Analysis of condensation and imidization of norbornene derivatives by ^{1}H NMR analysis effect of processing conditions

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The condensation and imidization reactions of norbornene derivatives have been analysed and the intermediates formed during the course of these reactions are identified. The mechanisms involved and the effect of the processing conditions are discussed.

1. Introduction

Thermosetting polyimide resins, and in particular systems of the polymerization of monomeric reactants (PMR) type such as PMR 15, are in full development because of their excellent thermal stability. These resins are generally obtained by an *in situ* reaction of three monomers, usually in an alcohol-based solvent. These three monomers are 4.4′-methylene dianiline (MDA), 5-alkyl norbornene-endo-2.3 dicarboxylate (NE), 3.3′, 4.4′-dialkyl benzophenone tetracarboxylate (BTDE 3 isomers).

A number of authors have pointed out the effect of the condensation and imidization reactions on the properties of the final material [1–5]. The literature mentions the analysis of condensation and imidization mechanisms mainly on aromatic compounds [6–9]. The scope of the present investigation was to analyse these reactions involving 4.4′-methylene dianiline (MDA) and acid and/or ester structures derived from norbornene (Fig. 1). With this ^{1}H nuclear magnetic resonance (NMR) analysis, attempts were made to confirm the condensation and imidization mechanisms proposed in the literature for aromatic compounds [9]. The effect of the processing conditions on the reaction scheme were studied.

2. Experimental procedure

The products required for this investigation (Aldrich company) were methanol (boiling point 64.7 °C, 99%), ethanol (boiling point 78.5 °C, 98%), isopropanol (boiling point 82.4 °C, 99.5%), 4.4′-methylene dianiline (MDA, melting point 90 °C, 99%); *cis*-5-norbornene-endo-2.3-dicarboxylic anhydride (NA, melting point 166 °C, 97%); *cis*-5-norbornene-endo-2.3-dicarboxylic anhydride (NA, melting point 166 °C, 97%); and *trans*-3.6-endomethylene-1.2,3.6-tetrahydrophtaloyl chloride (97%).

The monoesters of NA (NE) were synthesized by reflux in agitated alcohol for 2 h. The solvent was removed under vacuum. The products were then washed with petroleum ether. The diesters of NA (N(2 + ε)) were obtained in an acid medium and purified in a column of hexane and ether oxide (65/35) solvent. The NA diacid (N2A) was obtained by hydrolysis in a mixture of water and acetone.

The diacid (N2A*trans*) and diester (N(2 + ε)*trans*) of the *trans*-3.6-endomethylene-1.2,3.6-tetrahydrophtaloyl chloride were obtained by hydrolysis at 20 °C, in water–acetone and ethanol–acetone mixtures, respectively. The crystallized products were washed abundantly in water or ethanol and then vacuum-dried.

The "high-resolution" ^{1}H NMR spectra were recorded at atmospheric temperature on a Bruker AM 300 spectrometer with a Fourier transform attachment. The magnetic flux density was 7.05 T (proton Larmor frequency 300 MHz), pulse angle 90° (11.8 μs). The resolution was 0.256 Hz/point. The chemical shifts are given with respect to the solvent, dimethyl sulfoxide (DMSO) d_6, taken at 2.50 p.p.m.

3. Results and discussion

3.1. Identification of the reaction scheme

We used ^{1}H NMR to analyse the condensation–imidization reactions of different (2 +ε) NE/1MDA systems (methyl, ethyl, isopropyl) *in situ*, in solution in DMSO solvent, at a constant temperature of 100 °C. An acid-ester (NE) excess is desirable in order to avoid the secondary reactions of the amine on the amide-acid functions. DMSO was chosen as solvent in order to be able to analyse the reactions at high temperatures and avoid the esterification reactions of the amide–acid intermediates.

