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Polycondensation of bismaleimides with aromatic diamines

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Summary

The polycondensation (Michael addition) of a bismaleimide (BMI, N,N-4,4'-[(1-methylethylidene) bis (phenyleneoxyphenylene)] bismaleimide) with an aromatic diamine (DA, 4,4'-[1,3 phenylene bis (1-methylethylidene)] bisaniline), in a 1:1 molar ratio, was followed using SEC and FTIR techniques. The polycondensation followed a 2nd-order kinetics with an activation energy, $E = 51$ kJ mol^{-1}. The mass fraction of dimer varied with conversion following the statistical prediction for an ideal $A_2 + B_2$ polycondensation. At 60% conversion, gelation was observed. This was ascribed to a small advance in the BMI homopolymerization. Thermal degradation took place at $T > 200$ °C. The first step was, possibly, a reversal in the Michael addition reaction as revealed by the decrease in the concentration of CH_2 groups observed in FTIR spectra.

Introduction

Advanced composite materials based on bismaleimide resins (BMI) exhibit excellent thermal and mechanical properties together with a low moisture absorption. A major drawback is their brittleness, i.e. their low resistance to crack initiation and propagation. The fracture energy may be increased by introducing an aromatic diamine into the formulation. Chain extension through the Michael addition of the amine to the BMI double bond occurs at a faster rate than the homopolymerization of double bonds. This lowers the crosslink density and thereby increases the fracture toughness of the cured material. A commercially available resin, Kerimid 601 of Rhone Poulenc (1), is based on this concept. The formulation consists of a mixture of 1,1'-(4-methylene 1-phenylene) bismaleimide (BMPM) and methylene dianiline (MDA), in a BMPM:MDA molar ratio of 2.5 : 1. This system has been studied by several researchers, particularly regarding the effect of initial molar ratio

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and cure schedule on the reaction scheme and the thermal and mechanical properties of the resultant networks (2-12).

Main reactions taking place in the cure of a BMI with an aromatic diamine are shown in Fig. 1. The Michael addition proceeds at a very much faster rate than homopolymerization, particularly at low cure temperatures (10). Secondary reactions like the addition of secondary amine hydrogens (present in the polyaspartimide, Fig.1) to double bonds, and BMI ring opening by the attack of the amine at C=O leading to an amide (aminolysis), may be considered negligible (8,10,13-15).

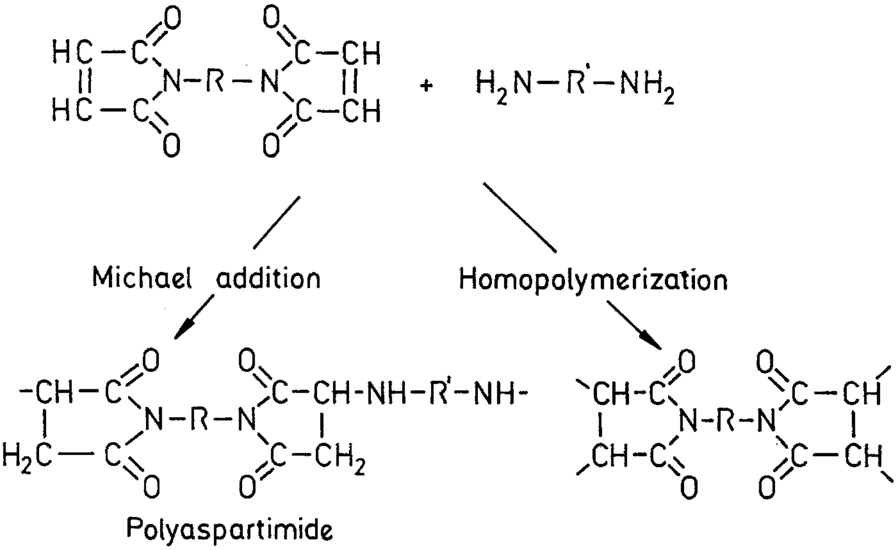


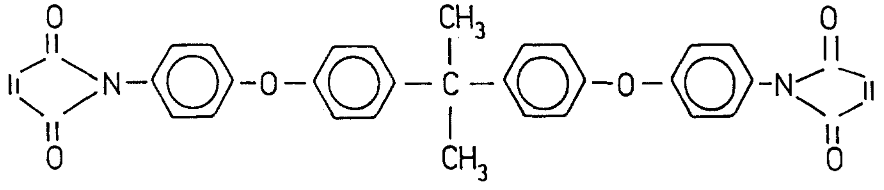
Fig.1 Main reactions in a bismaleimide - aromatic diamine system.

