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**UTILISATION DE LA REACTION DE CYCLOADDITION DE HUISGEN AFIN
D'AMELIORER LES PROPRIETES DES POLYMERES FLUORES**

JURY

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A mon épouse,

Avant-propos

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INTRODUCTION GENERALE

INTRODUCTION GENERALE

La chimie des azides et des nitrènes a attiré l'attention des chimistes depuis la découverte de l'azoture de phényle par Griess¹ il y a plus de 100 ans et la première proposition de la formation des nitrènes par Tiemann² en 1891. Pourtant, en dépit des importantes contributions de Bertho³ et de Curtius⁴ entre les deux guerres mondiales, l'intérêt pour ces espèces n'est réellement apparue qu'à partir des années 1960 suite aux articles de Smith⁵ (azoture d'acyle) et Boyer⁶ (azoture d'alkyle et d'aryle) qui ont montré le rôle majeur de ces substances dans le développement de la chimie des hétérocycles azotés.

Une grande variété de précurseurs permet de synthétiser ces composés. Parmi ceux-ci les halogénures d'alkyles, les époxydes, les alcènes et les alcools sont les espèces les plus communément utilisées. Les substances présentant cette fonction azide permettent, par des procédés simples, de préparer des composés impliqués dans la synthèse macromoléculaire tels que les amines ou les isocyanates par réduction ou réarrangement de Curtius. Un deuxième champ d'application très attractif de la réactivité des azides consiste en la formation d'hétérocycles azotés par réactions de cyclisation ou de cycloaddition. En effet, certains de ces cycles notamment les triazolines et les triazoles présentent des stabilités chimiques et thermiques remarquables. Leurs incorporations dans des chaînes macromoléculaires permettent d'améliorer les propriétés thermiques de macromolécules qui en découlent.

Dans ce domaine, Huisgen⁷ a développé la cycloaddition 1,3 dipolaire qui permet d'obtenir des composés contenant un ou plusieurs hétérocycles azotés. Cette réaction a récemment été revisité par Sharpless⁸ qui, en utilisant un système catalytique à base de cuivre, a permis d'optimiser la cycloaddition mettant en jeu un groupe alkyne et un groupe azide. Cette découverte a permis le développement du concept de « click chemistry » qui est très étudié actuellement et qui s'applique à d'autres types de synthèse tels que les thiol-ène par exemple. Dans le domaine de la chimie macromoléculaire, la « click chemistry » est très utilisée comme le montre les nombreuses revues⁹⁻¹³ publiées sur ce sujet dans les dernières années. Cependant, peu d'études de ce type de chimie portant sur les polymères fluorés ont été réalisées¹⁴.

L'objectif de cette thèse concerne l'utilisation de la cycloaddition 1,3 dipolaire organocatalysée ou non afin d'optimiser les propriétés de polymères fluorés. Deux différents types de réaction sont développés, le premier mettant en jeu un azide et un nitrile alors que la seconde utilise un azide et un alcyne.

Dans le premier chapitre, une étude bibliographique a été réalisée sur la réticulation chimique des polymères à température ambiante et à des températures inférieures à 150 °C.

Dans le deuxième chapitre, la réticulation d'élastomères fluorés grâce à la cycloaddition de Huisgen, entre un groupe nitrile et un groupe azidé a été étudiée, après avoir préalablement réalisés plusieurs études modèles. Ces études modèles ont permis d'obtenir des conditions de réactions permettant à la cycloaddition de se produire avec de bons rendements.

Enfin, dans le troisième chapitre, l'utilisation de la « click chemistry » entre les groupes alcynes et azides a été utilisée afin de greffer sur un polymère fluoré à base de chlorotrifluoroéthylène, un composé de type phtalocyanine. Ce greffage a pour but d'obtenir un composé possédant des propriétés photovoltaïques intéressantes.

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CHAPITRE 1

ETUDE BIBLIOGRAPHIQUE

CHEMICAL REACTIONS of POLYMER CROSSLINKING and POST CROSSLINKING at ROOM and MEDIUM TEMPERATURE

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Abstract: This review focuses on various strategies that enable the crosslinking and post-crosslinking of polymers, excluding crosslinking obtained by radiation (e.g., X ray, UV...) and that at high temperature. The review is divided into two main parts: systems enabling crosslinking at room temperature and those for which crosslinking occurs at intermediate temperatures (< 150 °C). In the first part, various key functional groups can be used, such as i) carboxylic acid involving reactions with compounds that bear carbodiimide or aziridine functions; ii) acetoacetyl groups (with isocyanate, activated alkenes, aldehyde, amines functions); iii) reactions involving activated amines with carbonyl functions (aldehydes, ketones...); iv) species bearing acetals as pH-sensitive crosslinking agents since they are stable in basic medium but they can self react under acidic conditions; v) acrylamide functions which are able to self-crosslink; vi) crosslinking agents able to react with water (such as species that bear a poly(alkoxy)silane for sol-gel process) and derivatives containing isocyanate functions and vii) systems that require oxygen, for example polymers bearing double bonds, boranes for generating hydroperoxides and acetylenic functions which undergo acetylenic coupling. The second series of systems, used at temperatures (below 150 °C) involving the following key functions: i) carboxylic acid that react with oxazoline, or epoxide function where specific catalysts are necessary; ii) alcohols reacting with protected urethanes, azlactones and methylol amide (for coating applications); iii) azetidines (obtained from a cyclic amine onto an activated double bond) which self-crosslink; iv) reversible Diels-

Alder reaction (such as furane/bismaleimide reaction), and v) Huisgen reactions between azido and triple bond.

Various examples are presented, along with a discussion of their properties and applications.

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Nomenclature:

AAEM:	acetoacetoxyethyl methacrylate
AA :	acrylic acid
ATRP:	atom transfer radical polymerization
BH:	blocking agent
CHA:	N-cyclohexylazetidine
DBN:	1,5-diazabicyclo(4.3.0)non-5-ene
DBU:	1,8-diazabicyclo(5.4.0)undec-7-ene
EPA:	Environmental Protection Agency
GMA:	glycidyl methacrylate
HEA:	2-hydroxyethyl acrylate
Highlink® AG:	acrylamidoglycolic acid monohydrate
Highlink® DMH:	N-(2,2'-hydroxy-1-dimethoxyethyl)acrylamide
HMM:	hexamethylol melamine
HPBd:	polybutadiene
IBMA:	isobutoxymethylacrylamide
IPDI:	isophorone diisocyanate
MAA:	methacrylic acid
MAAMA:	N-(2,2-dimethoxyethyl)methacrylamide
MAGME:	N-(methoxy methyl acetate) acrylamide
MMA:	methyl methacrylate
NMA:	N-methylolacrylamide
PAEK:	polyaryletherketone
PCL:	polycaprolactone
PDMS:	polydimethyl siloxane
PEO:	polyethylene oxide
PEs:	polyester
PFCB:	perfluorocyclobutane
PHEMA:	polyhydroxyethyl methacrylate
PMDETA:	pentamethyldiethylene triamine
PMMA:	polymethyl methacrylate
PMVE:	perfluoromethyl vinyl ether

PS :	polystyrene
PTFE:	polytetrafluoroethylene
PTMO:	polytetramethylene oxide
PVAc:	polyvinyl acetate
R _F :	perfluoroalkyl
REACH:	Registration, Evaluation, Authorisation and Restriction of Chemicals
TEOS:	tetraethoxysilane
TGIC:	triglycidyl isocyanurate
TMEDA:	Tetramethylethylenediamine
TMG:	tetramethylguanidine
TMI [®] :	m-isopropenyl- α,α -dimethylbenzyl isocyanate
VDF:	vinylidene fluoride

1 – Introduction

Improvement of the thermal, mechanical, physicochemical properties of polymers is a crucial challenge in both synthesis (by the insertion of a key function) and the quest for new search applications. Hence, researchers are in a scientific, economical and environmental context in which both modification and improvement of known polymers are preferred rather than the synthesis of polymers from new monomers. The properties of a polymeric material depend on its chemical nature, but, for a given polymer type, they also depend on their molecular weight and the functions borne by the polymer chain. In addition to the overall properties, the mechanical properties which are regarded as the most important properties of a material are of particular interest. In this context, polymeric materials can be conveniently divided into two main categories, dependent on their molecular weight:

- Those with a molecular weight higher than about 10^5 g.mol $^{-1}$; this value is not a strict limit since it depends on materials and on the intermolecular interactions which occur in these materials;
- Those which have low molecular weights, lower than 10^4 g.mol $^{-1}$, often in the range of 2 to 3.10^3 g.mol $^{-1}$.

According to the category, it is may be essential to carry out either crosslinking or post crosslinking. Indeed, polymer materials in the lower molecular weight range often require a crosslinking step to obtain satisfactory mechanical properties.

It is useful to recall the definitions and differences between crosslinking and post-crosslinking, the main difference arising from the way the material is processed. To obtain a final material in one step, either a very high molecular-weight material or a directly crosslinkable oligomer has to be used to fulfill the targeted properties. The preparation of an easily processed material requires the synthesis of an easily stored material possessing intermediate properties. If the desired performance is not reached, a further step to a post-crosslinking may be required, even though that the first step may have yielded a pre-crosslinked material). These statements concern all materials but they can be especially relevant for coatings since they must be deposited while they have no (or at most a few) crosslinks, to be must crosslink after they have been applied.

Since the fields of applications are various and numerous, crosslinking or post-crosslinking reactions have been intensively studied for a long time, and continue to this date. Studies to tune polymerization and crosslinking have as objectives methods to control when and at which rate both these steps take place, and how they can occur either separately or simultaneously.

Different types of crosslinkings are possible:

- i) covalent crosslinking (which is regarded as the most stable),
- ii) ionic bonds, and
- iii) physical crosslinking (via Van der Waals, hydrogen bonds or other interactions).

One of the most important parameters is, of course, the functionality of the reagents (oligomers and diluents) since crosslinked polymers are usually produced when this functionality is higher than two (even slightly so). Reactive groups are often introduced into the polymeric chains in the case of post-crosslinking. The reactivity and reaction rate of these groups can be controlled by different means:

- i) temperature,
- ii) radiation,
- iii) external reactants (such as moisture, O₂, H₂O...),
- iv) processing.

The objective of this review is to provide basic information to understand the phenomena of crosslinking, without claiming to be exhaustive in that very wide field. The focus is on some basic chemical reactions involving simple reactants, such as water or oxygen, but also some more complex reactants bearing key or specific functions. Various crosslinking and post-crosslinking processes have been excluded, such as those involving radiation, e.g., ultraviolet beams, which are commonly used to harden coatings, (paints, varnishes, etc.), or γ -rays, electron beams, ozone, X rays, etc.; many reviews have already been published on these methods [1-4].

2 – Crosslinking and post-crosslinking

For simplicity, the discussion of crosslinking and post-crosslinking reactions in the following is categorized by types of chemical functions, and discussed successively in two cases, according to the temperature range of the different reactions:

- i) room temperature,
- ii) intermediate temperature below 150 °C.

2.1 – Crosslinking at room temperature

Crosslinking reactions at room temperature are interesting for various reasons, such as network development in a heating-sensitive system or to gain energy savings. Several of these are discussed in the following.

2.1.1 Carboxylic acid

Two main intermediates are considered as crosslinking agents in this type: carbodiimides (the most common used) and aziridines.

2.1.1.1 Carbodiimides [5-18]

The use of carbodiimide as a crosslinker agent has been known since the late 60's [5], though deeper investigations started in 80's [6,7]. The general reaction involves the condensation of a carbodiimide reactant with a carboxylic acid, leading to an acetyl urea, as shown in Fig. 1.

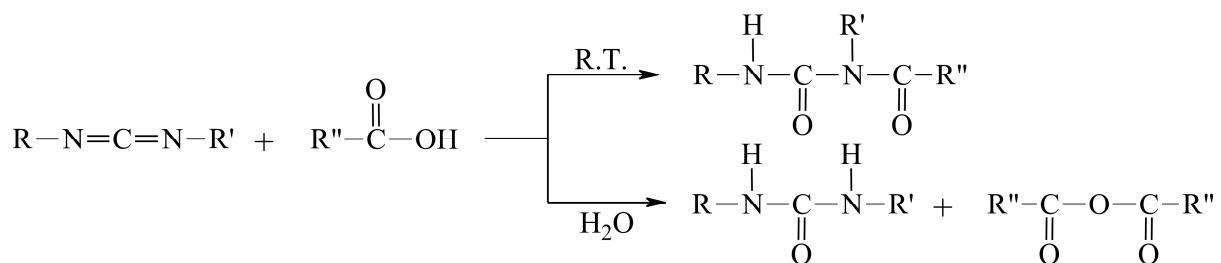


Fig. 1. Formation of acetyl urea compounds by condensation of a carbodiimide with a carboxylic acid and the side reaction in presence of water.

Such a condensation does not require any catalyst and this represents an advantage. However, in the presence of moisture, this reaction also competes with the classic reactivity of

carbodiimides, which are able to trap water and consequently generate anhydride acid and urea, as shown in Fig. 1.

Never the less, by adapting appropriate catalysis and reaction conditions, the reaction is directed towards the synthesis of N-acyl urea. In this way, Taylor and Bassett [8] have shown that the N-acyl urea/anhydride acid ratio increased on increasing the solvent polarity, the temperature, or even pouring a base into the reaction mixture. Moreover, their studies also reported that above 150 °C, N-acyl urea structure is not stable and this limits their uses to crosslinkers efficient at the lower temperature corresponding to most coatings.

According to Campbell and Smeltz's investigation [9], carbodiimides can be prepared from isocyanates in the presence of a catalyst such as phospholene oxide at 140-150 °C (Fig. 2).

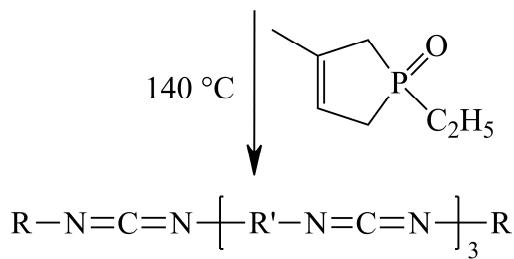
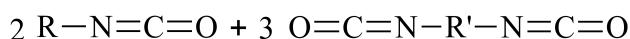


Fig. 2. Synthesis of a carbodiimide from isocyanate.

Other methods have also been described and are reported in the literature [5,10].

Studies on crosslinking have reported [11] that multifunctional carbodiimides are good crosslinking agents at low temperature in the field of emulsions. Hence, emulsion mixtures containing acrylic acid and multifunctional carbodiimides lead to paint films endowed with excellent properties (tensile properties and solvent resistance). Several patents [12-14] claim that carbodiimide agents can also be utilized in the fabrication of films.

This crosslinking method is also interesting because it can be used for *in vivo* conditions. Indeed, collagen matrices have been crosslinked to prevent their rapid degradation and to improve their mechanical properties. Several publications[15-18] describe the crosslinking of collagen by the reaction of a carbodiimide with carboxyl groups of aspartic and glutamic acid residues of the matrix.

