

## Effect of Amine Compounds on the Self-Polymerisation of Methyl Methacrylate

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This work is the result of the experimental analysis of the effect of different alkyl anilines (accelerators) on the self-polymerisation of methyl methacrylate. The state of the art before this study suggested that there should have been no significant increase in the rate of polymerisation reaction until the initiator (typically a peroxide) is added to the stabilised mixture of monomer and accelerator. All the experimental results found during this investigation indicated instead that the accelerators can affect the rate of polymerisation even if no peroxide is present in the system. Different kinds of alkyl anilines in methyl methacrylate have been tested by differential scanning calorimetry and adiabatic calorimetry. The experimental data allowed us to define safety ranges for the polymerisation reaction.

### 1. Motivations

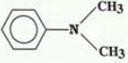
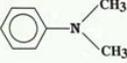
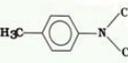
In the past, some accidents caused by runaway have occurred in polymerization plants (Nolan & Burton 1987). From an analysis of case histories, the development of incidents, in many cases, is found to be due to a lack of understanding of the process chemistry and thermodynamics and poor reactor design (Feliu et al. 1996). A recent analysis of ARIA Data Bank (French Ministry of Ecology Energy Sustainable Development 2001) showed that between 2005 and 2010 352 incidents involved sites of polymer production and manufacturing of plastic materials and resins. The incidents happened in either process, transport or storage operations, and caused fires and explosions. This study is itself based on the results from an investigation of an incident occurred in UK in 2009, when an explosion, followed by a fire, destroyed a resins manufacturing site. The polymerization of methyl methacrylate (MMA) represents a typical example of a diffusion controlled process. Reaction diffusion is of primary importance for termination at moderate and high conversion, which leads to fairly simple expressions for kinetic parameters even at conversions where the solution viscosity exceeds the initial monomer viscosity by several orders of magnitude (Soh and Sundberg 1982)(Louie et al. 1985). Diffusion control of the propagation rate becomes important at very high conversion where also the mobility of the monomer units decreases owing to the onset of the glass effect (Maschio and Moutier 1989): this phenomena produces a strong self-acceleration in rate that can generate a hazardous situation. Loss of temperature control is one of the major reasons that can lead to thermal runaway in chemical reactors carrying out exothermic reaction such as polymerisation (Copelli, Torretta, et al. 2013; Copelli, Dente, et al. 2013; Copelli, Storti, et al. 2013). In order to prevent the onset of runaway the knowledge of kinetic and the effect of diffusion control of the process are necessary (Ampelli et al. 2006). In the formulation of acrylic coatings, the use of accelerators allows the application of the coating at ambient temperature. Accelerators are designed to increase the rate of polymerisation by promoting the decomposition of the initiator employed (typically a peroxide) to initiate the polymerisation processes *at room temperature*. MMA is usually supplied with the addition of a chemical stabiliser (p-methoxy phenol, MeHQ) which inhibits the polymerisation of the monomer provided that oxygen is present (Schulze and Vogel 1998). Nising et al. (Nising et al. 2005) showed that MMA radical can react with oxygen to form peroxides which are stable below 100 °C,

concluding that even at ambient temperatures and with stabilized monomer, the formation of MMA peroxides takes place, leading to small quantities of peroxide species that can significantly influence the reaction kinetics. This peroxides present in the system could act as initiators in presence of accelerators, leading to undesired polymerisation reactions. With respect to the incident investigation itself, this study was aimed at more general conclusions about the effect of the accelerators on MMA polymerisation, so the analysis of samples containing different concentrations of various types of commercially available accelerators is proposed.

## 2. Experimental Investigation

The results discussed in this paper are based on data obtained by in Differential Scanning Calorimetry (DSC) and Adiabatic Calorimetry (ARC) (HarsNet 2002). The integrated use of calorimetry in polymerization of MMA is described in (Maschio et al. 1999). The different alkyl anilines tested (and shown in Table 1) were chosen on the basis of real industrial applications (CYTEC 2010). The monomer used for the experiment was commercially available (Sigma Aldrich pure 99% contains < 30 ppm of MeHQ as inhibitor).

Table 1: Characteristic and properties of the alkyl anilines tested.