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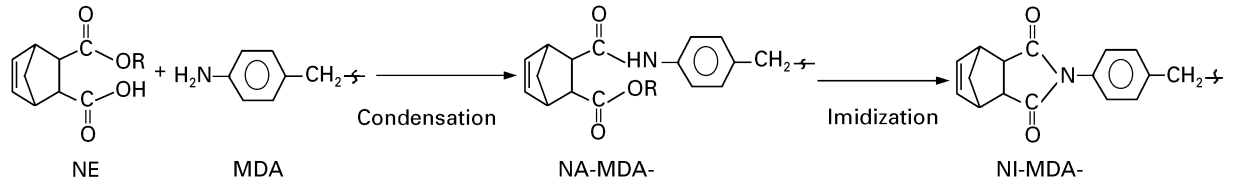

Figure 1 Condensation and imidization reaction in the case of norbornene structures.

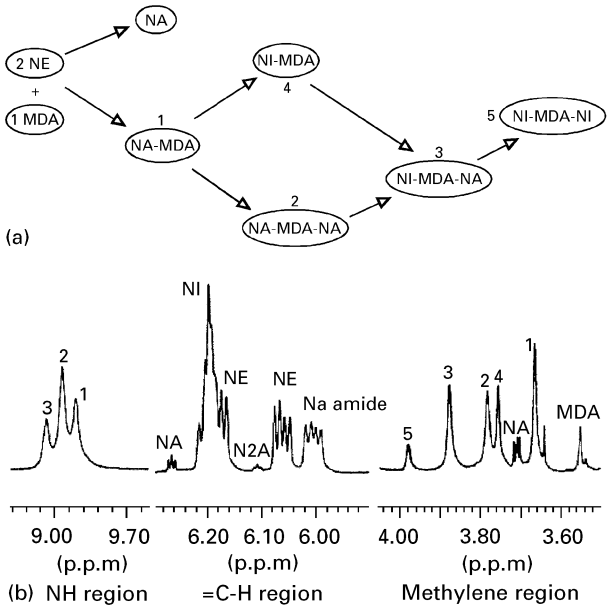

Figure 2 Condensation–imidization reaction. (a) Global reaction scheme. (b) Sensitive regions of the ^{1}H NMR spectrum of the 2 NE methyl/1 MDA system, 1600 min at 100 °C.

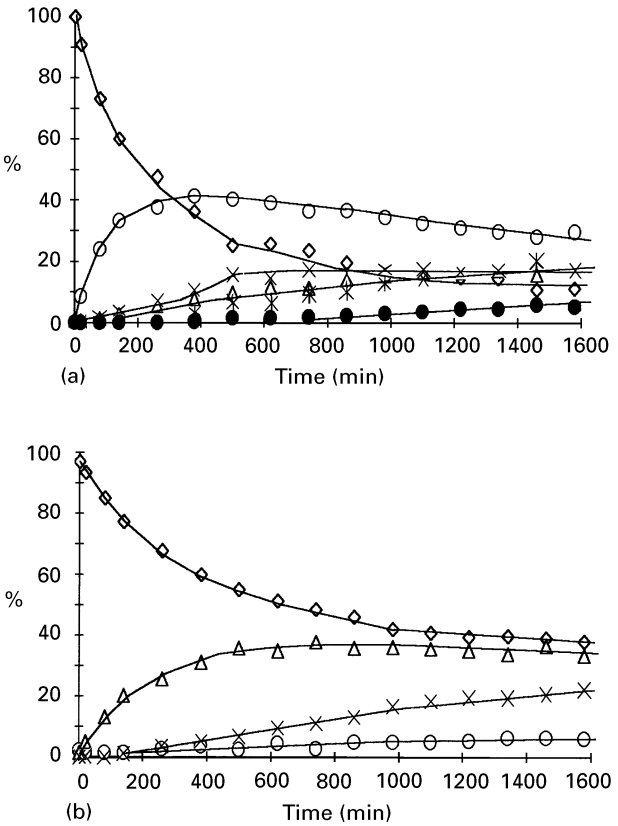

Figure 3 History of the methyl (2 +ε) NE/1 MDA systems at 100 °C in DMSO. (a) Analysis of the methylenic proton region (3.5–4.2 p.p.m). (◇) MDA, (○) NA-MDA, (△) NI-MDA, (×) NA-MDA-NA, (∗) NI-MDA-NA, (●) NI-MDA-NI. (b) Analysis of the ethylenic proton region (7–6 p.p.m). (◇) NE ester, (○) NA anhydride, (△) NA amide, (×) NI imide.