2.1.1.2 Aziridines [19-23]

The first paper that reports aziridine as crosslinking agent was published in the early 70's [19]. Roesler and Danielmeier [20] published a review on the reaction of aziridine with carboxylic acids, which spontaneously lead to an amino ester at room temperature, as shown in Fig. 3.

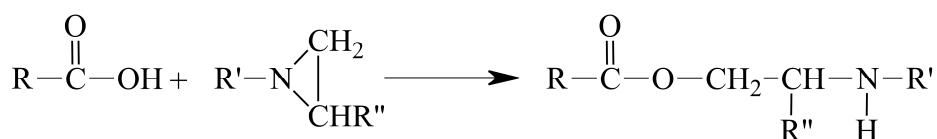


Fig. 3. Reaction between an aziridine and a carboxylic acid leading to an amino ester.

Polyaziridines used as crosslinkers can be obtained by the Michael reaction (Fig. 4), such as the addition of amine onto activated unsaturated groups (e.g., acrylics) [21]:

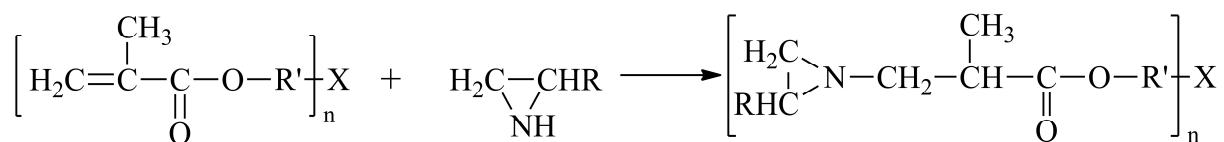


Fig. 4. Synthesis of polyaziridine by "Michael addition" between an amine and an acrylic alkene.

Fig. 5 shows a triaziridine that is soluble in several polar solvents including water, as described by Pollano [21]. This triazine has been used to improve the mechanical properties (lower elongation, higher strengthening) and the chemical resistance of various coatings, including wood varnishes [20] for interior applications.

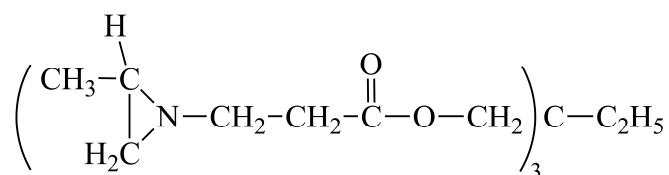


Fig. 5. Structure of trimethylolpropane tris(2-methyl-1-aziridine propionate).

Figure 6 illustrates the crosslinking of carboxylic acid terminated polymer with a triaziridine compounds, reported by Liu et al.[22].

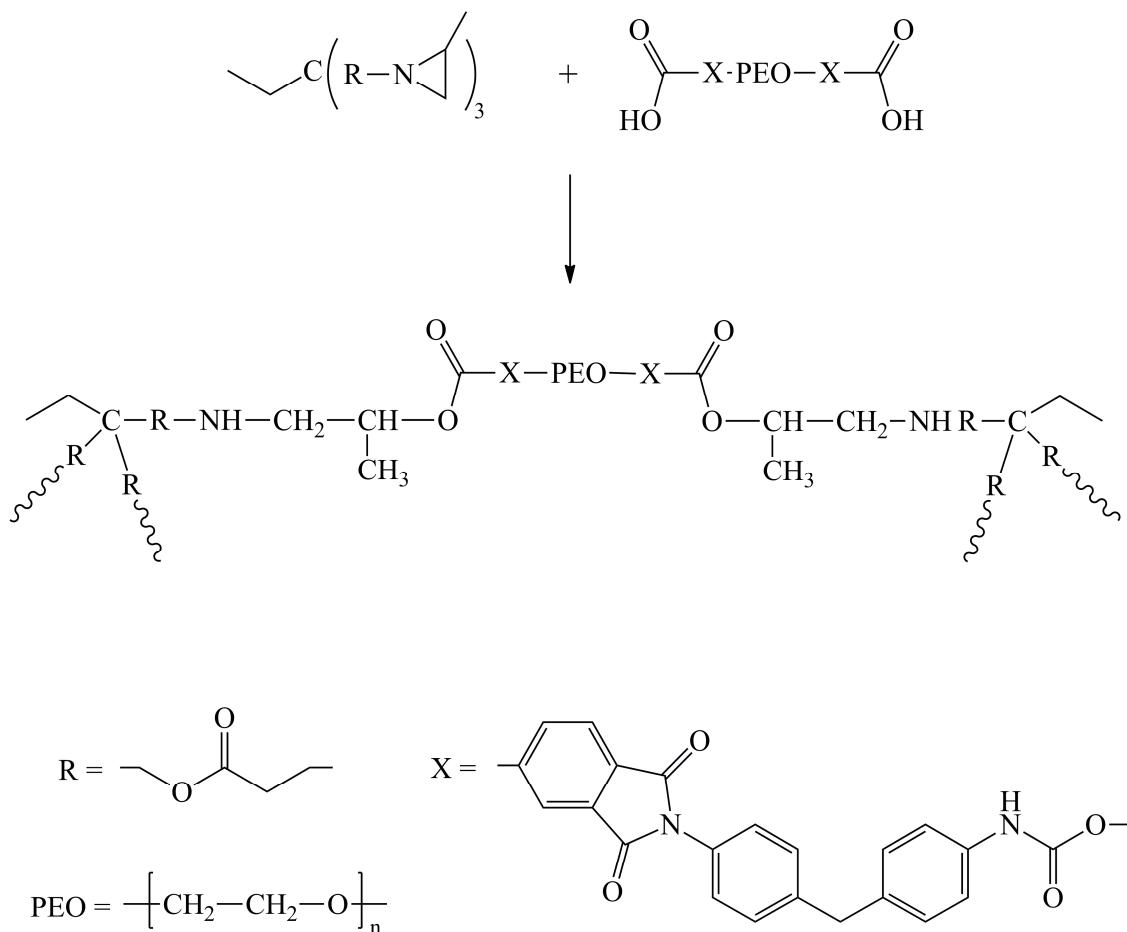


Fig. 6. Crosslinking example of a polymer bearing carboxylic acid functions with a triaziridine.

This reaction does not require any catalyst, and is carried out at room temperature, but its reaction rate is slower than that of the reaction involving carbodiimides. However, the reaction rate may be increased by the use of Cr(III) carboxylate as a catalyst [23]. Indeed, while it took one day in the absence of any catalyst, the reaction rate was reduced to one minute in presence of catalyst.

Two drawbacks were observed:

- As for their homologue carbodiimides, their poor water stability led to inactive amino alcohol. Nevertheless, this limitation can be overcome by adding the polyaziridine crosslinker prior to the processing of the oligomer.
- Aziridine compounds are irritant, toxic and mutagen.

2.1.2 Aceto acetyl function [24-31]

The aceto acetyl function (Fig. 7) is a relatively new function, offering interesting potential for wide chemical activity. This reactivity is partly due to keto-enol tautomerism (75% ketone / 25% enol) presented in Fig. 7. Indeed, the insertion of the aceto acetyl functionality in a polymer reduces both the viscosity and the glass transition temperature [24].

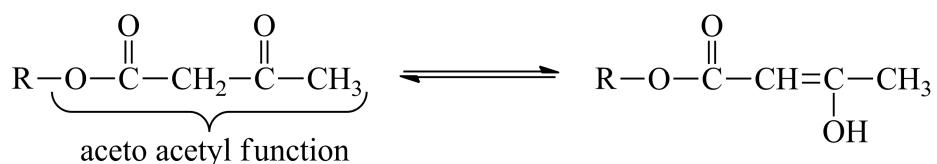


Fig. 7. Keto–enol tautomerism: chemical equilibrium between keto and enol forms.

The other part of the reactivity, shown in Fig. 8, arises from the metal chelation (with copper, silver, nickel...) by bisketones [25,26]:

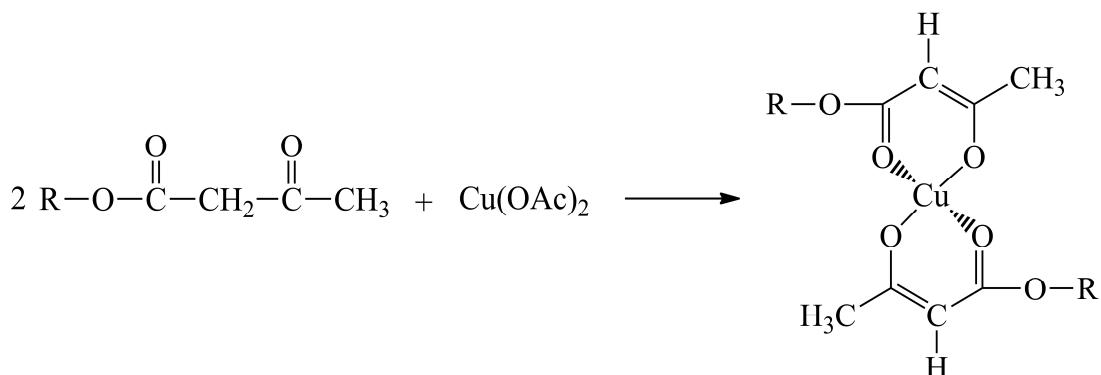


Fig. 8. Chelating of bisketone by copper acetate.

This reaction is quite interesting since it is able to enhance adhesion to metal.

Aceto acetyl derivatives can react with various groups, such i) as isocyanates, ii) activated alkenes, iii) aldehydes, and iv) amines, listed in the following:

i) Isocyanates

The active methylene group of acetoacetyl function can react with an isocyanate at room temperature like in the reaction of isocyanates with hydroxyls, as shown in Fig. 9.

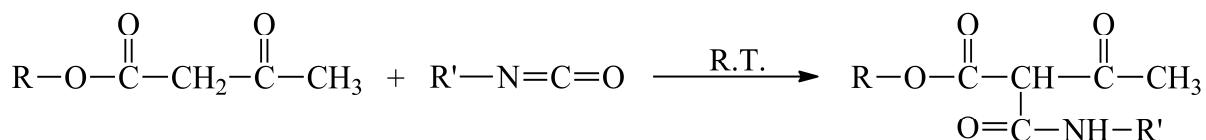


Fig. 9. Reaction between an isocyanate and an aceto acetyl compounds.

Del Rector *et al.* [24] have noted that this reaction occurred but with a lower reaction rate than that involving alcohols. In this case, a lower reaction rate is a benefit since it allows better control of the crosslinking, and also favors convenient conditions to process the final product.

ii) Activated alkenes (“Michael addition”)

A reaction between the methylene group and an electron deficient alkene can occur under strong basic conditions,. This reaction, reported by Clemens and Del Rector [27], is described in Fig. 10.

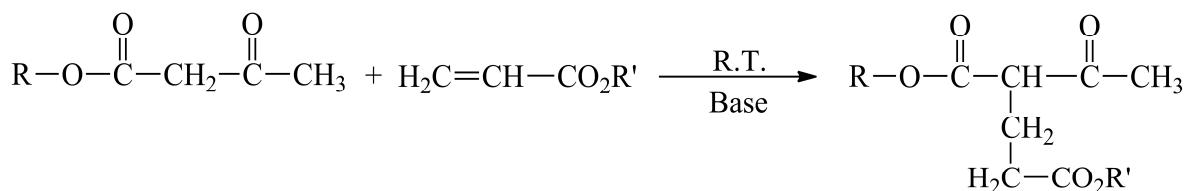
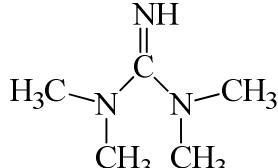
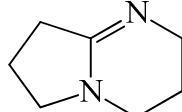
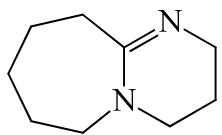


Fig. 10. “Michael addition” between an aceto acetyl compounds and an activated alkene.

These authors used strong bases ($\text{pK}_a > 12$), such as 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), 1,5-diazabicyclo(4.3.0)non-5-ene (DBN) and tetramethylguanidine (TMG), listed in Table 1. Indeed, the pK_a of such a acetylacetone derivative linked to the acidic protons of methylene between both ketone functions is estimated to 12 which explains the need to use such strong bases.

Table 1. Various bases involved in the reaction between acetoacetyl derivatives and acrylates (according to Clemens and Del rector [27]).

Structure	Acronym	pKa
	TMG	13.6
	DBN	12.7
	DBU	12.5

iii) Aldehydes and more especially formaldehyde

Similarly, acetyl acetone has also been used efficiently with formaldehyde to lead to short a link between two acetyl acetyl groups, as shown in Fig. 11:

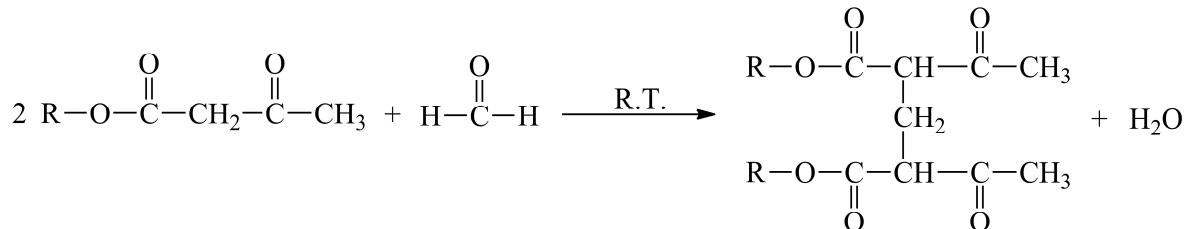


Fig. 11. Formation of a linkage between two acetylacetone groups by reaction with formaldehyde.

iv) Amines

By contrast, Fig. 12 illustrates the reaction of amines with the hydroxyl group of the aceto acetyl enolic form.

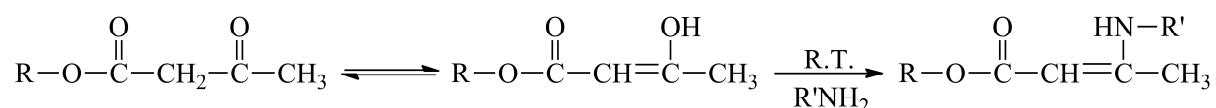


Fig. 12. Reactions between enolic form of aceto acetyl with an amine.

In this way, Mori et al. [28] synthesized “honeymoon-type” adhesives for wood products by crosslinking of acetoacetylated poly(vinyl alcohol) with diamines (these are adhesives consisting of two components, opposite components being applied to opposite adherends, the two brought together to form a joint). They propose the mechanism in Fig. 13 for this crosslinking.