There are several aspects of this reaction that merit further analysis. Regarding the course of the reaction at low temperatures (120 - 145 °C), it is not clear if gelation may occur due to the crosslinking introduced by the homopolymerization reaction. For example, Donnellan and Roylance (8) reported that resin mixtures with molar ratios BMPM:MDA equal to 1:1, 1.5:1, and 2.5:1, remained soluble after 6 h at 145 °C, indicating that extensive crosslinking did not occur. Similar observations were reported by Leung et al. (2,4), for a 7 h heating at 130 °C. However, Tungare and Martin (11) reported the presence of an insoluble fraction in tetrahydrofuran (THF) when curing during 4 h at 125 °C. Another aspect that is not clear is the stability of the polyaspartimide at high temperatures, due to the possibility of producing a reversal of the Michael addition reaction (13,15,16). This may lead to a change in the network topology before extensive degradation takes place.

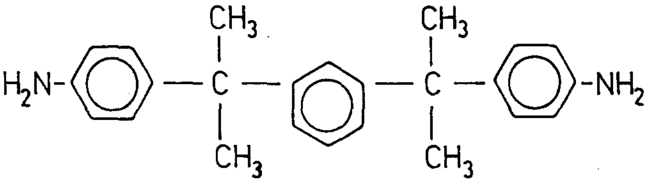
The aim of this paper is : i) to analyze the course of the reaction at low temperatures, ii) to study the stability of the network structure at high temperatures. To get a different perspective, both BMPM and MDA will be replaced by other monomers containing aromatic rings in their structures. Results for a molar ratio 1 : 1 will be discussed.

Experimental

Structures of the selected bismaleimide (BMI) and diamine (DA) are shown in Fig.2 BMI is N,N-4,4' [(1-methylethylidene) bis (phenyleneoxyphenylene)] bismaleimide (97% purity), and DA is 4,4'-[1,3 phenylene bis (1-methylethylidene)] bisaniline (99% purity). Both monomers were provided by Ken Seika Corp.(USA) and used without further purification. The melt point of the BMI was 83 °C and the one of the DA was 113 °C (determined by differential scanning calorimetry, DSC). Mixtures in molar ratios 1:1 were prepared by melting at 120 °C and keeping this temperature for about 2 min. This procedure advanced the addition reaction as will be discussed later.



Bismaleimide



Diamine

Fig.2 Structures of the selected bismaleimide and diamine monomers.

Size exclusion chromatography (SEC) was performed using a Waters 510 device provided with a refractive index detector, a set of ultrastyragel columns 100, 100, 500 and 10,000 A, and THF as a carrier at a rate of 1 ml min^{-1}. Mass fractions of monomers and the first addition product were obtained using the standard deconvolution technique of the integrator (Waters 745), coupled to the SEC device.

Infrared spectra of samples dispersed in KBr were obtained using a Bruker IFS 25 FTIR, in the transmission mode, with a standard resolution of 2 cm^{-1}.

Glass transition temperatures (Tg) were determined by DSC (DuPont 990 provided with a 910 DSC cell). Runs were carried out at 10 °C min^{-1} under a nitrogen flow. Tg was defined at the onset value of the transition.

The occurrence of gelation was determined from solubility tests in dimethylformamide (DMF) and tetrahydrofuran (THF).

Results and Discussion

Fig.3a shows SEC chromatograms of BMI:DA mixtures obtained by either melting or grinding. In this last process no reaction takes place (the small peak is an impurity present in the BMI monomer). Melting together both monomers leads to an advance in the extent of reaction as reflected by the appearance of a peak assigned to the first addition product.