The overall reaction scheme is given in Fig. 2. It was possible to identify the structures formed by ^{1}H NMR at the level of the ethylenic and methylenic protons [5]. The reaction scheme is independent of the type of ester used. That is, we were able to detect the formation of reaction intermediates carrying anhydride functions or amide–acid functions, regardless of the NE ester used. On the other hand, the ester considerably modifies the reactivity (see Fig. 5. later). Fig. 3 groups together the phenomena observed during the course of the kinetics at 100 °C (e.g. 2 NE methyl/1 MDA).

3.2. Condensation reaction mechanisms: formulation of the amide–acid intermediate

It may be surprising, when looking at the high reactivity of NA compared with the amine, given at low temperature [9], that it is possible to detect anhydride functions at 100 °C. The negligible quantity of anhydride observed during the course of the isothermal analysis at 100 °C cannot be due to the hydrolysis of the ester functions or the amide functions, by the water generated in the simultaneous imidization. It must be determined if the anhydride formed comes from the reaction mechanisms, as was proposed by Johnston *et al.* [9] on aromatic compounds. Moreover, the fact that the reactivity changes as a function of the ester grouping prevents us from deciding in favour of one of the two possible mechanisms (Fig. 4), which are (i) either a nucleophilic substitution of the function by the amine (process 1), (ii) or a nucleophilic substitution of the ester function of the carboxylate ion, with the formation of an anhydride function (process 2). That is, in both cases, the inductive effect, +I, of the alkyl groups, and the modification of the carboxylic function acidity by steric hindrance, are compatible with a modification of the reactivity, depending on the NE ester used.

The phenomena involved can be better understood by studying the amidization reactions described in Fig. 5, which also shows the relative variation of the systems (MDA here). In the diagram we can see that only the *cis*-ester acid (NE) and *cis*-diacid (N2A) configurations react with the diamine under these