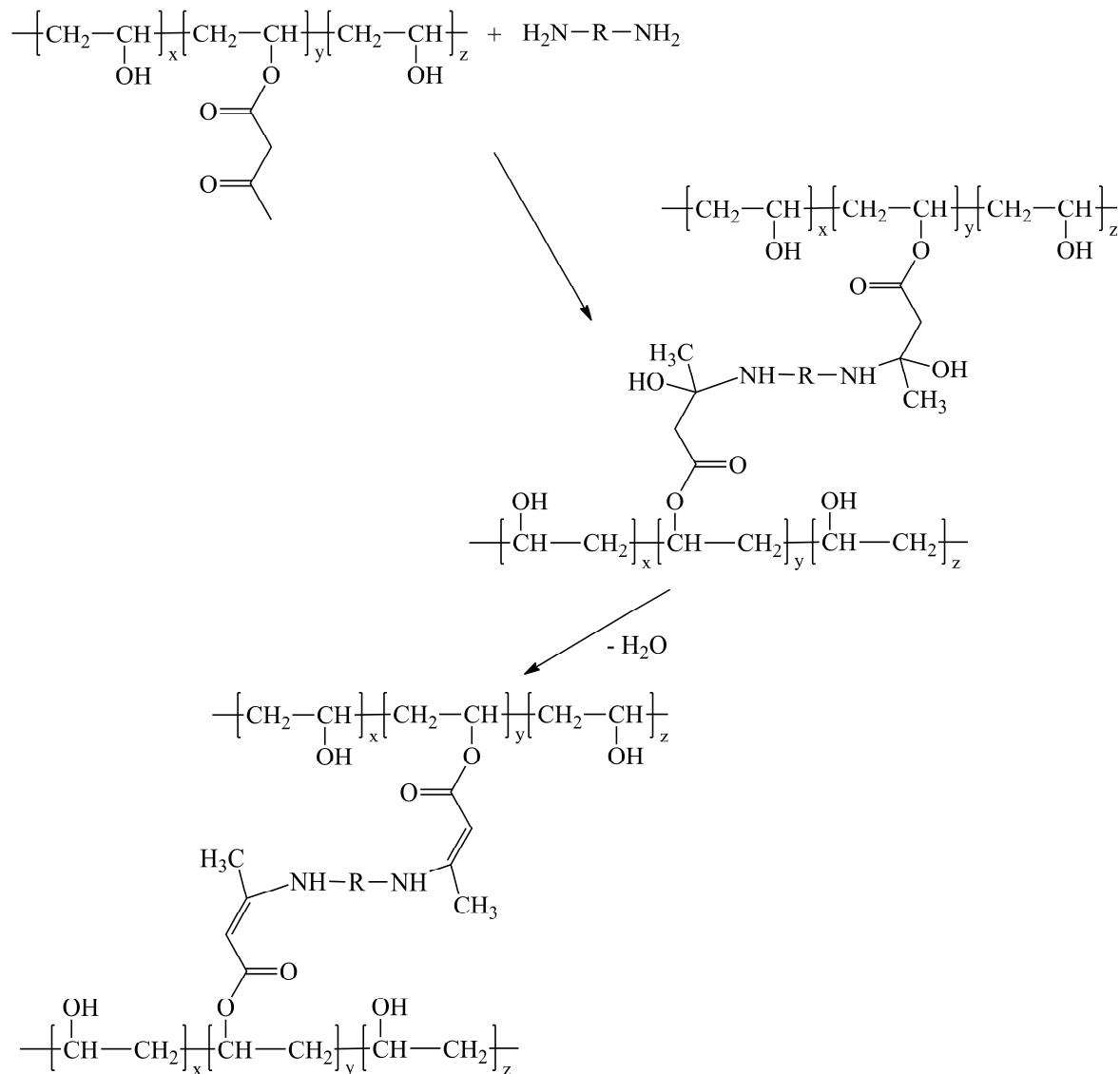


Fig. 13. Crosslinking of poly(vinyl alcohol) bearing aceto acetylated groups with a diamine.

Other reactions may occur when acetyl acetones are involved (in particular for reactions using melamines), but these reactions do not occur at room temperature, and in this case various examples are reported in section 2.2. It may be noted that the acetoacetoxyethyl

methacrylate (AAEM) monomer, with the structure given in Fig. 14, and has been marketed, and used in many fields, such as with acrylic latexes.,

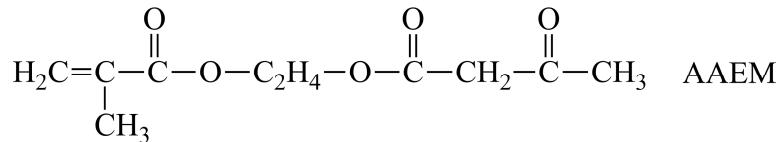


Fig. 14. Acetoacetoxyethyl methacrylate (AAEM) monomer bearing acetylacetone group.

The aceto acetamide function may also be used [29,30] because it should be less sensitive to hydrolysis which is an important feature as well during the polymerization reaction as for its storage [31].

2.1.3 Amines [32-40]

As amines exhibit high nucleophilicity, several reactions may occur at room temperature. In addition to the acetyl acetones reported in Fig. 15, aldehydes and ketones [32] are also featured reactants, and imine groups are also produced in this way:

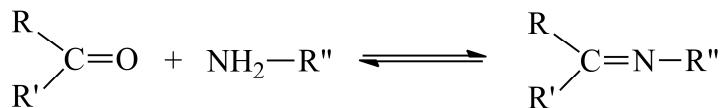


Fig. 15. Preparation of imines by reaction between an amine and a carboxylic group.

This reaction is acid-catalyzed, and it has been found that five days are required to reach satisfactory properties polyurethanes bearing two carbonyl groups.

Among amines, some hydrazine derivatives are able to react with ketones, as shown in Fig. 16.

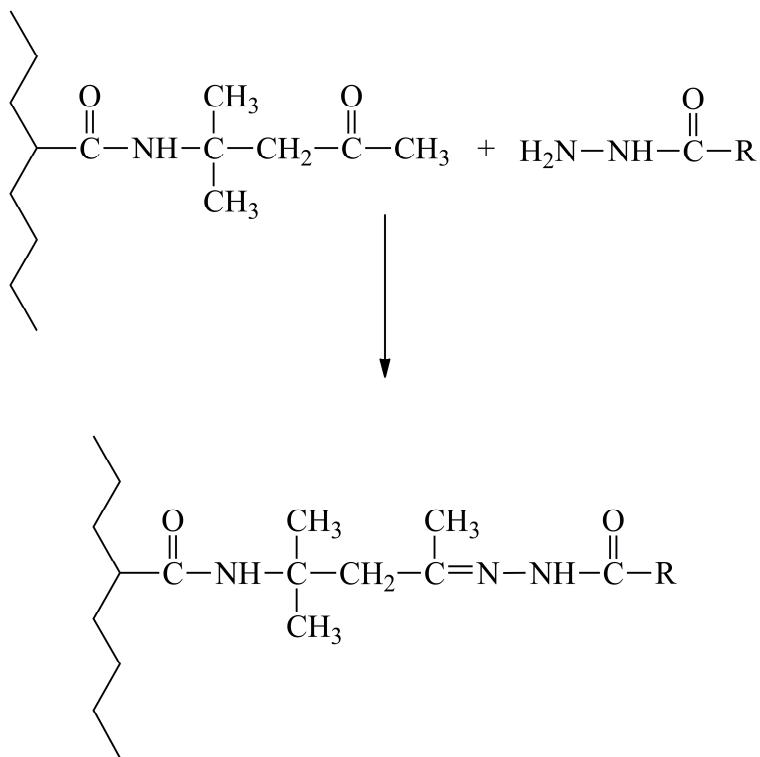


Fig. 16. Reaction of a hydrazine derivative with a polymer bearing ketones groups.

The introduction of ketone groups in the resin has been achieved thanks to the use of the N-(1,1-dimethyl-3-oxobutyl)acrylamide as shown in Fig. 17.

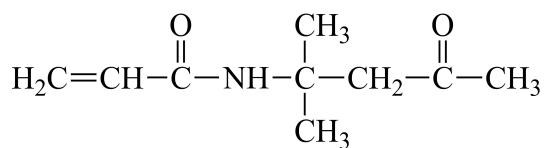


Fig. 17. Structure of N-(1,1-dimethyl-3-oxobutyl)acrylamide.

This reaction, discovered 40 years ago, has mainly been used in the field of crosslinking chemistry by Mestach *et al.* [33,34] in waterborne acrylic dispersions applications.

The second reaction involves amines reacting with epoxides. Several reactions have been published on this well known reaction [35-37]. Figure 18 illustrates the crosslinking between an amine terminated polysiloxane and polysiloxane bearing an epoxide.

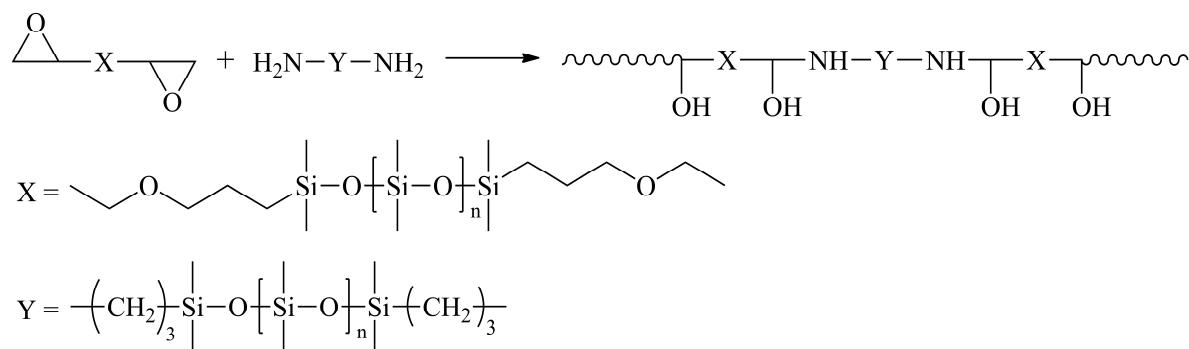


Fig. 18. Reaction between an epoxy and an amine often used to crosslink epoxy resins.

The epoxy/amine system has been developed for latex by Geurts [38]. In that case, the materials are separated into two different phases, called “the two in one system”. The main difficulty consists in incorporating amine groups in acrylic latexes. It is easy to insert epoxide groups thanks to the glycidyl methacrylate monomer (GMA). However, the use of GMA for latex synthesis raises a limitation (especially for precrosslinking) due to the instability of that monomer in aqueous medium. Therefore, O’Brien *et al.* [39] used the episulfide equivalent of an epoxide, synthesized as shown in Fig. 19. The episulfide is more stable towards water, limiting precrosslinking.

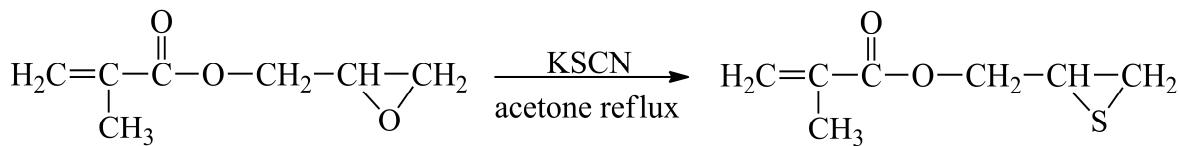


Fig. 19. Synthesis of thiirane from an epoxide.

The crosslinking of episulfides in the presence of piperazine is slower than that occurring in the presence of the oxygen containing derivative, and the best conditions of crosslinking are for 30 minutes at 65 °C. However, storage stability is not much improvement. This amine has been used for the hardening of both episulfide and epoxide because it is water soluble, and thus it can migrate into the particles.

Geurts [38] has reported an extensive and remarkable investigation of the synthesis of methacrylate amino monomers. The same group also prepared the corresponding salts of this amine. The best results were obtained when n = 5; for lower n a chemical rearrangement occurs (leading to amine), while for higher n, the monomer exhibits surfactant properties too high to enable suitable processing.

This system led to interesting results but Geurts noted the presence of an unavoidable Michael reaction in the course of latex synthesis that contains this amine, as shown in Fig. 20.

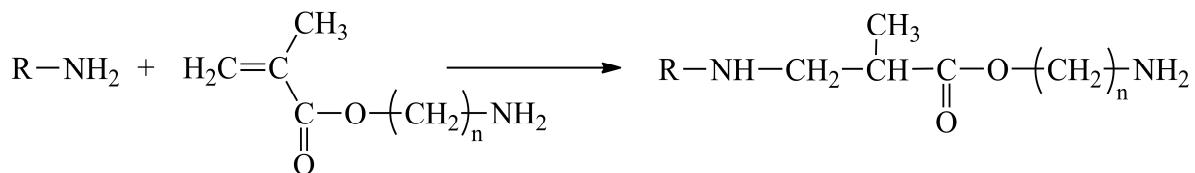


Fig. 20. “Michael reaction” between an amine and a methacrylate amino monomer.

The preceding reports the use of primary amines, but extensive researches also deal with the efficiency of tertiary amines and their reactivity with epoxides. Van de Ven et al. [40] have compared the reactivity of model epoxide molecules in the presence of water, tertiary amine, acid and alcohol, noting that, at room temperature, both the quaternization reaction and the direct polymerization of epoxide mainly occurred, in contrast to the acid/epoxide reaction, which requires heat.

2.1.4 Acetal function [41-45]

The acetal function represents the protected form of an aldehyde group and this protects the aldehyde function from amines. However, for lower pH values, the aldehyde is regenerated and the reaction with amine can lead to the corresponding imines. In this case, the driving force is the pH variation. Fig. 21 displays both reactions.

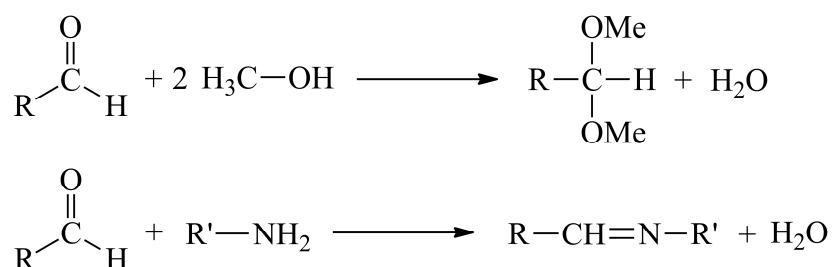


Fig. 21. Protection reaction of an aldehyde by alcohol, reaction between an aldehyde and an amine.

Pichot's group [41] was one of the first team that's to apply this concept using monomers with acetal groups to trap amino-acid, and this strategy was applied in the field of Life Science.

Another French team [42] used this concept in the field of acrylic coatings. Further progress was developed by Charleux's group [42] and also claimed in a patent deposited by Elf Atochem [43].