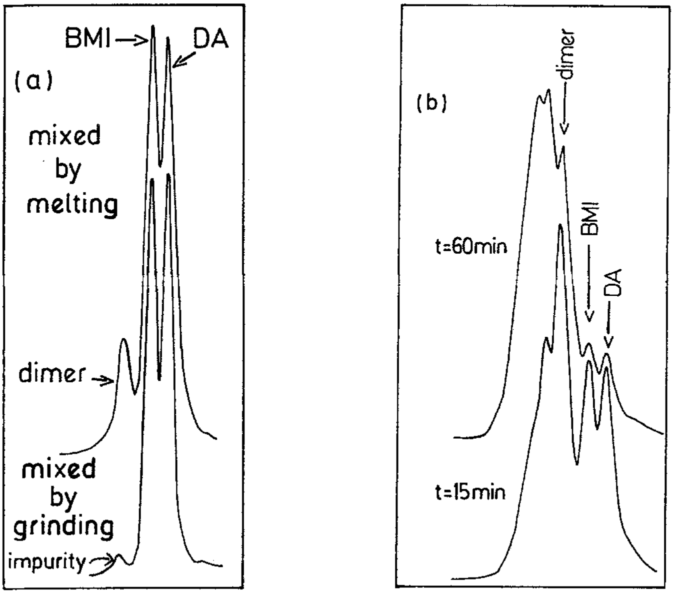


Fig.3 SEC chromatograms:a)initial mixtures, b)reaction products at 123 °C (15 and 60 min)

Fig.3b shows SEC chromatograms of mixtures polymerized at 123 °C for different times. An increase in the peak of dimers and higher oligomers, together with a decrease in the peaks of both monomers, reveals that the Michael addition is the main reaction taking place at low temperatures.

FTIR spectra shown in Fig.4, confirm that the addition of the primary amine to the BMI double bond is the prevailing reaction. Using the assignation of bands reported by DiGiulio et al.(3), it is observed that NH_2 peaks at 3415 and 3446 cm^{-1}, the maleimide double bond at

3100 cm^{-1} and the C-N-C peak of maleimide at 1150 cm^{-1}, disappear during polymerization. At the same time, there is an increase in the intensity of peaks assigned to the addition products; i.e. NH at 3373 cm^{-1}, CH_2 at 2856 and 2923 cm^{-1} and the C-N-C peak of succinimide at 1182 cm^{-1}. The reaction is not complete after 4 h at 120 °C (curve 2), due to the occurrence of vitrification. After 2h at 190 °C (curve 3), the reaction is practically complete and the maximum glass transition temperature of this particular system is attained, i.e. Tg = 156 °C, as measured by DSC.

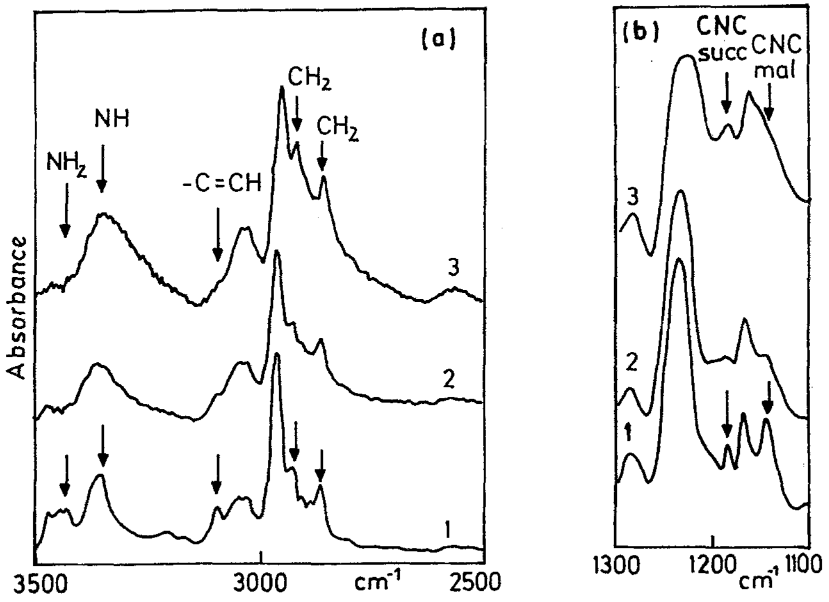


Fig.4 FTIR spectra (a) 2500 - 3500 cm^{-1} range, (b) 1100 - 1300 cm^{-1} range; (1) initial mixture obtained by melting, (2) after reaction during 4 h at 120 °C, (3) after reaction during 2h at 190 °C.