Chemical	N,N-dimethylaniline DMA	N,N-diethylaniline DEA	N,N-dimethyl-para-toluidine DMPT
			
Cas. No.	121-69-7	91-66-7	99-97-8

For the DSC tests the mass of the sample was approximately 3 mg (~ 50 % of the total volume of the sample holder – i. e. 60 µL). Medium pressure stainless steel crucible sealed with Viton O-rings were used (maximum pressure allowed is 2 MPa and maximum temperature is 250 °C). The results obtained from DSC allowed us to define a critical concentration for each accelerator in MMA (corresponding to the maximum heat evolved) so a more detailed calorimetric analysis could then be performed on them in the ARC (heat-wait-and search mode). Adiabatic calorimetry simulates to certain extent the worst case scenario for the reaction, allowing the determining of a more accurate onset temperature, the adiabatic temperature rise and the Time to Maximum Rate. In the ARC, 1/8" stainless steel bombs were used and the mass of sample analysed was ~ 5 g. The main objective of the adiabatic experiments was to evaluate the influence of the diffusion controlled regime on the extent of the polymerisation. The maximum conversion achievable in the system is an important parameter in order to estimate the free monomer that could evaporate as a consequence of the overheating of the system.

## 3. Results and discussion

This part of the study focused on the effect of the type and quantity of accelerator added to commercial methyl methacrylate. In the formulation of the batch involved in the incident, the accelerator was the 1 % by weight of the mixture; the companies producing accelerators suggest using them up to 5 % by weight (CYTEC 2010). First of all the effect of the concentration of the accelerator on the polymerisation was investigated: solutions containing 0.5 %, 1 %, 2 %, 5 % and 10 % by weight of different types of accelerator were tested by DSC scanning (25-300°C, heating rate 5°C/min). The main result was that a concentration lower than 2 % by weight increased the heat evolved by the reaction (Figure 1-I). Further tests were therefore performed on the range up to 2 % by weight (Figure 1-II) to identify a critical concentration of each accelerator (the one at which the heat evolved by the reaction is greatest); for all the accelerators tested the critical concentration was found to be 0.75 % by weight.

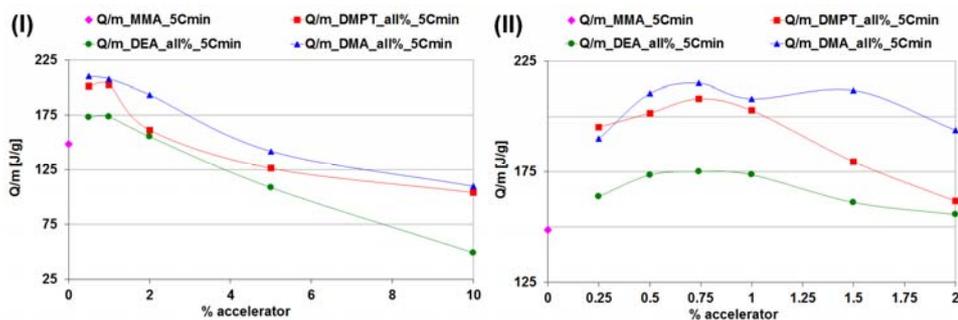


Figure 1: DSC scanning tests (5°C/min) of solutions containing up to 10 % by weight (I) and 2 % by weight (II) of accelerators.

### 3.1 Differential Scanning Calorimetry: Isothermal tests

The isothermal tests at 120°C performed on the same solutions described in the previous section showed that increasing the quantity of accelerator up to 10 % by weight, seemed to cause it to start to behave as an initiator for polymerisation. Figure 2-I shows the comparison of the profiles for DMPT (the other amine accelerators gave similar results): when the concentration of the accelerator is high, the induction period is small and, after the kinetic controlled step of the polymerisation, no self-acceleration due to gel effect occurs. This can be attributed to the effect of accelerator in activating polymerisation: a larger number of lower molecular weight chains causes a lower viscosity in the system (production of oligomers). When lower concentrations of accelerator are used, the results are affected by the gel effect: this increases the final conversion of the reaction (Table 2 and Figure 2-II).

Table 2: Final conversion of isothermal DSC polymerisation (120°C) with different quantities of DMPT.

	MMA	DMPT 0.25 %w/w	DMPT 0.50 %w/w	DMPT 0.75 %w/w	DMPT 1 %w/w	DMPT 5 %w/w	DMPT 10 %w/w
Q/m [J/g]	531.7	532.8	513.80	507.73	459.64	311.03	114.36
Final conversion	97.9 %	98.1 %	94.6 %	93.5 %	84.6 %	57.3 %	21.1 %

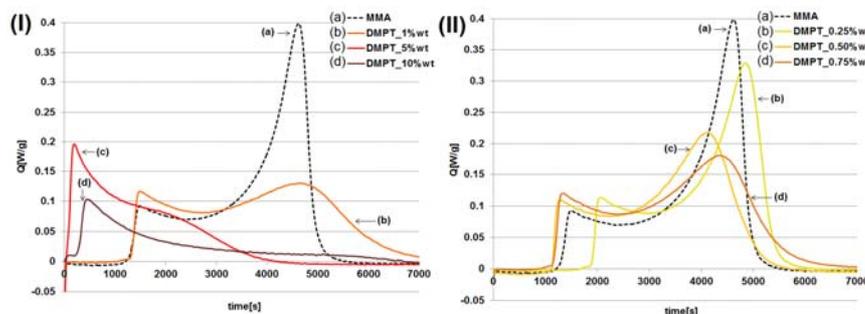


Figure 2:

DSC isothermal tests (120°C) of solutions containing up to 10 % by weight (I) and up to 1 % by weight (II) of DMPT.