The development of latex for paints, able to undergo further reaction at room temperature during the film forming step, but remaining chemically stable during the latex synthesis and its storage, is obviously very delicate. That balance requires the use of protected chemical groups in the latex, which are deprotected during the film forming, and hence become reactive. Such a concept also occurs for acetal functions which are stable and inert in basic media [44]. However these functions undergo hydrolysis in acid medium to lead to self-reactive aldehyde functions at room temperature. Fig. 22 displays this concept from N-(2,2-dimethoxyethyl)methacrylamide (MAAMA).

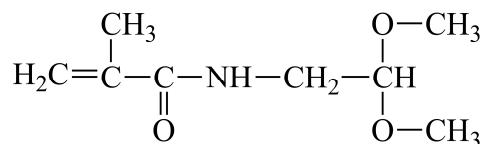


Fig. 22. Structure of *N*-(2,2-dimethoxyethyl)methacrylamide (MAAMA).

Such a reaction is possible and studies with model compounds have shown that the dimerization of the amido group with aldehyde leads to the cyclic structure shown in Fig. 23.

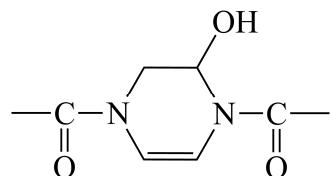


Fig. 23. Cyclic structure after the dimerization of an amido group with an aldehyde.

This explains the crosslinking obtained thanks to this kind of latex, but this latter must be prepared under basic medium and it has to be acidified during the film forming to carry out the hydrolysis of acetal into aldehyde. In fact, the acetal function is interesting because it acts as a pH-responsive crosslinking agent as Li et al. [45] have shown.

2.1.5 Acrylamide derivative [46-50]

Acrylamide and aldehyde derivatives have been well-known for decades because they are able to self-crosslink at high temperatures. The chemical reaction arises from the self-condensation of the alcohol function [46] on the acrylamide monomer, as is found in urea/formaldehyde or melamine/formaldehyde resins. Likewise, monomers bearing these groups have been synthesized for incorporation in latexes, such as N-methylolacrylamide (NMA), isobutoxymethylacrylamide (IBMA), acrylamidoglycolic acid monohydrate (Highlink® AG) or N-(2,2'-hydroxy-1-dimethoxyethyl)acrylamide (Highlink® DMH), illustrated in Fig. 24.

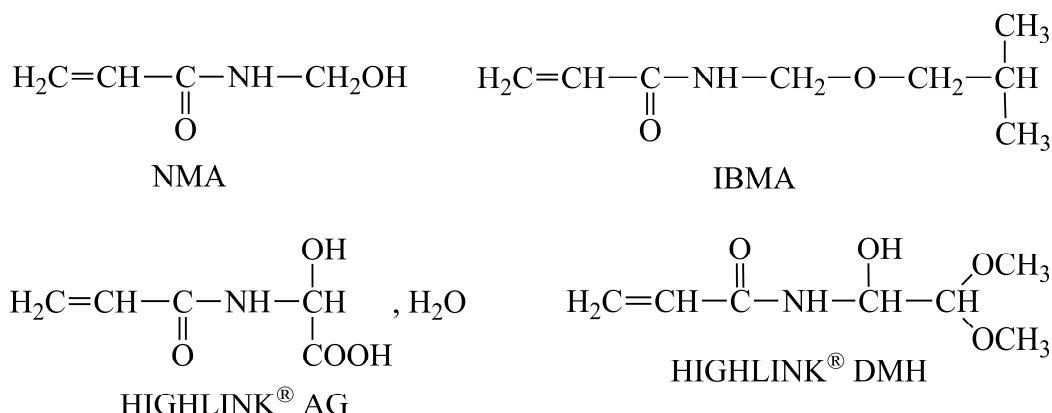


Fig. 24. Structure of some acrylamide monomers.

In addition to the above monomers, many others are commercially available or synthesized. The use of a catalyst enables one to decrease the self-reaction temperature to room temperature, but post-curing is often necessary. These catalysts are either AlCl_3 or strong organic acids such as paratoluene sulfonic acid or orthophosphonic acid [47]. However, several side reactions are also involved, leading to the formation of formaldehyde by-products, as shown in Fig. 25, which is undesirable because of its toxicity.

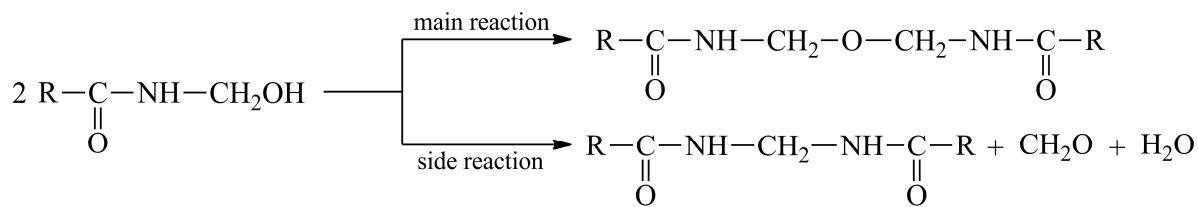


Fig. 25. Self-reactions of acrylamide compounds.

Monomers such as N-(methoxy methyl acetate) acrylamide (MAGME) have been copolymerized with monomers containing hydroxyl groups, such as 2-hydroxyethyl acrylate (HEA), to obtain self-crosslinkable latexes [48]. Indeed, Fig. 26 shows the presence of three potential crosslinking sites borne by the monomer, including NH, CH and OMe. Such a chemistry is promising and undergoes a fast development [49,50].

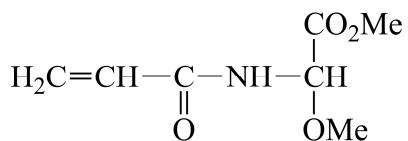


Fig. 26. Structure of *N*-(methoxymethyl acetate)acrylamide monomer.

2.1.6 Other crosslinking moieties

This section describes a peculiar process that allows a post-crosslinking process at room temperature. However, it requires the participation of a chemical agent (and from neither thermal nor from photochemical effects). Typically, the use of oxygen and water are reported below.

2.1.6.1 Water [51-100]

i) Sol-Gel reactions

The chemical reactions of the sol-gel process were reported almost four decades ago [51], but this technique has gained increasing interest. The sol-gel process makes it possible to produce at low temperature networks with high purity and high homogeneity. Although many studies have been carried out on sol-gel processes involving organic compounds, a few investigations involve polymers to lead to hybrid materials for which organic and inorganic phases coexist. Furthermore, some multicomponent systems which cannot be made by conventional methods due to crystallization can be produced in a sol-gel process [52]. Although shrinkage and fracture during the curing process limit the widespread applications of these techniques, much success has been achieved in producing monolithic solids by controlling the diffusion rate of volatile components in the system [53]. Two methods exist to obtain organic/inorganic materials. The first method is based on a mixture of a metal alkoxide [such as Si(OR)₄,

Ti(OR)_4 , Zr(OR)_4 , Al(OR)_3] and a polymer. For example, Blanchard *et al.* [54] reported an extensive study on the hydrolysis and condensation reaction of different metal alkoxides M(OR)_n (where M represents Si, Ti, Zr atoms, etc... and OR is an alkoxy group). Then, the metal alkoxide undergoes a hydrolysis reaction followed by a polycondensation to form a three dimensional network containing the polymer. The hydrolysis and polycondensation reactions are described in Fig. 27.

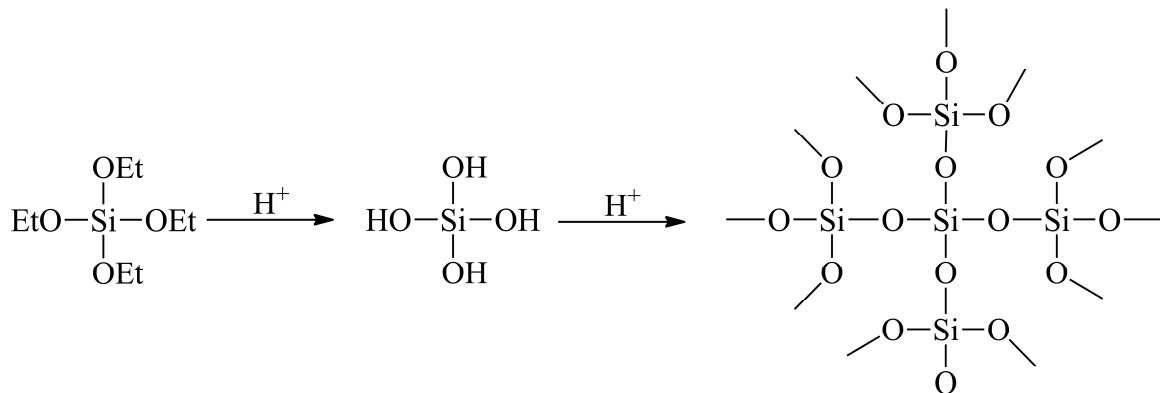


Fig. 27. Hydrolysis and polycondensation of tetraethoxysilane.

The resulting materials, initially called “ceramers” by Wilkes *et al.* [55], should reflect some of the properties of the sol-gel glass and the incorporated polymeric reactant. However, the completion of the hydrolysis reaction depends upon the amounts of water and acid added to the system. Because of the nature of that process, several authors [56-58] have incorporated polymeric or oligomeric species into a glassy network when these components exhibit appropriate functional groups to undergo co-condensation.

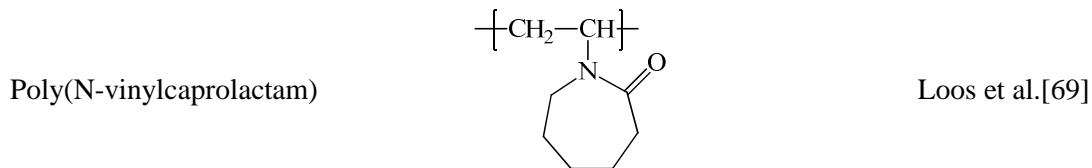
Mechanical properties (torsion, compression, strain and rupture modulus) of the polymers are usually improved [59] (about ten-fold) when inorganic fillers are generated *in situ*. The mechanical modulus increases with the amount of inorganic fillers in a hybrid system, with the increase being greater than for the homologues reinforced by fillers.

In contrast to most materials achieved from a process which leads to brittle pure silicone glasses, inclusion of polydimethyl siloxane (PDMS) [60], hydrogenated polybutadiene (HPBd) [61] induced a significant flexibility. These studies showed that the rubbery PDMS or HPBd reactants have been incorporated into the networks. In addition, Wilkes *et al.* [55] obtained transparent materials, which indicate that no phase separation occurred (or at least

did not produce large phase separated domains). However, some microphase separation could be noted [52] according to the acid content. Several examples of polymers [56,57,62-74] used to create original networks by sol-gel with tetraethoxysilane (TEOS) are given in Table 2.

Table 2. Examples of polymer containing various base unit used to create networks in mixture with TEOS by sol-gel reaction (PMMA, PHEMA, PVAc, PDMS, PTFE and MAA stand for polymethyl methacrylate, polyhydroxyethyl methacrylate, polyvinyl acetate, polydimethylsiloxane, polytetrafluoroethylene and methacrylic acid, respectively).

Polymer	Base unit	References
PMMA		Landry et al.[51]
PHEMA		Kaddami et al.[57]
PVAc		Girard-Reydet et al.[58], Landry et al.[59] Yano et al.[60]
Polyester		Frings et al.[61]
Polyphosphazene		Coltrain et al.[62]
Polyimide		Kaddami et al.[63], Morikawa et al.[64,65]
Hydroxypropyl Cellulose		Yano[66]
PDMS		Pinto et al.[67]
PTFE		Chen et al.[52]
R _F (MA) _n R _F		Sawada et al.[68]



The second method is based on hydrolysis followed by the polycondensation of telechelic oligomers or polymers bearing metal alkoxide at both ends of the chain; the resulting materials are called “oxo-polymers”. This process facilitates creation of a crosslinked network formed by the polymeric chains linked by M-O-M covalent bonds. Many types of telechelic polymers, ranging from aliphatic to aromatic and to specialty polymers (Table 3), [75-92] have been used for this process, showing the adaptability of this method. Our research team[89] used such a method that employed fluorinated model compounds, as shown in Fig. 28.

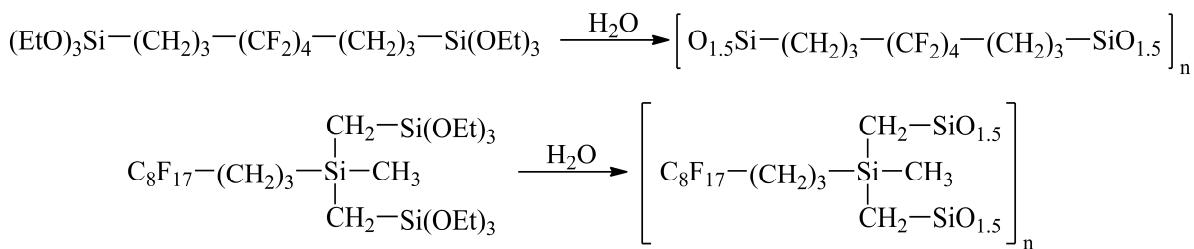


Fig. 28. Sol-gel model reaction of fluorinated compounds.

Table 3. Examples of telechelic bis(trialkoxy) silane polymers containing various base units crosslinked by sol-gel reaction (PEO, PTMO, PCL, PDMS, H-PBd, PMMA, PAEK, PS, PFCB, RF and Poly(VDF-co-PMVE) stand for polyethylene oxide, polytetramethylene oxide, polycaprolactone, polydimethylsiloxane, hydrogenated polybutadiene, polymethylmethacrylate, polyaryletherketone, polystyrene, perfluorocyclobutane, perfluoroalkyl group and poly(vinylidene fluoride)-co-perfluoromethyl vinyl ether) respectively).

Polymer	Base unit	References
PEO		Kweon and Noh[70,71]
PTMO		Huang and Wilkes[72], Trossaert and Goethals [73]
PCL		Kaddami et al.[74], Cuney et al.[75], Messori et al.[76]
PDMS		Surivet et al.[77]
H-PBd		Surivet et al.[77], Kaddami et al.[78]
PMMA		Coltrain et al.[79]
Polyoxazoline		Chujo et al.[80]
PAEK		Wang et al.[81]
PS		Mourey et al.[82]
Ar-PFCB-Ar		Rizzo and Harris[83]
R-RF-R		Ameduri et al.[84], Zhao et al.[85], Michalczik[86]
Poly(VDF-co-PMVE)		Hung et al.[87]

A similar strategy involving longer fluorinated compounds (C_8F_{17} , $C_{10}F_{20}$) was also claimed by the DuPont de Nemours Company [91]. This process was recently investigated using telechelic bis(triethoxysilane), bis(methyldiethoxysilane) or bis(dimethylethoxysilane) with poly(VDF-co-PMVE) elastomers (where VDF and PMVE stand for vinylidene fluoride and perfluoromethyl vinylether, respectively) leading to original crosslinked fluorosilicon elastomers [92] endowed with T_g lower than -30 °C, satisfactory mechanical properties (high modulus), and no swelling in oil.

