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On the Hazard Investigation of Polymerizing Substances through Experimental Methods and Theoretical Chemistry

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Polymerizing substances can undergo strongly exothermic reactions under specific conditions such as transport. For this reason, they are considered under specific classification and safety recommendations. But their classification is mainly based on criteria initially intended for self-reactive substances and organic peroxides. So, considering their specific reactivity mechanisms, adaptations of the test methods and classification criteria could be needed and proposed.

In this context, Ineris engaged efforts to evaluate the possible limits of experimental methods and the potential of theoretical chemistry tools to investigate the hazards and reaction mechanisms associated to polymerizing substances and to their self-polymerization.

1. Introduction

Among the chemical reactions involved in industrial accidents, uncontrolled polymerizations of substances like unsaturated hydrocarbons (ethylene, propylene, styrene, butadiene, etc.) and unsaturated nitriles (acrylonitrile, etc.) are found. In particular, accidentology highlights cases of polymerization runaway during the use of such substances in chemical industrial processes or their transport in tankers. (BARPI, 2021)

For a long time, these substances were not specifically classified in regulations. Since only 2013, these materials are classified as "Polymerizing substances and mixtures (stabilized)" of Division 4.1 (with generic UN numbers 3531 to 3534) for the Transport of Dangerous Goods (TDG) (United Nations, 2019b) but they are not yet recognized in other regulations, such as the GHS (Globally Harmonized System of Classification and Labelling of Chemicals) (United Nations, 2019a) or the European CLP (Classification, Labelling and Packaging) (2008).

Defined as substances which, without stabilization, are likely to undergo a strongly exothermic reaction leading to the formation of larger molecules or to the formation of polymers under specific conditions such as transport, their classification is based on several criteria initially intended for self-reactive substances and organic peroxides. However, these materials have specific reactivity mechanisms and adaptations of the tests and classification criteria may be necessary.

After a summary of the accidentology, the regulatory framework applied to polymerizing substances is discussed with an analysis of the testing methods used in existing classification schemes. Their adequacy and practical drawbacks when characterizing the properties of polymerizing substances were analyzed. The completeness of the classification testing procedure was also criticized regarding the specificities of polymerizing substances and notably the efficiency of stabilizers and the prescription and sizing of decompression devices on packaging. At last, the use of quantum chemical methods for the theoretical study of self-polymerization mechanisms was investigated with the toluene and its derivatives as a reference case study.

2. Accidentology

The ARIA (Analysis, Research and Information on Accidents) database (BARPI, 2021), supported by the French Ministry in charge of the Environment, catalogues 85 accidents caused by or involving self-polymerizing substances between 1962 and 2019. 65 of them took place in France and 20 abroad. The distribution of the number of accidents per ten-year period is shown in Table 1 and demonstrates their stable occurrence over the last three decades.

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Table 1: Distribution of number accidents by ten-year period

Period	Number of accidents
1960-1969	1
1970-1979	1
1980-1989	7
1990-1999	26
2000-2009	30
2010-2019	20

Due to the multiple applications of polymerizing substances, accidents/incidents affect many economic areas like rubber and plastic manufacturing, chemical industry, textile manufacturing, transport or waste treatment.

The accident causes found in these 85 accidents were proposed as related to:

- Material failures,
- Process control defaults leading to polymerization,
- Containers without decompression devices or not checked,
- Loss of stabilizer,
- Presence of contaminants,
- Handling and traffic accidents,
- Causes directly involving the organizational or human factor,
- External causes.

The consequences of these events are very diverse from one accident to another, depending on its context and situation. They are often associated to increases in temperature and pressure, which can lead to fires, mechanical breakages and releases of products. The products released by these accidental polymerization events are often toxic and, depending on the quantities, can affect the company's staff as well as surrounding local residents.