In all of the experimental curves reported in Figure 2-II, it is possible to recognize the typical shape of an isothermal polymerisation affected by the gel and glass effects: there is an induction period due to the presence of the inhibitor after which a first order reaction starts. In this step the reaction is controlled by the kinetics. The profile then moves away from this trend: the reaction rate undergoes the self-acceleration caused by the gel effect until a point at which the polymerisation stops (glass point). During the last two steps, the polymerisation is diffusion controlled: in homogeneous bulk polymerisation, with increasing viscosity of the reaction medium, the diffusion of the macro radical and so the termination of the reactive chains are strongly reduced whereas the diffusion of the smaller monomer molecules to the reactive centres at the chain ends continues undisturbed. The reason for this apparent increase in the reaction rate and degree of polymerisation is a drop in termination of polymerisation. On the basis of the results

obtained, tests were performed with 0.75 % by weight solutions of DEA, DMA, DMPT and 1% by weight solution of DIPPT either isothermally (with DSC) or adiabatically (with ARC) in order to study the kinetics of MMA polymerisation in the presence of accelerators. The isothermal experiments for samples with critical concentrations of accelerator were carried out in the 100-140°C temperature range. Figure 3 shows the comparison between the solution of the accelerator and pure MMA for the different isothermal tests in the case of presence of DEA.

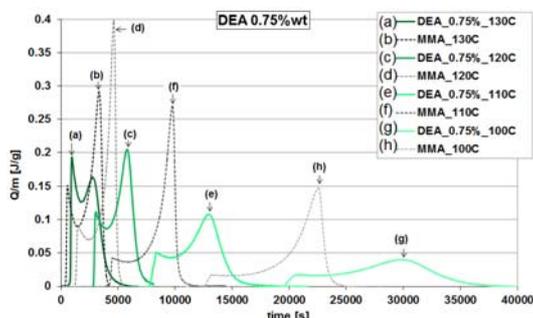


Figure 3: DSC isothermal tests: MMA and 0.75 % by weight DEA solution.

According to experimental data reported in Figure 3, the polymerisation of MMA happens at each successively higher temperature tested with lower induction periods and higher final conversion. In particular, the gel effect seems to be reduced in presence of accelerator. This suggests a possible explanation for the role for DEA as an initiator: its presence activates a larger number of chains compared with MMA alone, so that the viscosity of the system during the process is lower and the gel effect appears smoothed. The first peak (representing the reaction rate for the kinetic controlled step) is greater in presence of accelerator. The profile of the heat evolved by the reaction in the presence of DMA (Figure 4) can be discussed with similar considerations to DEA, with the main difference being that DMA and MMA have nearly the same induction time and final conversion for each test.

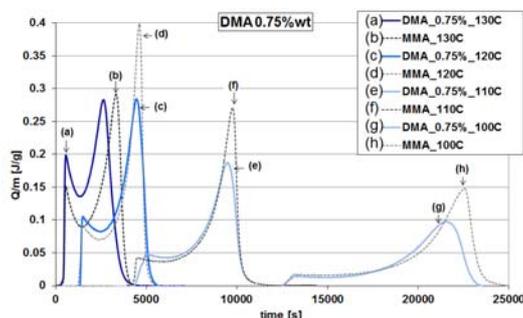


Figure 4: DSC isothermal tests: MMA and 0.75 % by weight DMA solution.

One of the main differences for DMPT compared with previous accelerators is its capacity to reduce drastically the induction time: this is evident in the test carried out at 130°C (Figure 5), for which the polymerisation had already started before the data logging was initiated so that the first peak was not completely recorded. However it is still apparent that most of the polymerisation reaction happens in the kinetic controlled step and that the gel effect is reduced because of the dependence of viscosity on temperature. The first peak of the profile for the solution with accelerator is greater than that of MMA for every test, even if there is a clear dependency of this behaviour on temperature. The value of the final conversion for each experiment is similar to that of the MMA tested alone.