Kinetic and statistical aspects of the reaction were obtained from SEC chromatograms of mixtures heated during predetermined periods of time at 123 °C and 142 °C. Assuming an A_2 + B_2 ideal polycondensation, the mass fraction of both monomers is related to conversion by (17):

$$w_{A2} + w_{B2} = (1 - p)^2 \qquad (1)$$

Then, the particular conversion attained at any reaction time, may be obtained from SEC chromatograms as:

$$p = 1 - (w_{A2} + w_{B2})^{1/2} \qquad (2)$$

The reaction could be followed up to conversions close to 0.6 where an insoluble fraction was observed. In a short conversion range after this point, macroscopic gelation took place. Two experimental facts have to be reconciled. On the one hand, FTIR spectra showed an almost complete reaction of primary amine groups and maleimide double bonds. This constitutes a proof of the $A_2 + B_2$ linear polycondensation. But, on the other hand, gelation takes place. This can be explained by a small conversion in the homopolymerization of maleimide double bonds (gelation takes place at very low conversions for an A_4 chainwise homopolymerization).

Therefore, the BMI-DA system in a 1:1 molar ratio undergoes a linear polycondensation (Michael addition), with a very small extent of BMI homopolymerization taking place in parallel. This leads to gelation at an overall conversion close to 0.6.

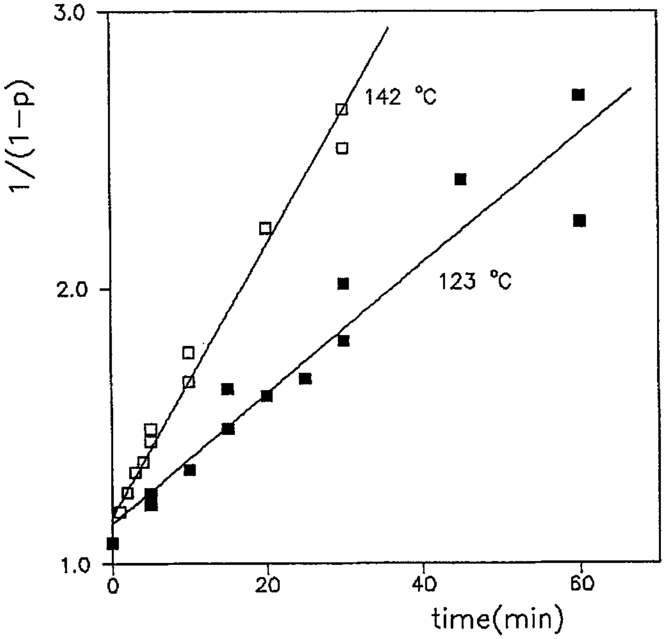


Fig.5 2nd-order kinetic regression for runs carried out at 123 °C and 142 °C.

As shown in Fig.5, a 2nd-order kinetics could be fitted to the experimental p vs t points in the pregel stage (the initial conversion, $p_0 = 0.10 - 0.15$, arises from the selected mixing procedure as shown in Fig.3a). Similar 2nd-order kinetic equations for the BMI-DA polycondensation, were reported by Crivello (13) and Tungare and Martin (10). The activation energy (based on only two temperatures), is $E = 51$ kJ mol^{-1} , comparable to a value of $E = 62.3$ kJ mol^{-1} reported in the literature (10) for the commercial BMPM-MDA system.

For a stoichiometric $A_2 + B_2$ system undergoing a linear polycondensation, the mass fraction of dimer is given by (17):

$w_2 = 2p(1 - p)^2$ (3)

Experimental points arising from SEC chromatograms (2 runs at 123 °C and 2 runs at 142 °C), are represented in Fig.6, together with the theoretical prediction. The reasonable fitting constitutes an extra proof that the linear polycondensation is the main reaction taking place in the system.