An example of event with significant consequences is an accident occurred in Himeji (Japan) on September 30th 2012. The explosion of a tank containing acrylic acid was followed by a fire in a chemical plant resulting in 37 deaths, 5 seriously injured and 31 slightly injured people. From an economic point of view, the production losses and damages were estimated at 450 M€ and 15 M€, respectively.

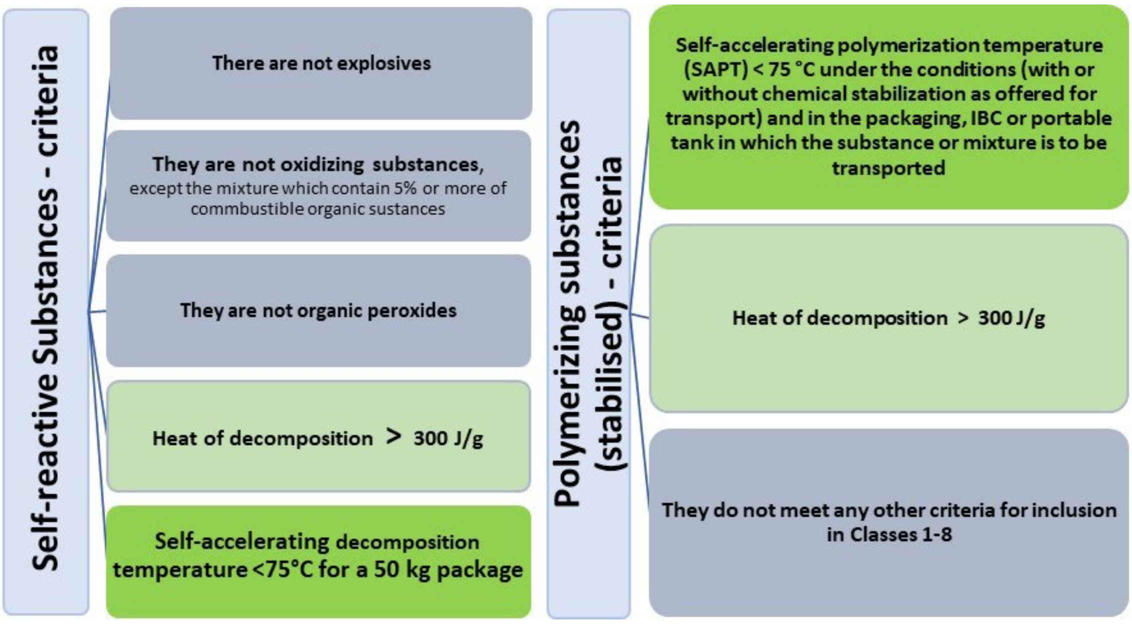


Figure 1: Flow chart for classification of self-reactive and polymerizing substances

3. Critical analysis of testing methods to classify polymerizing materials

To be classified as "Polymerizing substances and mixtures (stabilized)" of Division 4.1 (with generic UN numbers 3531 to 3534) for the TDG, a substance must meet the criteria detailed in the flowchart presented in Figure 1. In case where the substance presents hazards of classes 1 to 8, it will be classified according to those hazards which are predominant but with the word "STABILIZED" in the proper shipping name to indicate the risk of polymerization.

Polymerizing substances are distinguished from self-reactive ones by the knowledge of their subjacent mechanisms (polymerization rather than decomposition). Otherwise, as the classification criteria are very similar to those for self-reactive substances, a polymerizing substance could be classified as self-reactive.

Indeed, the classification of polymerizing substances is based on test results recommended in the UN Manual of Tests and Criteria, developed for organic peroxides and self-reactive substances, which are subject to decomposition rather than polymerization. These tests are listed in Table 2.

However, due to the specific behaviors of polymerizing substances, some difficulties may be encountered in their experimental implementation. For instance, the tests using single-use containers (UN H.1, UN H.3 and DSC) do not pose any problem with sample “solidification” during polymerization whereas, this is not the case for UN H.2 and H.4 tests, which use a fragile apparatus (Dewar vessel) that can be impossible to clean after the tests. For these lasts, alternative tests would deserve to be proposed and validated.