The self-condensation of the silanol terminated polymer may take place and thus can affect the network structure. In this context, Bourne *et al.* [93] explored the use of silanol to prepare crosslinkable emulsions nearly three decades ago.. Two main unsaturated monomers are commercially available: i) triethoxyvinylsilane is not very reactive during the polymerization, but it has sufficient reactivity for use in material crosslinking (such as polyolefins), ii) γ -methacryloyl-propyl trimethoxysilane is quite reactive in radical polymerization. The only limitation concerns the hydrolysis of siloxane groups during the synthesis of the latex, which is not desired (since they lead to crosslinkable latex). The resistance to hydrolysis can be adjusted according to the nature and the number of alkoxy group, as follows:



In this way, Chen *et al.* [94] prepared tri(propioxy) silane latex which was not pre-crosslinked.

More recently, terpolymers containing a few triethoxysilane side groups located randomly in the backbone based on units of VDF and a perfluorovinylether bearing an ω - SO_2F group (i.e., Nafion® monomer) have been synthesized and chemically modified to obtain crosslinked membranes for fuel cell applications [95].

Hence, the sol-gel process affords the means for an excellent compromise of the suitable properties brought by both the organic and the inorganic moieties. Moreover, it can be regarded as a “green process” which needs only water and acid (or base) to lead to a three dimensional network, that often may be developed at room temperature.

ii) Isocyanates

Isocyanates are the second group which enables a self-reaction at room temperature in two steps as illustrated by Fig. 29.

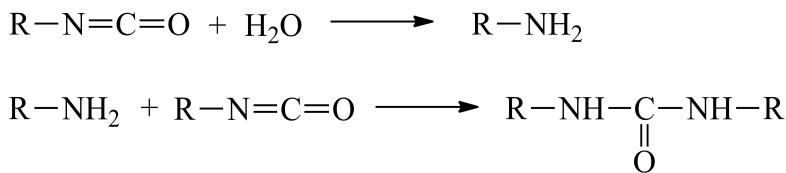


Fig. 29. Self-reaction of an isocyanate in presence of water.

As with the triethoxyvinylsilane , a limitation concerns the stability of the isocyanate group in an aqueous medium. Thus, it has usually been preferred to protect this function during polymerization, and then to carry out a thermal deprotection during the crosslinking. This aspect will be developed below. However, m-isopropenyl- α,α -dimethylbenzyl isocyanate (Fig. 30) or TMI[®], an unsaturated isocyanate, has recently become commercially available.

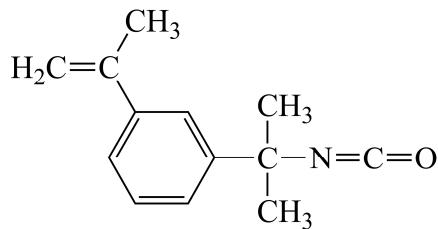


Fig. 30. Structure of m-isopropenyl- α,α -dimethylbenzyl isocyanate.

This monomer is much more stable in aqueous medium than classic isocyanate monomers and this property permits its use in a polymerization process in dispersed medium [96,97]. In these conditions, and in spite of the loss of some isocyanate groups during the latex synthesis, enough intact functions remains to favor the formation of urea groups, and hence to induce the self-crosslinking of the latex [98,99]. Yoon and Lovell [100] used acetic acid as the catalyst to increase the otherwise very slow reaction rate with this isocyanate.

2.1.6.2 Oxygen

i) Reaction generating peroxide: [101-108]

Finally, involving oxygen has long been used in post-crosslinking reactions in coatings and particularly in alkyde resins. Indeed, such a process was already used in Egypt in antiquity for

mummification. This system has mainly been applied for solution resins and mainly with alkyde resins modified by unsaturated fatty acids. Actually, the presence of linolenic acids (three double bonds), linoleic acids (two double bonds) and oleic acids (one double bond) allows the action of oxygen in the presence of a catalyst, which enable the generation of peroxy radicals responsible for crosslinking. Interest in the study of these complex mechanisms, ignored for years, returns from time-to-time [101-103].

One interesting strategy was to modify the polymer by the insertion of peroxides or hydroperoxides able to generate radicals, and thus to initiate the crosslinking. This is illustrated by Fig. 31, for the case of non-conjugated double bonds (e.g., oleic acid), for which the mechanism shows the formation of an allyl hydroperoxide. These hydroperoxides then undergo decomposition to induce interchain crosslinking through various side reactions, as shown in Fig. 32. This reaction can be catalyzed by metal salts or complexes (cobalt, lead or manganese octoates, naphthenates, or linoleates) which are soluble in the medium.

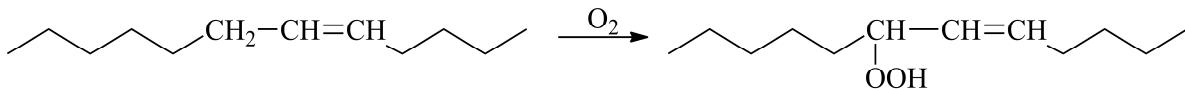


Fig. 31. Formation of an allylhydroperoxide by reaction of a non-conjugated double bond with dioxygen.

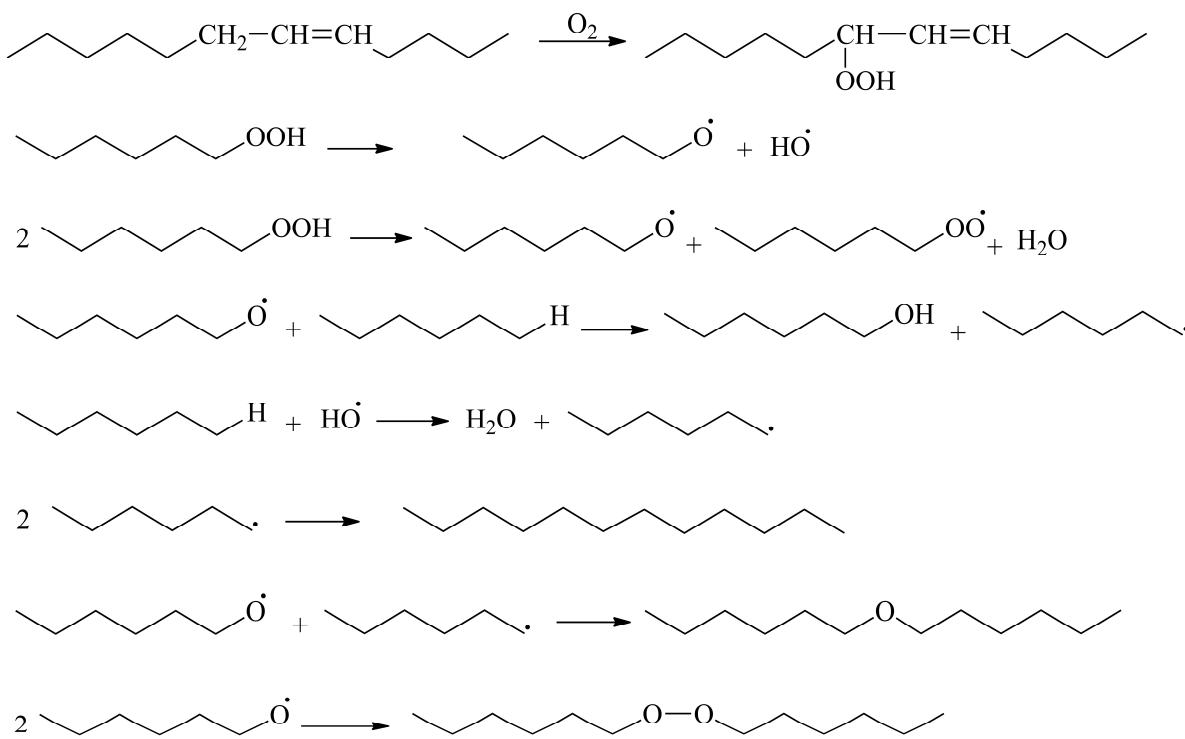


Fig. 32. Different reactions after decomposition of hydroperoxides.

The number of bridges, and hence the crosslinking density, is higher with conjugated double bonds (e.g., linoleic acid). First, the formation of cyclic peroxides is observed, followed by their subsequent decomposition leading to the same type of reactions, as presented in Fig. 33.

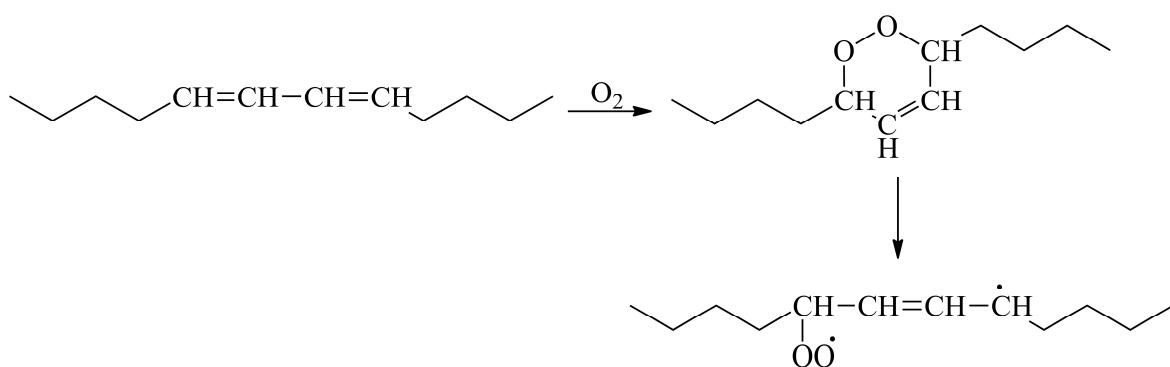


Fig. 33. (a) Formation of cyclic peroxide by reaction of dioxygen with conjugated double bonds and (b) decomposition of cyclic peroxide.

In 1985, Chen and Bufkin [104] used fatty acid acrylates in acrylic latexes in the presence of lead or tin salts. These authors showed that the obtained films underwent crosslinking at room temperature after two weeks. To limit the plasticizing effect of these long side chains, new monomers have been synthesized such as cyclohexene methylacrylate. However, the optimization of the structure has not been realized to supply a monomer that possesses two double bonds: the first one is reactive in polymerization to achieve the latex while the other is able to allow post-crosslinking with oxygen in the presence of catalysts.

Finally, systems containing boranes stable in the absence of oxygen, can lead to peroxides able to favor crosslinking at room temperature when they react with oxygen. Fig. 34 exhibits the reactions involving borinated compounds[105,106].



Fig. 34. Formation of peroxide borinated derivatives.

Indeed, borane is chemically modified into non-toxic borinate, and radicals can be generated at low temperature (from -35 °C to room temperature) [107,108]. This type of system has been used to prepare dental printings directly on a patient. To our knowledge, such a strategy has never been proposed in the field of coatings.

ii) Acetylenic coupling: [109-113]

In 1869, Glaser[109] pioneered the coupling of acetylenic functions. This reaction named “Glaser coupling” occurs with acetylenic compounds in the presence of oxygen and copper (I) catalysts, at room temperature as shown in Fig. 35. Siemsen et al. [110] provides an extensive overview of acetylenic coupling used in the field of material chemistry.

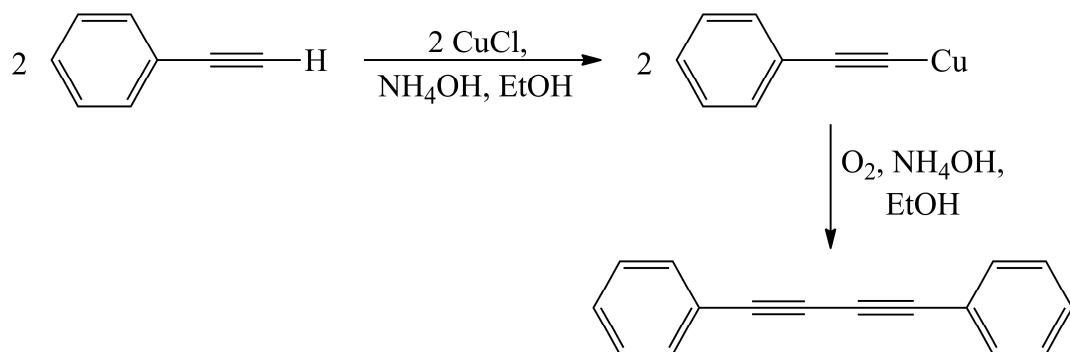


Fig. 35. Mechanism of “Glaser coupling” reaction with an acetylenic compound in presence of O₂ and Cu(I).

In the 60s, Hay [111,112] improved this coupling by addition of a tertiary amine, which complexes the copper salts. Dirlikov et al. [113] subsequently claimed the crosslinking of poly(propargyl methacrylate) in the presence of copper (I) and tetramethylethylenediamine as displayed in Fig. 36.

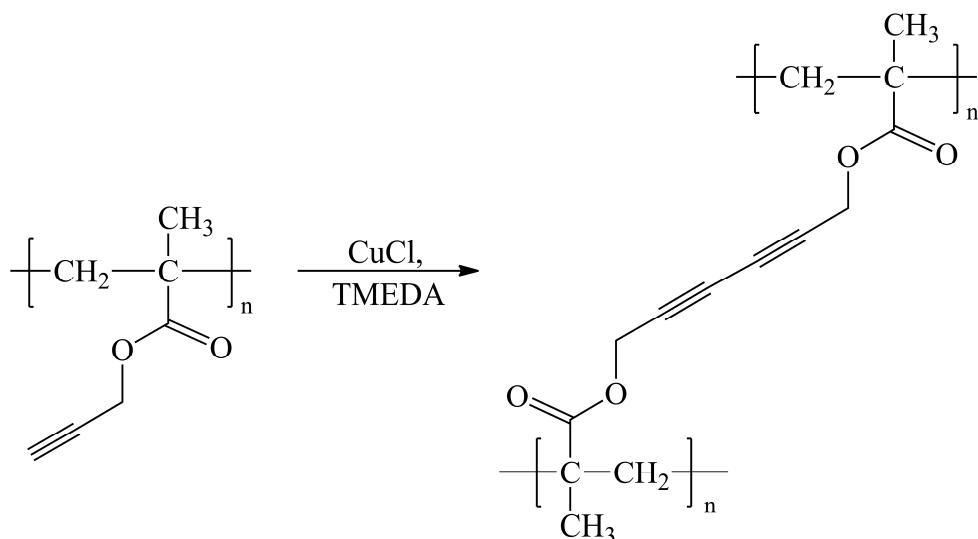


Fig. 36. Crosslinking of poly(propargyl methacrylate) by “Hay coupling” reaction.