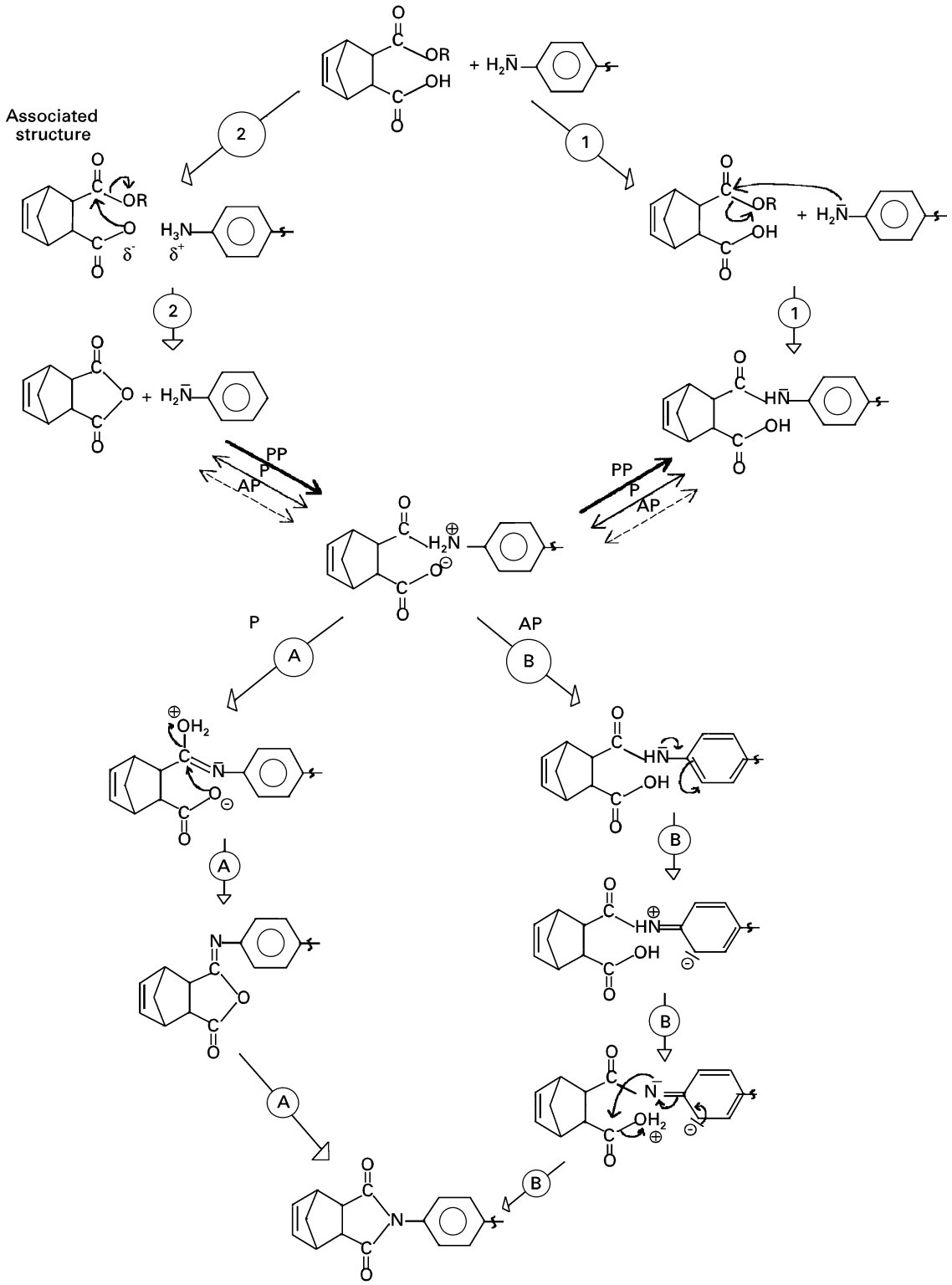

Figure 4 Presumed mechanisms for the condensation imidization reactions for norbornene structures. PP, protonic polar; P, polar; AP, apolar.

processing conditions. Because the *trans* structures (N(2 +ε)*trans* and N2A*trans*) cannot form anhydride, they give rise to no reaction with the diamine. In the same way, the *ortho*-diester compound (N(2 +ε)) does not react with the diamine. The mechanism, therefore, does not involve a nucleophilic substitution of the ester function (process 1).

These observations show that the production of amide–acid structures from ester–acid compounds necessarily implies the formation of an anhydride intermediate, on which the kinetics depend. It can be said that the reaction of such an *ortho*-ester–acid grouping with respect to the amine depends only on the aptitude of these groups to dehydrate, i.e. on the electrophilic character of the ester function and on the nucleophilic character of the carboxylic function. For this reason, the reactivity is predictable by ^{13}C NMR, using the chemical shift of the ester carbonyl. This was also confirmed by Ando *et al.* [10] on aromatic compounds.

The amine would contribute strongly to the dehydration of the acid–ester by "doping" of the