Table 2: UN test methods used for the classification of polymerizing substances

Heat of reaction	DSC calorimeter tests	
	Test Code	Name of test
Self-Accelerated Polymerization Temperature (SAPT)	UN Test H.1	United States SADT test,
	UN Test H.2	Adiabatic storage test (AST)
	UN Test H.3	Isothermal Storage Test (IST)
	UN Test H.4	Heat accumulation storage test

Then, Model Regulation requires substances with a polymerization hazard (even those with additional hazards of classes 1 to 8) to be transported in specific packaging with different requirements depending on whether the substances are in solid or liquid form. Among these requirements, two parameters would require further analyzes:

- **Check the effectiveness of the stabilizer to avoid uncontrolled polymerization during transport.**
  It depends on different factors and in particular on the type of stabilizer (e.g. thermal stabilizers, antioxidants). It also requires the consideration of criteria representative of the conditions of transport, whatever the mode used (road, rail, sea and air transport), including its duration and the climatic conditions.

- **Check that the packaging is designed to allow gases/vapors releases in order to avoid overpressure or if it needs a pressure relief device and size it.**
  Upon their specific reaction mechanisms, polymerizing substances may release a certain amount of gas with a flow rate depending on the substance. So, it could be important to check that, in case of polymerization, the pressure relief devices are correctly sized to avoid mechanical rupture.

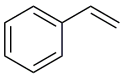
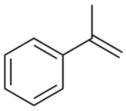
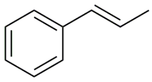
Unfortunately, no specific regulatory tests are nowadays implemented to guide the verification of these two safety points for polymerizing substances.

4. Theoretical study of self-polymerization reactions

Knowledge of reaction mechanisms (decomposition or polymerization) is a key information to well classify the substances as polymerizing or not (for instance as self-reactive). As a complement to experimental testing, quantum chemical methods have been successfully used to evidence the subjacent mechanisms of other hazardous reactions (like peroxidation (Di Tommaso et al., 2011) or chemical incompatibilities (Cagnina et al., 2014; Menicacci et al., 2020). So, works were engaged towards their use for the theoretical study of possible self-polymerization of these materials with the toluene and its derivatives as a reference case study (Fayet and Rotureau, 2022).

Indeed, calorimetric data are available for the toluene, α-methylstyrene (AMS) and *trans-β*-methylstyrene (TBMS) demonstrating a thermal polymerization at an onset temperature of 103°C for toluene (with a heat of reaction ΔH of 602 J/g) compared to more than 350°C for both AMS and TBMS (with $\Delta H < 280$ J/g) by differential scanning calorimetry at a 4°C/min temperature rate, as shown in Table 3 (Lin et al., 2008). It should be noticed that, for AMS and TBMS, a first exothermic pic of low heat (proposed as associated to a dimerization process) is observed prior to polymerization, at lower temperature.

Table 3: Experimental onset and peak temperatures (T_o and T_p) and heat of reaction ΔH obtained from the DSC tests (Lin et al., 2008)

	Styrene	AMS	TBMS
			
T_o (°C)	103.3	136.5 356.3	74.6 385.4
T_p (°C)	205.8	140.5 402.9	97.6 415.6
ΔH (J/g)	601.7	17.6 266.3	29.8 277.3

At first, the detailed reaction mechanisms involved in the self-polymerization of toluene were theoretically investigated by use of the density functional theory (DFT). These mechanisms were already investigated in literature using the B3LYP/6-31G* and BPW91/6-31G* methods (Khuong et al., 2005) but this study presented some failures. In particular, the calculated diradical transition state of one main reaction of the mechanism (a Diels-Alder type reaction) was found as presenting unstable wave functions.

For this reason, these mechanisms have been analyzed again using a more recent functional, M05-2X, identified as more relevant for Diels-Alder reactions in benchmark studies (Johnson et al., 2008; Zhao and Truhlar, 2011). Finally, the new theoretical study (at M05-2X / 6-31+G(d,p) level) overcame the limits of the study of Khuong since the corresponding Transition States were found stable.