2.1.7 Conclusion

This section reports many reactions that enable crosslinking at low temperature by means of various groups such as acetate, isocyanate, or even in the presence of oxygen (boranes) or water (for sol-gel systems). As has been seen, the reactivity is a key parameter, but extreme care is required in both the processing and processes which avoid components too reactive that are too reactive before processing. These crosslinking methods are used in several areas, such as biology, coatings, paints, especially to improve mechanical properties and chemical resistance.

2.2 – Crosslinking at intermediate temperatures

In the context of this review, intermediate temperatures are in the range between 40 and 150 °C, whereas high temperatures range 150 to 300 °C. As in the previous section, the following is organized by the chemical functions involved in the reactions, taking into account carboxylic acid reacting with various complementary functions, such as hydroxyl groups, azetidines, or various key functions involved in Diels Alder reactions.

2.2.1 Carboxylic acid function

The carboxylic acid function has extensively been investigated since it is easily introduced into the polymers either by radical polymerization (of acrylic acid for example) or by polycondensation (e.g., in the case of diols containing an acid function or of triacid derivatives that bear different reactivities). Carboxylic acids are known to react with many functions and the examples below consider epoxide and oxazoline mainly.

2.2.1.1 Reaction with epoxides [114-134]

The general reaction is illustrated in Fig. 37.

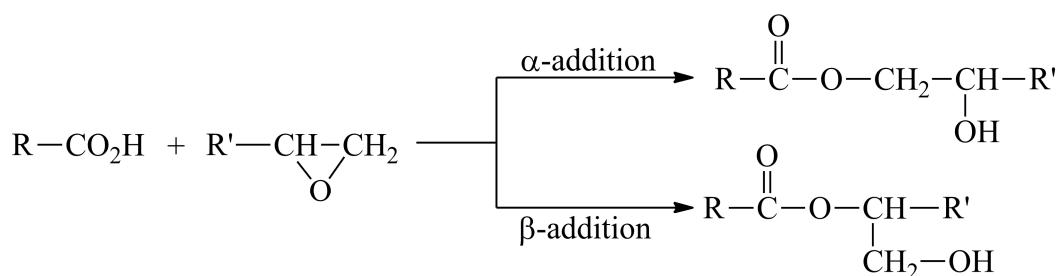


Fig. 37. α - and β -Addition between a carboxylic acid and an epoxy.

This reaction has led to extensive studies over the range of temperatures discussed in this section. On the one hand, research has focused on catalysis. On the other hand, studies have been devoted to the selectivity of the addition, since, besides α -addition to the carbon atom of the methylene group, β -addition is also possible to the carbon atom of CH groups. This addition easily reaches 20 % [114,115], leading to isomers shown in Fig. 37, depends on the reaction conditions [116,117]. Indeed, several catalysts have been successfully used such as:

- i) Tertiary amines [118,119] are the most commonly used catalysts, and have been involved in several studies, particularly to avoid possible side reactions [120]. The most frequently used amines are triethylamine [121], N,N-dimethylbenzylamine [122] and N,N-dimethyldodecylamine [123,124].
 - ii) Tertiary amine salts [125-127] such as tetrabutylammonium bromide are advantageously used in latex because of their solubility in water.

iii) Metallic complexes are another catalyst class, among which diisopropyl salicilate chromium is the best known [128]; its structure is shown in Fig. 38.

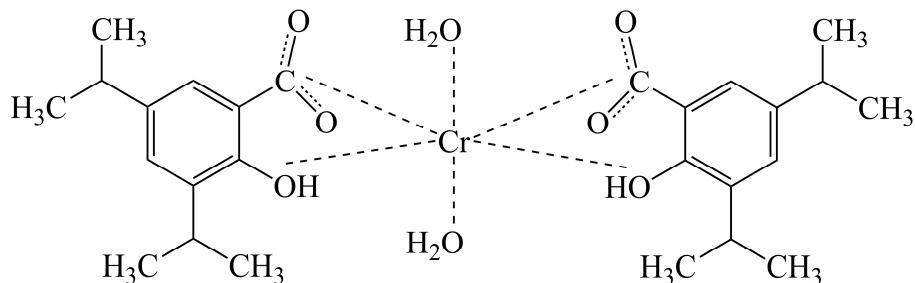


Fig. 38. Structure of diisopropyl salicilate chromium complex.

The application of the epoxide/acid reaction is important in powder coatings, to enable the crosslinking of polyesters which bear carboxylic end-groups. The most popular crosslinking agent is triglycidyl isocyanurate (TGIC) (Fig. 39) [129,130].

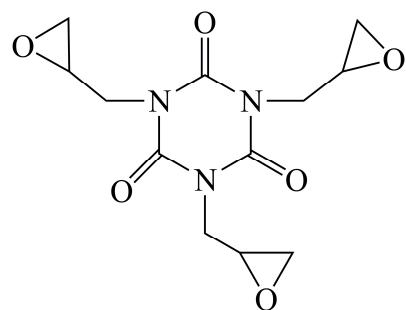


Fig. 39. Structure of triglycidyl isocyanate (TGIC).

This compound can be synthesized by several methods, including one that starts from 1,3,5-trichlorotriazine (Fig. 40). However, the most frequent reaction requires the addition of epichlorohydrin to an isocyanurate [131] derivative. These strategies are illustrated in Fig. 40.

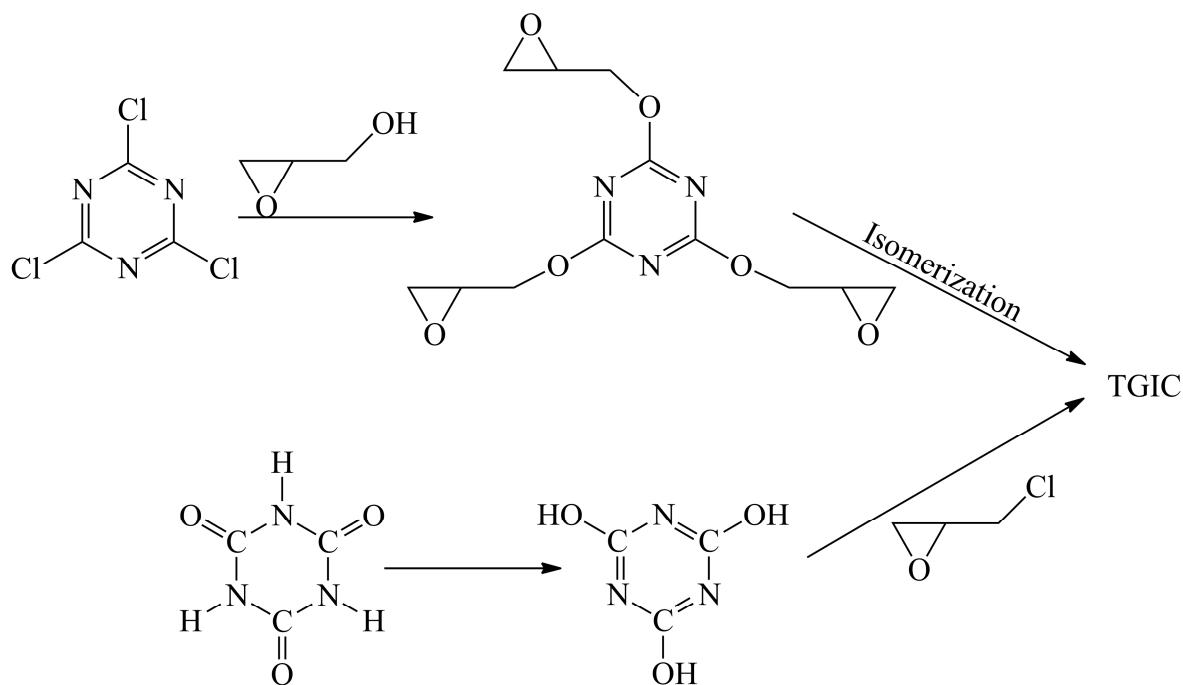


Fig. 40. Synthesis of TGIC from 1,3,5-trichlorotriazine and from an isocyanurate derivative.

This hardener is a complex mixture composed of several diastereoisomers, the properties of which vary according to the supplier [132-134]. TGIC is a more reactive crosslinker than the classic bisphenol-A based diepoxy. Less than 10% is usually required, taking into account that T_g of the coating decreases by about 2 °C per percentage of TGIC in the process. Coatings using this system exhibit good durability.

2.2.1.2 Reaction involving oxazolines [135-137]

Reaction with oxazoline is a less known reaction although it has been developed by the Dow Chemical Company [135] as shown in Fig. 41.

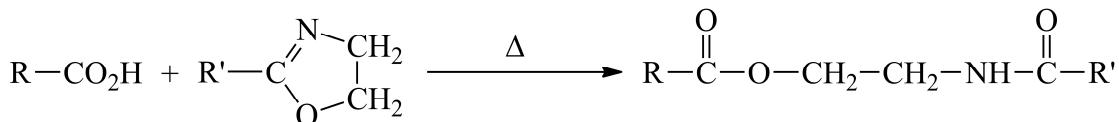


Fig. 41. Reaction of an oxazoline with a carboxylic acid.

In this reaction, the acid group is protected by an amino salt. Indeed, this protection avoids the reaction with oxazoline [136], but, in the course of the heating, the salt decomposes to regenerate the acid (concomitant with the vaporization of amine) and the acid/oxazoline

reaction can occur. This type of protection has been used for the crosslinking of polyester [137].

2.2.2 Alcohol function [138-139]

For the reasons discussed above, the crosslinking reactions involving an alcohol function are diverse and versatile. The synthesis of acrylates containing lateral hydroxyl groups (such as $\text{CH}_2=\text{CH}-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{OH}$, HEA) is possible. Some secondary alcohols, produced from poly(vinyl acetate) after hydrolysis [138,139], can also be used. In addition, triols and diacid alcohol have also been prepared.

2.2.2.1) Protected urethanes [140-154]

Isocyanates are well known to react with alcohols at room temperature [140,141], but if protected urethanes (which are thermally unstable) are prepared it is possible to induce crosslinking with alcohols (or amines, of course). The mechanism is shown in Fig. 42.

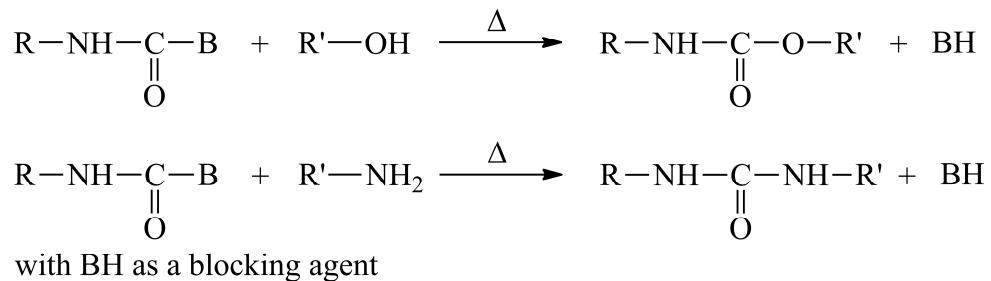


Fig. 42. Reactions of protected urethane with alcohol or amine.

Numerous investigations on the generation of various BH molecules, named “blocking agents”, which lead to relatively unstable urethanes. Examples include phenols, oximes [142] and, more recently, amides (or lactames). These may lead to the reverse reaction as a function of temperatures. Exhaustive and excellent reviews have been written by Wicks and Wicks [143,144].

The main drawback concerns the evolution of generated BH agent. Among marketed products, DESMOCAP® 11 [145] (produced by the Bayer Company) requires nonyl phenol

as the protected agent, which remains in the polymer as a polyurethane plasticizer. Other patents registered by Cray Valley [146], Rhodia-Cray Valley [147] and Rhodia [148] companies claim other protected agents, such as methyl parahydroxybenzoate which can be deprotected from 120 °C. They are used in paint applications, named “glass or glossy coatings”.

In powder paints or high-solid resin coatings, considering the targeted applications, isophorone diisocyanate (IPDI) is mainly used because it exhibits better UV-proofing [149] properties than its aliphatic homologues. Moreover, lactames are used as protected agents because they lead to compounds possessing suitable melting points, about 65 °C. Huels company [150-152] used caprolactame in order to block isocyanates in the field of polyurethane coatings, the temperature of deprotection, which varies from 130 to 165 °C. The deblocking mechanism is described in Fig. 43.

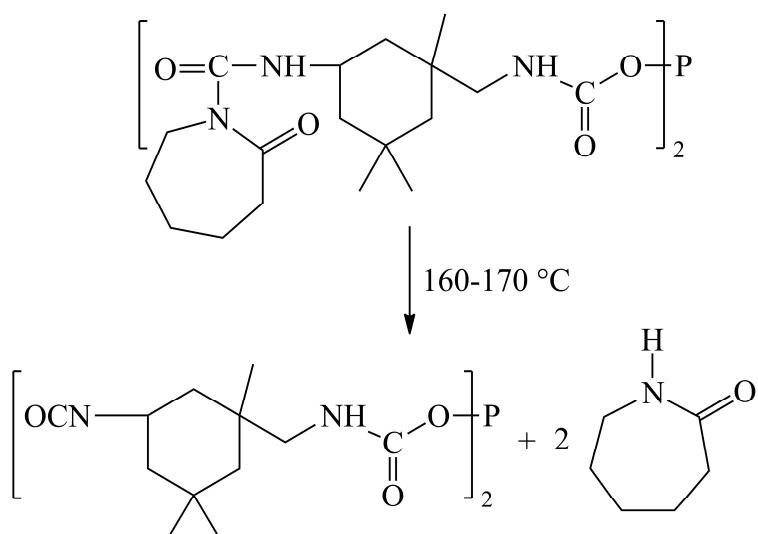


Fig. 43. Deprotection mechanism of a polymer bearing isocyanate functions blocked by caprolactame (where P stands for a polymeric structure).

Investigations on protected or “blocking agent”, which enable lower deprotection temperature, have been reported by Cooray and Spencer [153] for the use of pyrazole with aliphatic diisocyanates at 120 °C, or Engbert *et al.* [154] for diethyl malonate, with a deblocking temperature of 104 °C.

2.2.2.2 Azlactone function [155-157]

Using derivatives containing azlactone function for crosslinking is a more recent chemistry, similar to that of oxazolines; the basic reaction is presented in Fig. 44.

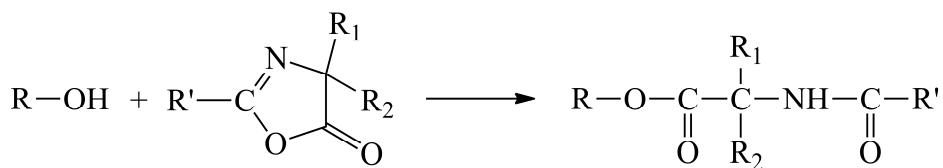


Fig. 44. Reaction between an azlactone and an alcohol.

