking place (the "ene" reaction and radical polymerization) equals 22.0 kcal mol^{-1}. Note that the incomplete conversion of maleimide groups observed at T<180 °C is due to kinetic reasons (vitrification of the curing systems) and not a thermodynamic one.

Taking into account all the data, the only possible explanation of the observed reaction kinetics of the nonstoichiometric blends with excess maleimide groups can be that the thermal initiation of the radical polymerization of maleimide groups occurs by biradical formation from donor-acceptor pair generated by maleimide and propenyl groups. Such a reaction requires considerably smaller activation energy and can proceed at rather low temperatures. Further chain growth occurs by homopolymerization. Thus, the excess of maleimide groups in BMDM/DABPA and the corresponding model systems reacts at rather low temperatures due to the acceleration of radical polymerization initiation via a mechanism similar to the initiation of the alternating copolymerization of maleimide and propenyl groups. In this case, the maleimide polymerization proceeds as an autocatalytic reaction. It should be emphasized that there is no thermally-induced homopolymerization of maleimides itself under these conditions.

The preceding conclusion also helps one to understand kinetics peculiarities of the investigated system. In particular, why the second-order reaction law, which should be characteristic for stoichiometric systems of reagents, is not obeyed. If the bimolecular "ene" reaction occurs and the product of this reaction stimulates the polymerization of maleimide groups, the following kinetic equation should apply:

$$\frac{d\alpha / dt}{M_0(1-\alpha)} = k_1 - (k_1 - k_2)\cdot\alpha \qquad (1)$$

Here, k_1 is the rate constant of "ene" reaction for a stoichiometric system, k_2 is the effective rate constant of chain polymerization of maleimide groups, α is the conversion and M_0 is the initial concentration of maleimide groups. At $k_2/k_1 = \gamma \approx 1$ equation (1) transforms to the first-order rate equation, at intermediate γ values, the observed reaction order will be between the first and second, and at $\gamma = 0$, the equation transforms to the second-order rate equation.

For the experimental verification of equation (1), we have used the results of a kinetics study of model equifunctional PMI/DABPA system at 200 °C.[8)] It was shown that, in this model system, the maleimide groups are consumed completely, whereas 30% of the allyl groups remained intact. Thus, part of the maleimide groups are consumed in the "ene" reaction with the rate constant k_1, and the remainder of these groups are consumed in radical polymerization with the effective rate constant k_2. As expected, equation (1) describes quite well the reaction kinetics over the complete reaction (Fig. 6).

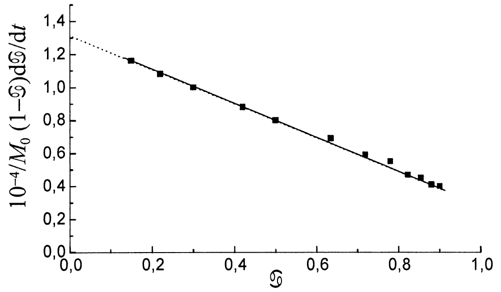


Fig. 6: Kinetics of reaction of an equifunctional PMI/DABPA system at 200°C in coordinates of equation 1.

The negative slope of the straight line testifies that $k_1 > k_2$. The values of the rate constants found for the specified equifunctional system are $k_1 = 1.31\cdot10^{-4}$ l mol^{-1}s^{-1} and $k_2 = 0.3\cdot10^{-4}$ l mol^{-1}s^{-1}.

Conclusions

It has been established that the cure mechanism of the investigated bismaleimide systems consists of a unique combination of all known ways of polymer formation: the "ene" polyaddition reaction of allyl groups to maleimide ones and the consecutive and parallel chain polymerization of maleimide and propenyl groups generated by the first reaction. The homopolymerization of maleimide groups proceeds autocatalytically, initiated by free-radicals generated by the thermal decomposition of the maleimide-propenyl donor-acceptor pairs. In addition, the dehydration reaction of phenol groups takes place during curing and proceeds with the participation of the 1:1 "ene" adduct. A difference in reactivity between real and model systems in the Diels-Alder reaction is revealed. Some thermodynamic and kinetics parameters of the reactions taking place are determined.

Acknowledgements

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