Moreover, some deviations were found between the new method and the results of Khuong, in agreement with the observations made in the benchmark studies (highlighting an underestimation of reaction exothermicity using B3LYP). However, the global reaction mechanism and relative balance between the different reactions remained the same.

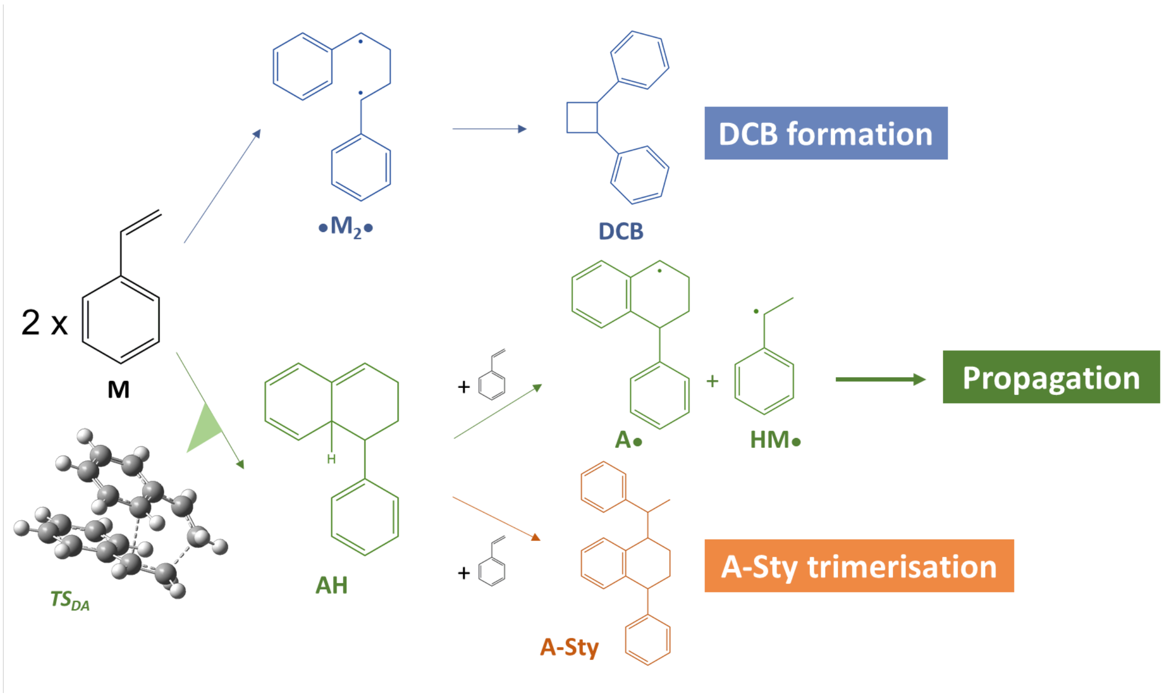


Figure 2: Reaction mechanisms involved and in competition with the initiation of styrene thermal polymerization, as proposed by Khuong (2005)

Figure 2 shows a summary of the main mechanisms involved and in competition with the initiation of a self-polymerization of styrene. This initiation is proposed as based on a Diels-Alder reaction between two styrene monomers M. The diradical transition state associated to this reaction, TS_{DA}, was found as unstable in the study of Khuong.

This reaction leads to the AH dimer intermediate from which two different reactions can occur in contact with another toluene monomer. An ene reaction leading to the 1-phenyl-4-(1'-phenylethyl)-tetralin trimer (A-Sty) or an H-abstraction (Habs) from the AH dimer by the additional toluene monomer to produce the $A^\bullet$ and $HM^\bullet$ radicals from which propagation begins. Another reaction was found in competition with this initiation mechanism in which two toluene monomers form 1,2-diphenyl cyclobutene (DCB) through a diradical intermediate $^\bullet M_2{}^\bullet$.