This reaction, that leads to an ester/amide derivative, has been studied to determine the influence of the nature of R_1 and R_2 groups onto the reactivity. In certain conditions, the final product can lead to a reverse reaction at higher temperature as reported by Wagener [155,156] in his interesting review on the thermal uncrosslinking reaction. Hence, thermo-crosslinkable gels can be obtained by reaction of a bisazlactone with an activated phenol (such as bisphenol AF, $\text{HO}-\text{C}_6\text{H}_4-\text{C}(\text{CF}_3)_2-\text{C}_6\text{H}_4-\text{OH}$ [157]).

2.2.2.3 Crosslinking from methylol amide function [158-165]

This reaction is well-known for the crosslinking of polyol by hexamethylol melamine (HMM Fig. 45) or its derivates (methylic ester) for coating applications [158,159]. It is based on the reactivity of amide-formaldehyde derivatives with alcohols, shown in Fig. 46, though formaldehyde has recently been banned by REACH regulations.

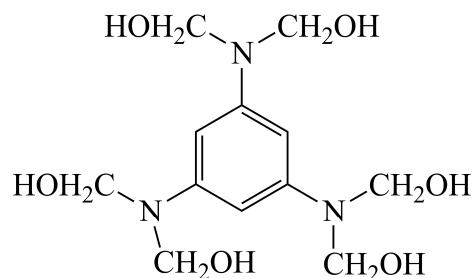


Fig. 45. Structure of hexamethylol melamine (HMM).

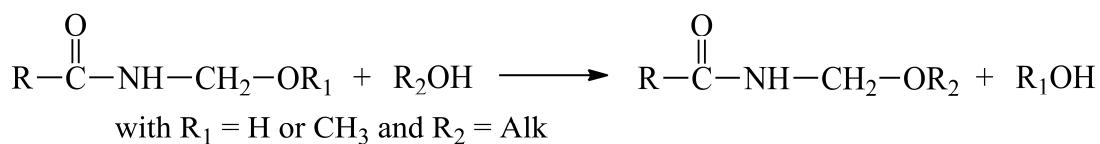


Fig. 46. Reaction between an amide and an alcohol.

This reaction is possible at high temperatures [160,161] (ca. 150 °C), but it can be carried out at lower temperatures with the use of a catalyst, in particular, acidones, such as phosphonic acid.

A crosslinking reaction developed by the EXXON Company [162,163] and Subrayan and Jones [164] is shown in Fig. 47.

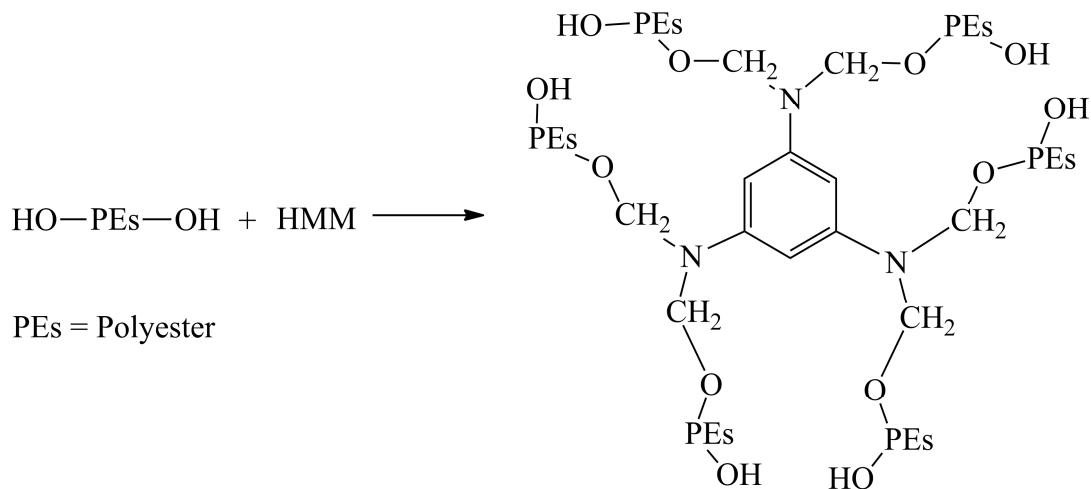


Fig. 47. Crosslinking reaction, developed by Exxon, between HMM and alcohol terminated polyester (PES).

This reaction is the hardening of high-liquid resin coatings free from solvent, composed of a low viscosity diol prepolymer (ca. 300 mPa.s at 25 °C) and a reactive diluent monomer. Hexamethylol melamine is added to achieve the final crosslinking. The same group [165] performed additional investigations on the reaction of HMM with parahydroxybenzoic acid derivatives leading to 1,3-benzoxazines, as shown in Fig. 48.

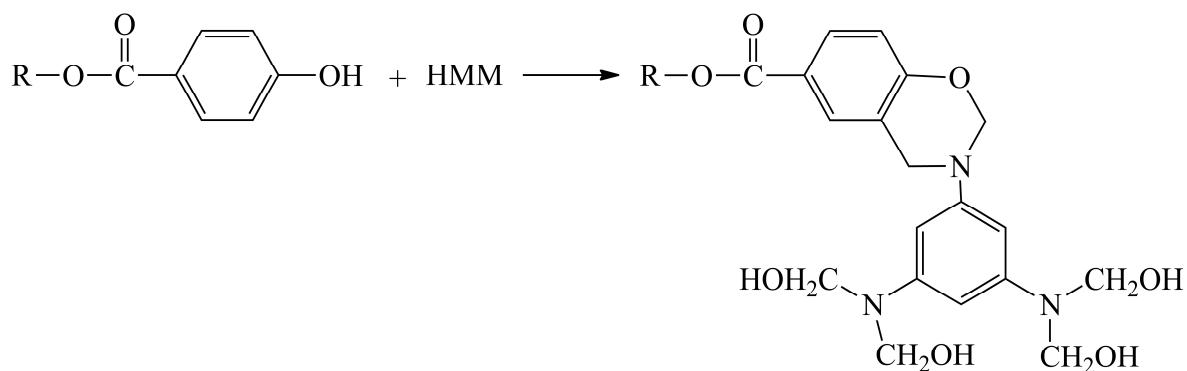


Fig. 48. Reaction between HMM and a parahydroxybenzoic acid derivative.

2.2.3 Azetidine functions [166-169]

Azetidines represent a class of very interesting compounds possessing a double reactivity. They are obtained from the reaction involving a primary amine and epichlorohydrine, as illustrated in Fig. 49.

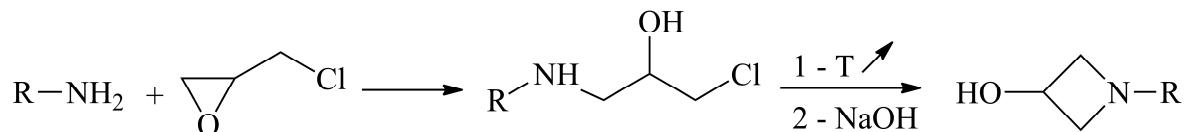


Fig. 49. Reaction of a primary amine with epichlorohydrine to obtain azetidinol.

They can react either i) by cationic homopolymerization [166] to give original polyamine compounds bearing secondary alcohols (Fig. 50), or ii) by copolymerization with acrylic acid to lead to a nitrogenated polyester also containing secondary alcohols, as illustrated by Fig. 50.

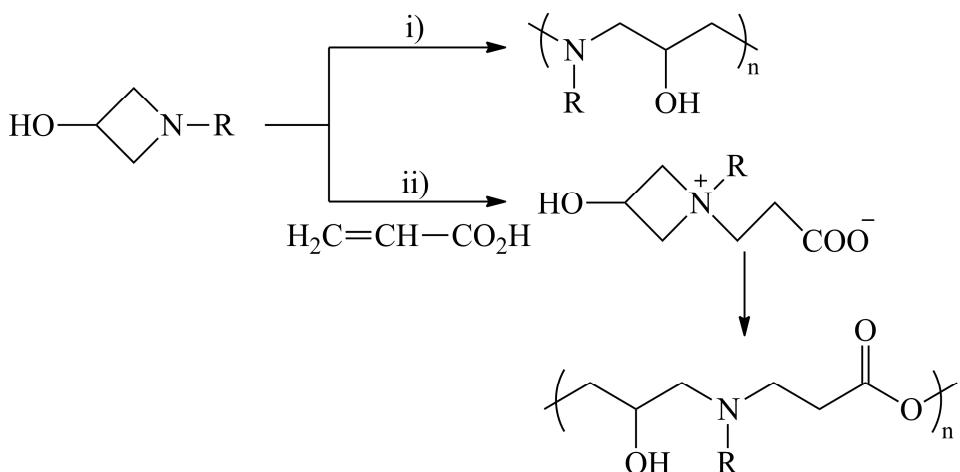


Fig. 50. Azetidinol involved in (i) cationic homopolymerization or in (ii) copolymerization with an acrylic acid.

Transesterification of the alcohol function gives the corresponding acrylate or methacrylate monomers, as shown in Fig. 51.

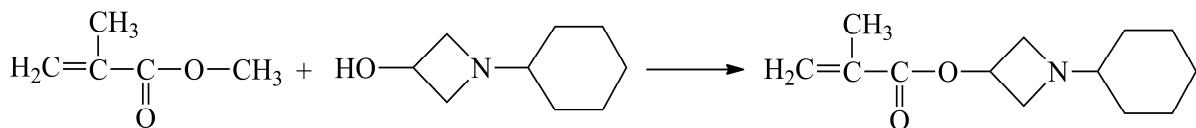


Fig. 51. Formation of a methacrylate monomer bearing an azetidine function by reaction between a methacrylate and an azetidinol.

This monomer easily copolymerizes with methyl methacrylate (MMA) to give water soluble polymers when the N-cyclohexylazetidine (CHA) content is higher than 40 %. Fig. 52 illustrates the quaternization of nitrogen atom by a proton or an alkyl group, which allows the subsequent crosslinking of the copolymer. Hence, the resulting amino group can attack another azetidinyl site. This crosslinking reaction occurs from about 95 °C for copolymers based on MMA, whereas it starts from 61 °C for butyl acrylate copolymers [167]. This property of self-crosslinking has been used to avoid wool-felting during washing [168,169].

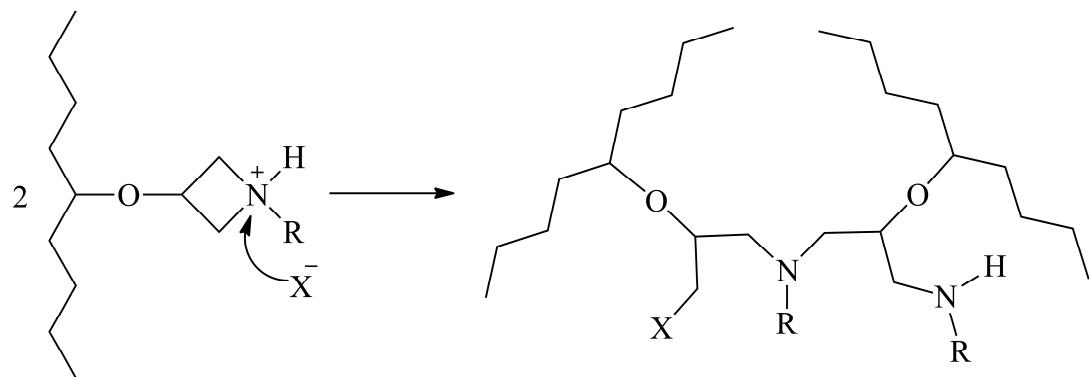


Fig. 52. Crosslinking of a polymethacrylate polymer bearing quaternized azetidine.

2.2.4 Diels-Alder reactions [170-176]

Diels-Alder system can also lead to crosslinked products. The Diels-Alder [4+2] crosslinking and step polymerization reactions are schematically represented in Fig. 53. This reaction scheme offers a wide variety of functional groups suitable for both polymerization and crosslinking.

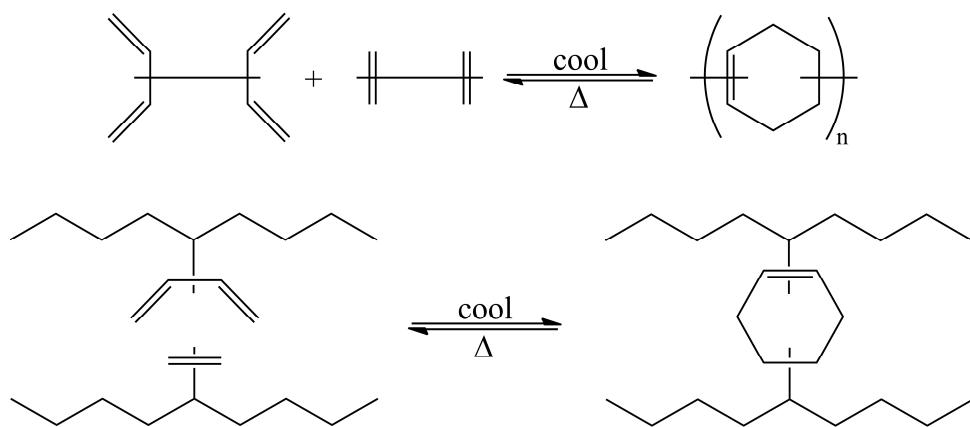


Fig. 53. Example of Diels–Alder [4 + 2] reaction in polymer chemistry.

An example of a telechelic poly(butyl acrylate) including the structure prepared by Edelmann and Ritter [170] is shown in Fig. 54.

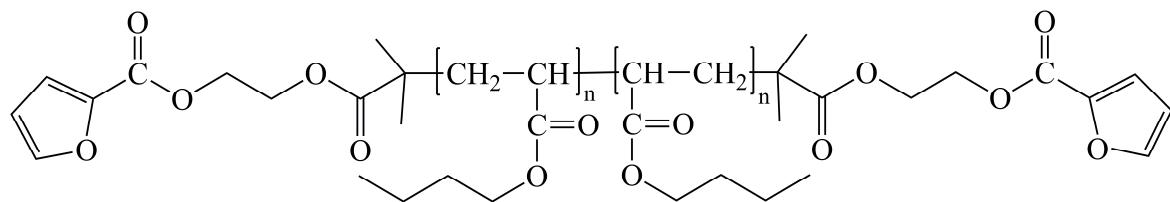


Fig. 54. Structure of telechelic difuranic poly(butylacrylate).

The dienophile used is an unsaturated copolyester, and the film hardening is obtained at 100 °C. Such a strategy has also been applied successfully from polymers bearing furan dangling groups. Indeed, polyacrylic-type coatings have been crosslinked with maleimides [171,172], such as those reported in Fig. 55.