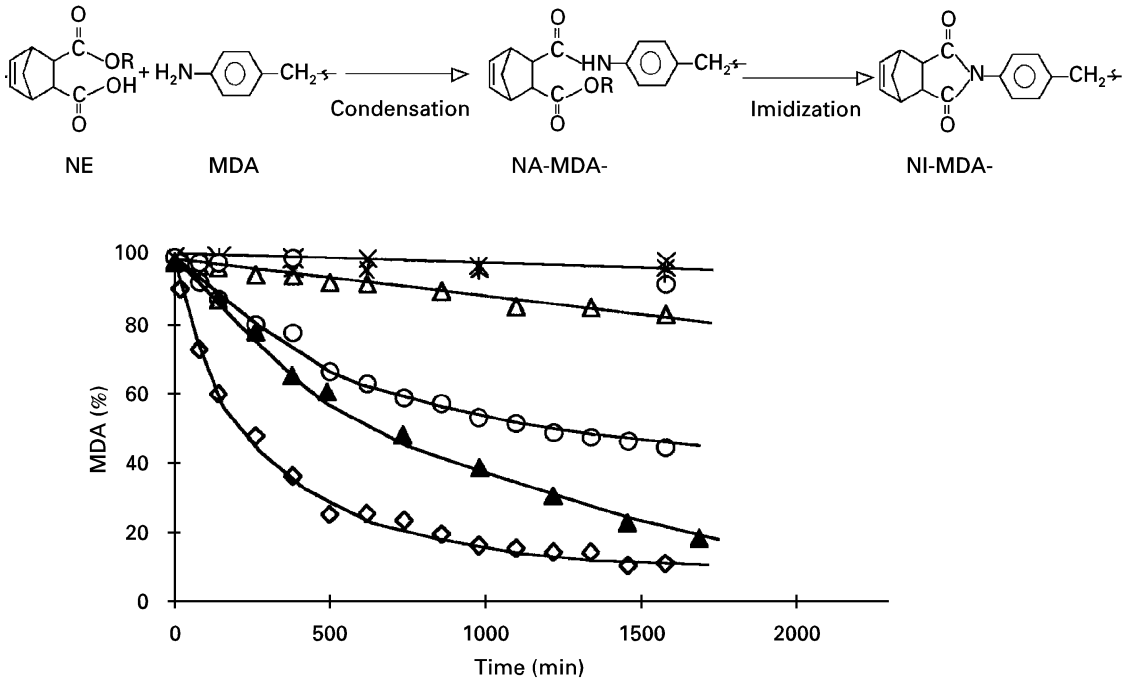

Figure 5 Condensation reactions of derivative structures of norbornene at 100 °C in DMSO. History of MDA (band at 3.55p.p.m). Systems: (◇) NE meth., (○) NE eth., (△) NE isop., (×) N2ETH., (∗) N2E*trans*, (●) N2Atrans, (▲) N2A.

nucleophilic character of the carboxylic function, after a basic attack of it, leading to the formation of an associated structure (Fig. 5). The formation of this structure is then very much dependent on the processing conditions, and would be compatible with the mechanisms proposed by Johnston *et al.* [9].

3.3. Imidization reaction mechanisms

The dehydration leading to the formation of imide functions is performed starting with structures exhibiting the particular feature of having an amine and acid group in the *ortho* position. It may rightly be assumed that electron interactions occur between these two groups participating in the imidization mechanisms. Furthermore, the processing conditions affect the formation of the acetone and enol mesomeric forms of the amine function [11, 12]. Depending on which mesomer form is more stable, two mechanisms are possible, using the competition of the nucleophilic character of the carboxylic function (process A) and of the amide function (process B, Fig. 4).

Mechanism A is favoured by a polar medium, which in this case leads simultaneously to the formation of a structure containing a carboxylic function and an enolized amide function, for which the electrophilic character of the carbonyl is relatively weak (it is known that this mesomer of the amide function is possible in a polar medium [11]).

Mechanism B is favoured by a slightly polar medium. Under these conditions, the conformation of the amide function allows, by its mesomer character, +E, the delocalization of the nitrogen doublet with the aromatic cycle. In this case, this has the effect of activating the electrophilic character of the carbonyl of the amide function. It is remarked, on the whole, that the association is stabilized by the proximity of the aromatic cycle.

Some information concerning the probable mechanism can be obtained by studying the dehydration reactions under several processing conditions. To do so, we compare the reactions occurring in a methyl (2 +ε) NI/1 MDA system, either by solvent process (toluene, DMSO, butanol/DMSO) or by condensate process at 100 °C.

It is seen that the reaction scheme varies considerably depending on the conditions. By increasing order of reactivity, the processing conditions are [DMSO] > [butanol/DMSO] > [toluene] > [condensate system] (see Fig. 6). The imide production is maximum for systems by condensate process and in toluene (Fig. 7). The formation of amide functions is observed mainly in the systems dissolved in the butanol/DMSO mixture or in DMSO. The formation of the NA-MDA-NA oligomer is observed only in the system dissolved in DMSO (Fig. 8). For this reason, mechanism B seems to be the most consistent with the processing conditions.

Two reactions should be considered in explaining why the reaction scheme changes with the processing conditions.

(i) The condensation reaction of the reaction intermediate NA (nadic anhydride) on the diamine MDA. This reaction is balanced, and is favoured by a proton medium [5]. Experimentally, we were not able to observe the formation of the nadic anhydride in the proton system (butanol/DMSO). This further explains the rapid disappearance of the diamine in this system, compared with a polar system (DMSO). Owing to the displacement of this equilibrium, imide production starting with this system is relatively favoured.