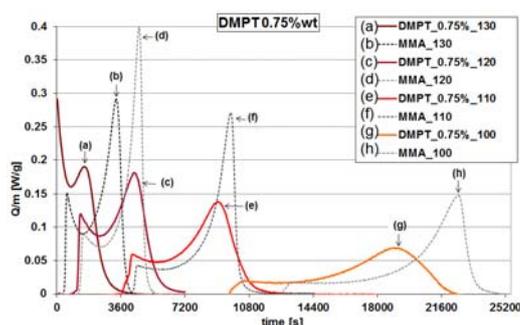


Figure 5: DSC isothermal tests: MMA and 0.75 % by weight DMPT solution.

### 3.2 Adiabatic tests of solutions with critical concentration of accelerators

The same solutions tested isothermally by DSC were also analysed adiabatically by ARC calorimeter, with the aim of studying the influence of diffusion control on the polymerisation reaction. The maximum conversion achievable in adiabatic conditions is an important parameter in order to estimate the quantity of monomer free in the system that could evaporate as a consequence of the runaway reaction. In most of the isothermal tests just described, the final conversion was near to completion, especially at high temperature. The mass of the samples in DSC experiments was approximately 3 mg; under these conditions it is easier to keep the reagent fluid just by the effect of temperature on viscosity. A chemical reactor in which a runaway reaction is occurring is similar to an adiabatic system and, when a polymerisation is going on, the effect of the fluid dynamic should not be neglected. The changes in the viscosity of the system as the reaction progresses have an important effect on the heat transfer coefficient that worsens the heat removal from the reactor to the jacket. As can be seen from Table 3, in which the main data obtained by the adiabatic tests are reported, when adding accelerators the detected onset temperature of the polymerisation decreases: in particular for the case of DMPT it is 36.5°C lower than MMA. The adiabatic temperature rise is, in the majority of cases, increased, apart from with DEA. In every case the final conversion is larger in presence of accelerators, but the maximum value does not go beyond 60 % leading to 40 % of free monomer in the system; in the case of the incident, this would correspond to ~ 1,100 kg. As the temperature rises above the ceiling temperature for the material in all these tests, the reversion of polymer to monomer also limits the final conversion. Another important parameter is the maximum rate of temperature change which increases when accelerator is added to MMA except in the case of DEA. In every case the Time to Maximum Rate is between 45 min and 3 h shorter with respect to MMA, depending on the type of accelerator tested.

Table 3: ARC tests results.

ARC (5°C steps)	$\Delta T_{ad}$ [°C]	Tonset [°C]	TMAX [°C]	(Q/m) <sub>ad</sub> [J/g]	(dT/dt) MAX [°C/min]	TMR [min]	Xf
MMA	153	106.5	188	314	3.1	729	53 %
DMPT 0.75 %	169	70	173	348	5.4	561	61 %
DMA 0.75 %	158	81	176.5	323	4.67	563	60 %
DEA 0.75 %	135	96	177	277	2.96	685	60 %

## Conclusions

The principal aim of this work was to understand the role of a range of accelerators in the polymerisation of methyl methacrylate with no initiator present, on the basis of an investigation of an incident in a resins manufacturing site. The isothermal and adiabatic data support the conclusion that the explosion at the time of the incident was due to the ignition of a large volume of a fuel-air mixture formed from the discharge of flammable vapour from the mixing vessel when the contents became overheated due a runaway exothermic reaction. In most of the isothermal tests, the final conversion was nearly 100 %, increasing at higher temperature. The mass of the samples for those experiments was approximately 3 mg; under these conditions, it is easier to keep the reagent fluid just by the effect of temperature on viscosity. In the case of scanning tests and adiabatic tests carried on in the ARC calorimeter, the maximum conversion reached was 60%. The presence of a ceiling temperature for the monomer could also be an explanation for the lowest final conversion as, after ceiling temperature, the polymer tends to revert to monomer. The adiabatic data showed also substantial reductions in onset temperature associated with the addition of

accelerators and this effect, along with the observation of increased self-heat rates, is likely to lead to substantial reductions in the safe process temperature. The adiabatic tests confirm the presence of the ceiling temperature and the thermal polymerization of MMA in the presence of accelerators. The isothermal tests showed the typical shape of a polymerisation affected by the gel effect. The diffusion controlled step was smoothed in presence of accelerators but, on the other hand, the rate of the kinetic controlled step and total heat output were increased when accelerators were added to the monomer. The presence of the accelerators decreased the induction time. A further development of this work will be the building of an ad hoc detailed kinetic model to account for the effects of accelerators in all the stages of MMA polymerisation.

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