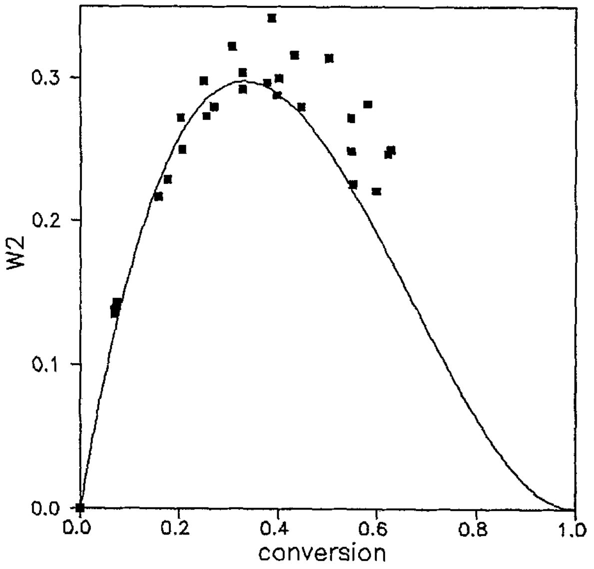


Fig.6 Mass fraction of dimer as a function of conversion (full line = theoretical prediction).

The high temperature stability of cured products was determined from the Tg decrease after a predetermined heating schedule. At T > 240 °C, thermal degradation took place as revealed from a Tg decrease coupled to mass losses. For example, samples cured at 260 °C during 2 h under nitrogen, showed a Tg = 122 °C with a 5.5% mass loss.

In order to get some idea of the first stages of thermal degradation, fully cured samples exhibiting a Tg = 156 °C, were heated up to 275 °C at 10 °C min^{-1}, under nitrogen, and rapidly cooled. The glass transition temperature decreased to 138 °C without mass losses. FTIR spectra of samples before abd after the heating period, were substracted in an absorbance scale, using as a reference the band at 1500 cm^{-1}(1,4-substituted benzene ring). Fig.7 shows the difference spectrum in the 2000 - 3900 cm^{-1} range. A decrease in the absorbance of peaks at 2853 and 2922 cm^{-1} may be associated with a decrease in the concentration of CH_2 groups pertaining to succinimide rings (Fig.1). This may be explained by a reversal of the Michael addition reaction (13), which is possibly the first step involved in the thermal degradation. The fate of the resultant amine and double bond is masked within the experimental error. It may be speculated that aminolysis of the regenerated bismaleimide ring may take place under these conditions (12).

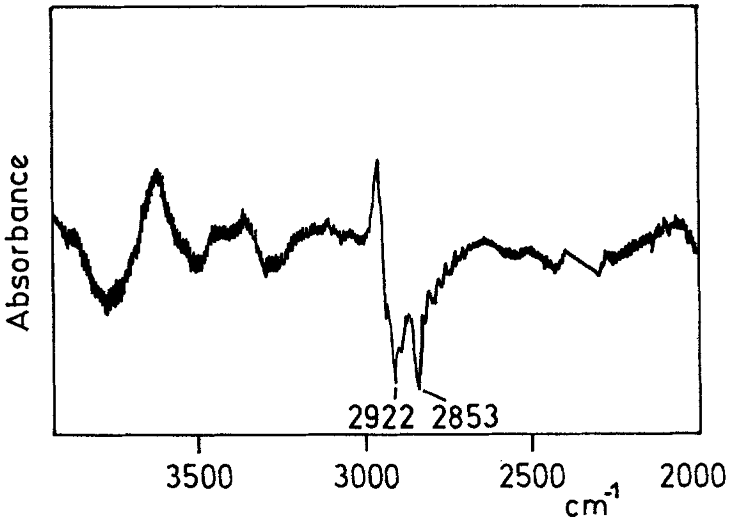


Fig.7 Difference FTIR spectrum for a fully cured sample after a degradation step.

This paper is dedicated to Prof. Eloisa B. Mano (IMA, UFRJ, Brazil) for her pioneering work in the development of the polymer field in Latin America.

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