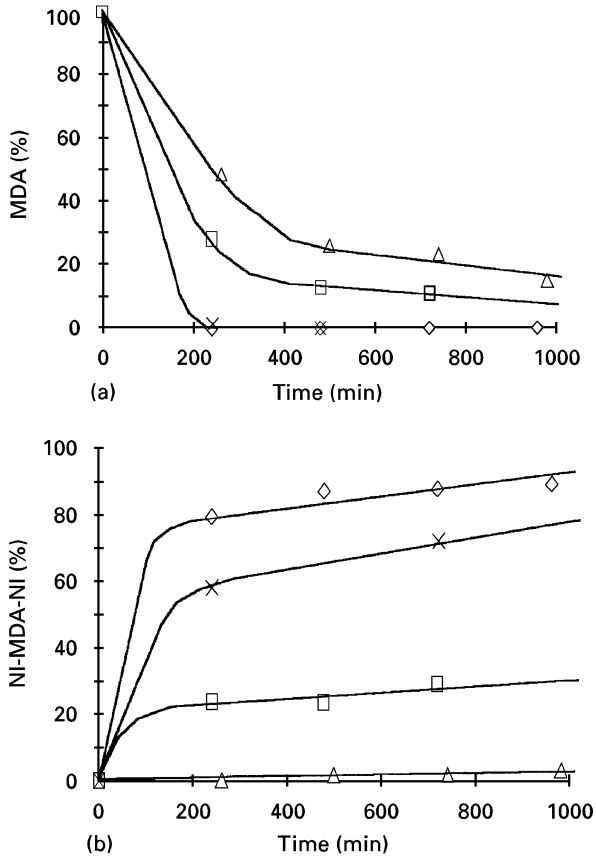

Figure 6 History of (a) MDA and (b) NI-MDA-NI according to processing conditions (^{1}H NMR, methylene region). (◇) Solid, (□) butanol/DMSO, (△) DMSO, (×) toluene.

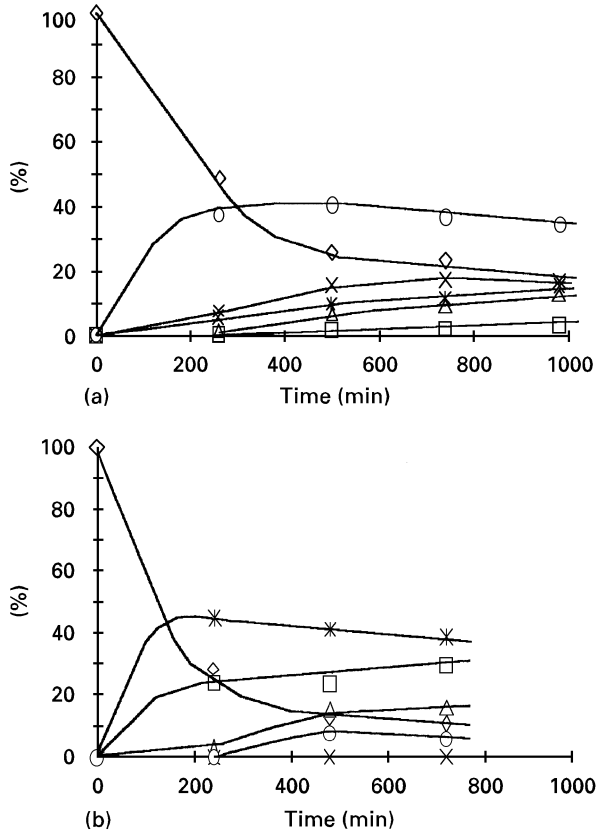

Figure 8 History of the (2 +ε) NE/1 MDA system in solution in (a) DMSO and (b) a butanol/DMSO mixture at 100 °C (^{1}H NMR, methylene region). For key, see Fig. 7.