As shown in Figure 3, the formation of DCB and the Diels-Alder reaction present similar activation energies (associated to their respective transition states TS_1 and TS_{DA}). Then, formation of the monoradicals (responsible for polymerization propagation) is slightly more difficult than trimerization, which agrees with experimental data evidencing an higher production of A-Sty trimers than polymers during the polymerization process (Khuong et al., 2005).

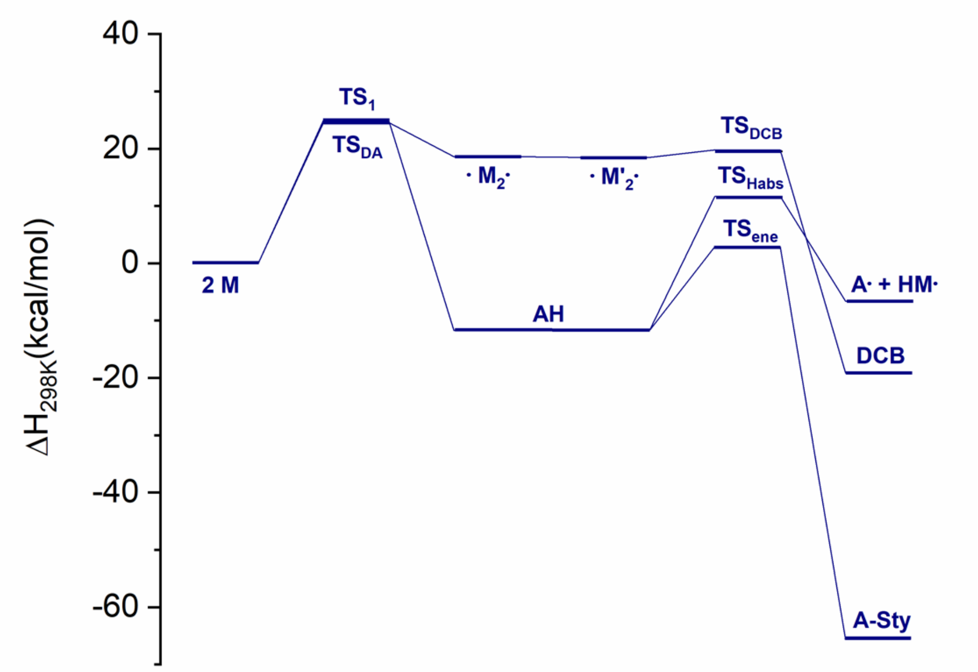


*Figure 3: Energetic profile of the mechanisms involved and in competition with the initiation of styrene thermal polymerization, as calculated at M05-2X/*6-31+G(d,p) level (Fayet and Rotureau, 2022)

The next step of the study now consists in computing these main mechanisms for AMS and TBMS. These calculations are under progress and may help to understand why self-polymerization occurs at higher temperature for these compounds than for styrene despite their similar structures. For instance, the relative activation energies could be influenced making the propagation less favorable compared to the two other mechanisms, or the presence of additional methyl groups in AMS and TBMS could favor other reactions compared to styrene.

5. Conclusions

The new classification framework proposed for the transport of polymerizing materials encourages some adaptations of the testing methods and criteria for their classification. They concern both the feasibility of the testing methods already implemented in the TDG regulation but also additional testing methods to fulfill the requirements of the classification (notably regarding the efficiency of stabilizers and the need and sizing of pressure relief devices).

The use of theoretical chemistry also opens new perspectives towards an in-depth understanding of their thermal self-polymerization mechanisms and a better identification of compounds subject to possible hazardous polymerization issues. These theoretical studies could, for instance, be the basis of development of practical tools complementary to experimental methods, to support the identification of reaction types (e.g. self-polymerization rather than self-decomposition) within the classification process.

Acknowledgments

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