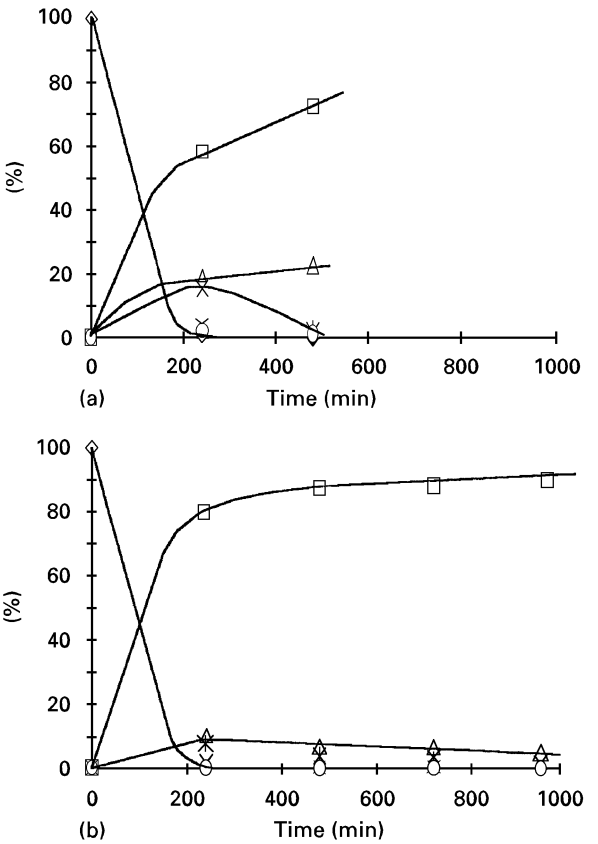

Figure 7 History of the (2 +ε) NE/1 MDA system in solution in (a) toluene and (b) the condensation process at 100 °C (^{1}H NMR, methylene region). (◇) MDA, (□) NI-MDA-NI, (△) NI-MDA-NA, (×) NA-MDA-NA, (∗) NI-MDA, (○) NA-MDA.

(ii) The imidization reaction. This reaction is favoured by a slightly polar medium and by condensate process. For the system in toluene, it may be surprising to observe such an advancement of the reactions, because the first equilibrium is disfavoured in this medium. Just one alternative way of explaining such a reactivity of this system consists in imagining a dehydration reaction activated by an apolar medium. This activation of the dehydration has the effect of displacing the equilibrium, thereby conferring an enhanced global reactivity to the system. In practice, in such a medium, the formation of amide functions is negligible.

In addition to the considerations of viscosity and dilution, the condensate process system seems to offer the ideal compromise, because the advance of the reactions is large. In this particular case, it might be thought that the condensation reaction is activated by the interaction of the ester–acid with the amide, and also that the intermediate is not stabilized by the dissolution effects. Moreover, the association of the amide proton with the carboxylic function is a widely known phenomenon in the condensate process, and might be one explanation for the differences in reactivity with the liquid (e.g. toluene) and solid processes.

It might be pointed out that, whatever mechanism is considered, the hypothetical isoimide intermediate always results from a nucleophilic attack by the carboxylic function, while the imide comes from a nucleophilic attack by the nitrogen doublet. This means that, whatever the reaction medium, the doublet of the

amide function is more nucleophilic than in the case of the carboxylic function. The mobility of this doublet, depending on the structure and processing conditions, therefore turns out to be a major parameter in the reactivity. This is in agreement with the works of Dickinson and Sung [13], who correlated the electron charge of the nitrogen with the stability of the bonds. The formation of isoimide functions was never observed during the course of the experimental analysis of the systems.

4. Conclusion

The condensation and imidization mechanisms are difficult to dissociate from each other. It can be said that the processing conditions greatly influence the kinetics, which gives rise to systems of variable reactivity. The maximum advancement is observed for reactions in the condensate process and in a slightly polar system.

The condensation reaction is favoured by a proton medium, while the imidization reaction is activated by any localizer effect of the doublet on the nitrogen (e.g. a slightly polar medium).

The condensation mechanisms bring an anhydride intermediate into play by prior dehydration of the acid–ester. Amidization occurs at the same time, by nuleophilic attack of the amine on the anhydride function. This reaction is an equilibrium that depends on the processing conditions.

The imidization mechanisms use a complex with the adjacent aromatic nucleus, which favours the nucleophilic attack of the doublet on the carboxylic function.

It is not certain if the isoimide compound (not observed) is a reaction intermediate, but rather a product of a parallel mechanism involving, in all cases, a nucleophilic attack of the carboxylic function on the amide function.

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