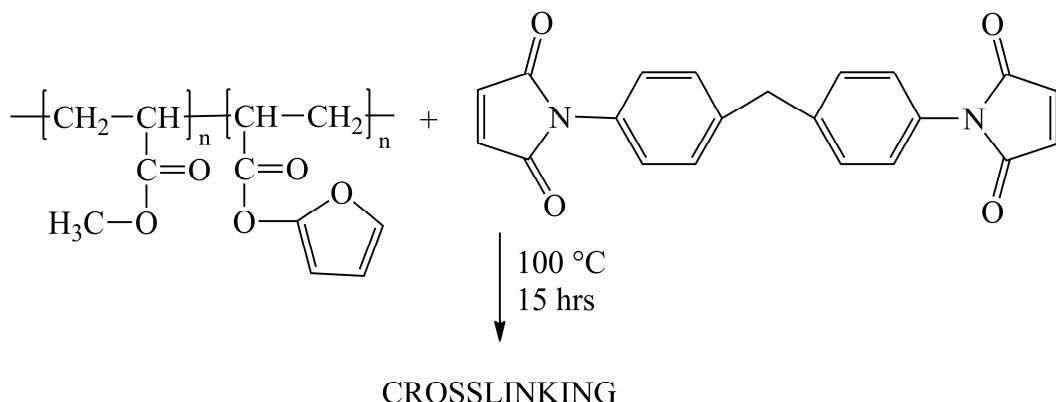


Fig. 55. Crosslinking of polyacrylic bearing furan group with maleimides telechelic compounds.

The reaction between a furan (or difuran) compound and a bismaleimide has been implemented to obtain thermally reversible crosslinked polymers [173,174]. Chen et al. [175] developed self healing polymers using the reversibility of the Diels-Alder reaction, such as that shown in Fig. 56. The crosslinking obtained is thermally reversibility, but this reversibility is not quantitative. After 15 minutes at 150 °C, 25 % of the linkages were lost, returning to the initial state on cooling to 80 °C.

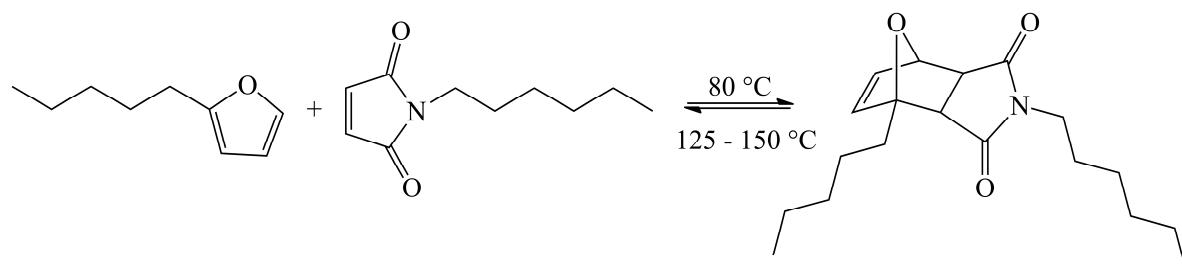


Fig. 56. Reversible Diels–Alder reaction between furan and maleimide compounds.

A French team[176] also developed the same type of reversible crosslinking for silicone bearing furan side groups using the reaction scheme displayed in Fig.57. The results showed that T_g of the crosslinked copolymer ($-111\text{ }^{\circ}\text{C}$) was very close to that of its linear precursor ($T_g = -112\text{ }^{\circ}\text{C}$), indicating that PDMS soft segments were preserved.

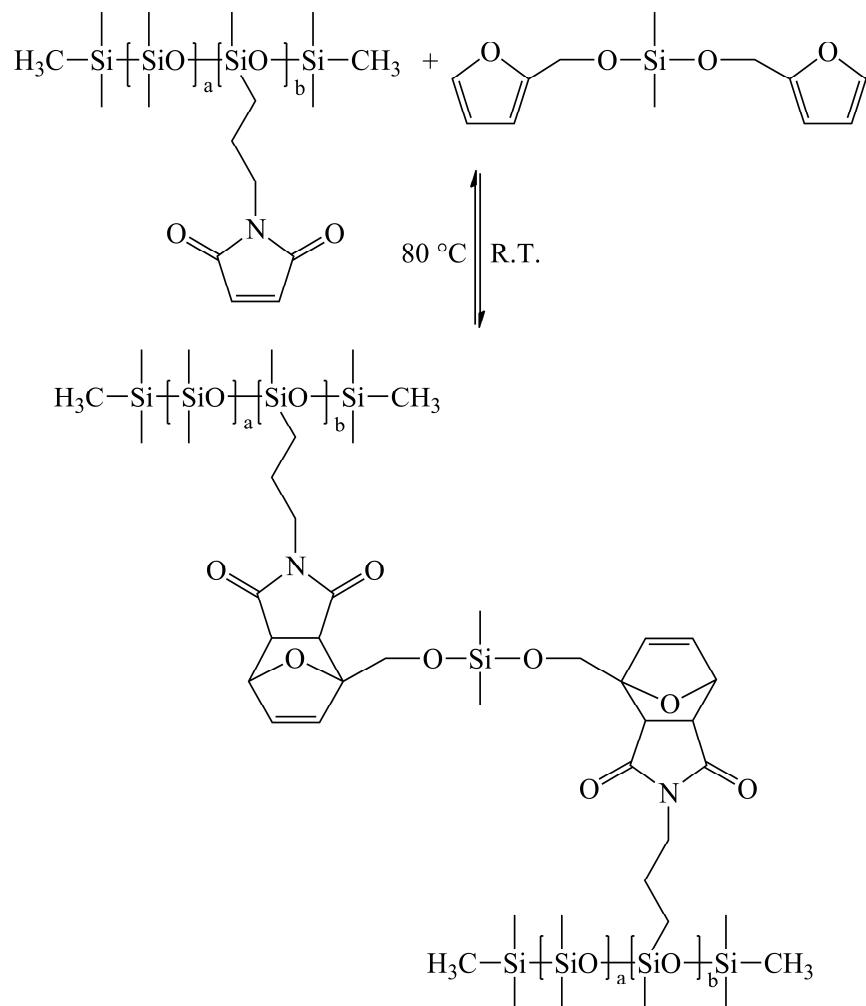


Fig. 57. Crosslinking of a silicone polymer bearing furan side groups by Diels–Alder reaction.

The reversibility of crosslinking is very important because it can give many benefits. For example, the reversibility can enhance the recyclability of polymers and can also facilitate its process.

2.2.5 1,3-Dipolar cycloaddition and “Click chemistry” reaction [177-187]

The concept of “click chemistry” based on a 1,3-dipolar cycloaddition was first pioneered by Huisgen et al. [177] in 1967 and then revisited and developed by the Sharpless group [178]. As illustrated in Fig. 58, the principle of “click chemistry” which can be explained by the condensation reaction between an azido group and a triple bond in the presence of catalyst.

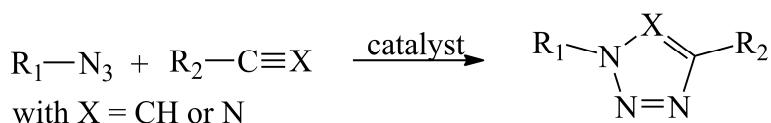


Fig. 58. General reaction illustrated the principle of “click chemistry”.

This method possesses several benefits because the reactions occur at low temperatures (< 100 °C), give high yields and are tolerant to the media since they can be carried out in the presence of oxygen and even in water. The reaction needs a catalytic system, such as Cu(I)/pentamethyldiethylene triamine (PMDETA) or Cu(II)/Ascorbic acid.

Various authors [179-183] have published reviews on the use of “click chemistry” in the field of polymers. Diaz et al.[184] utilized the “click” concept to synthesize some organogels, as shown in Fig. 59. Jonhson *et al* .[185] crosslinked polyacrylates, synthesized by atom transfer radical polymerization (ATRP), *via* the “click chemistry” concept to obtain a star polymer (Fig. 60).

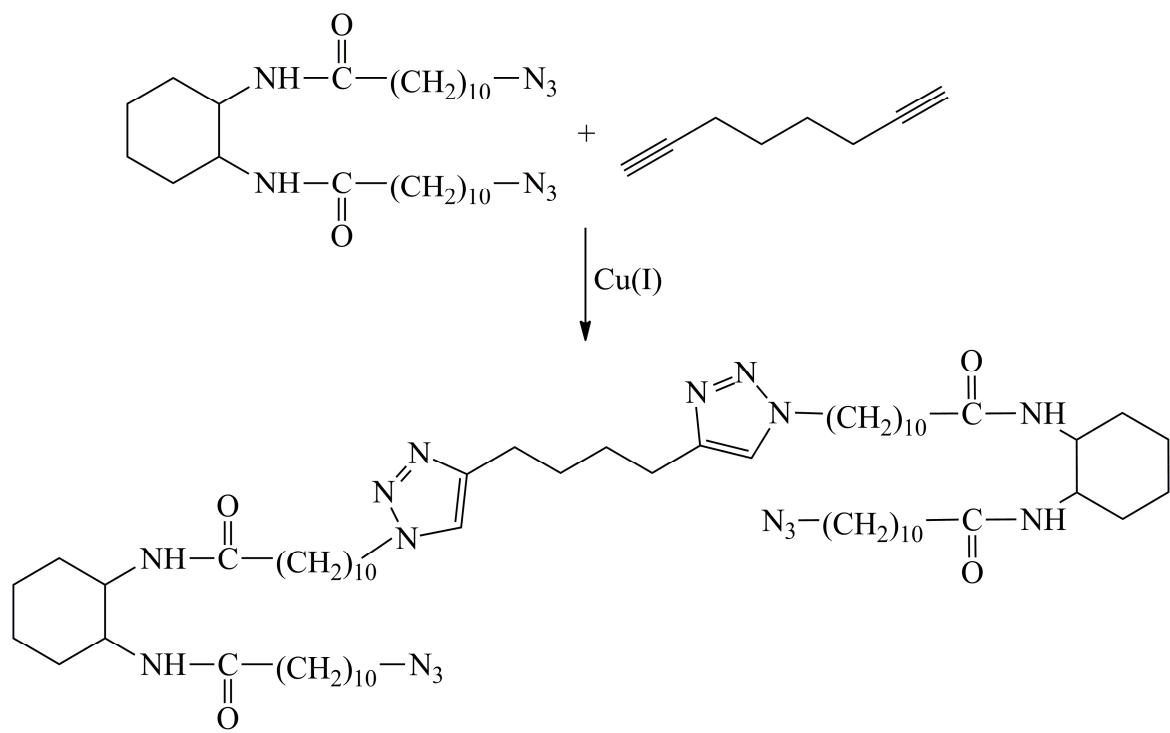


Fig. 59. Synthesis of organogel by click chemistry.

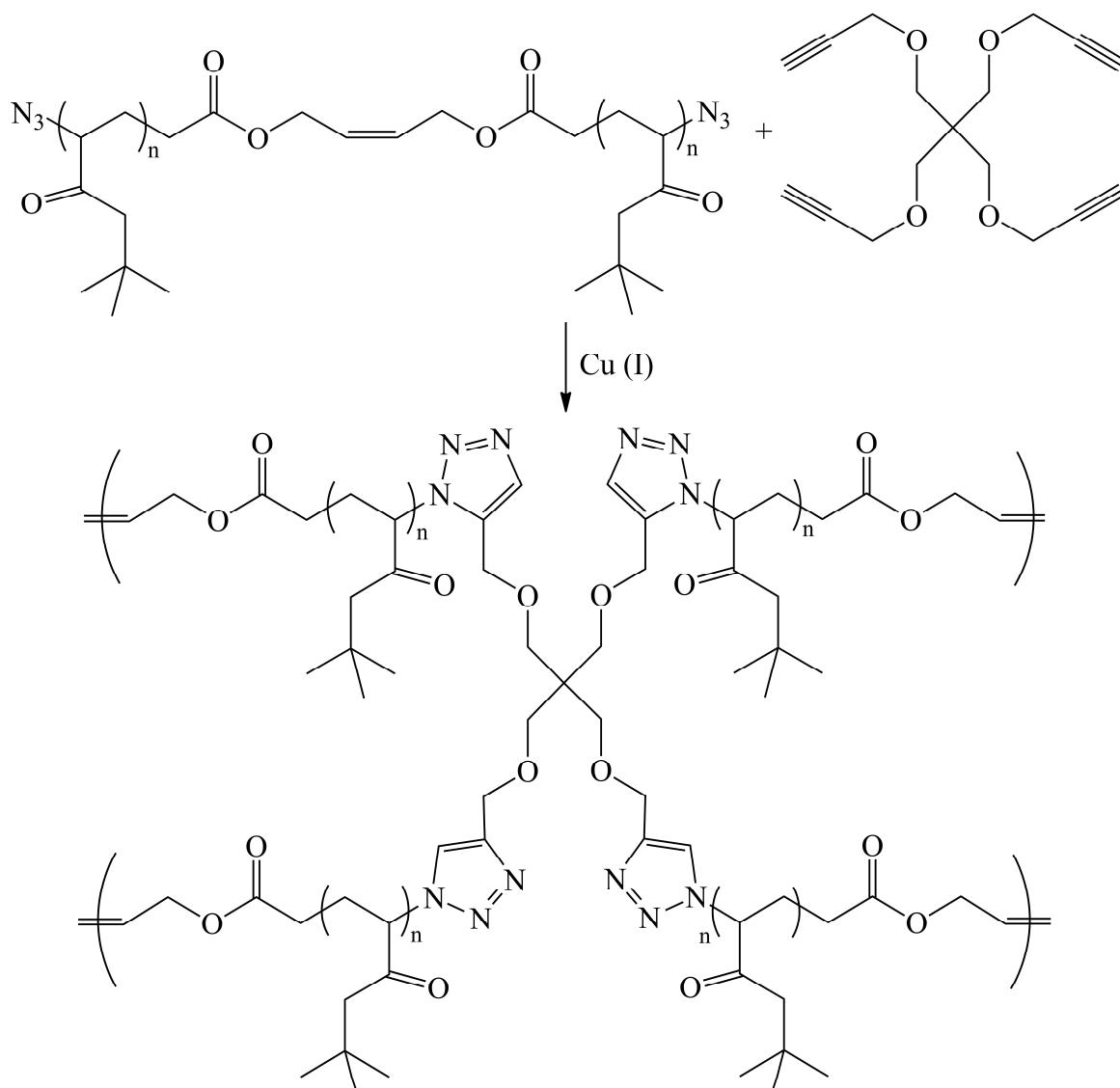


Fig. 60. Crosslinking of end-azido polyacrylate with an acetylenic crosslinker agent.

Nowadays, the “click chemistry” is extensively used and its development is very fast. However, main issues on the explosiveness and toxicity of azides must be overcome for a suitable adaptability of the “click chemistry” towards industrial scales. Several studies consist in searching for catalytic systems to improve the yield and to decrease the reaction temperature. For example, a catalytic system adapted to crosslink a fluorinated polymer bearing nitrile functions (e.g., Kalrez® marketed by DuPont Performance Elastomers) and a telechelic bis-azido perfluoroalkane [186] is in progress in order to decrease the crosslinking temperature, see Fig. 61.

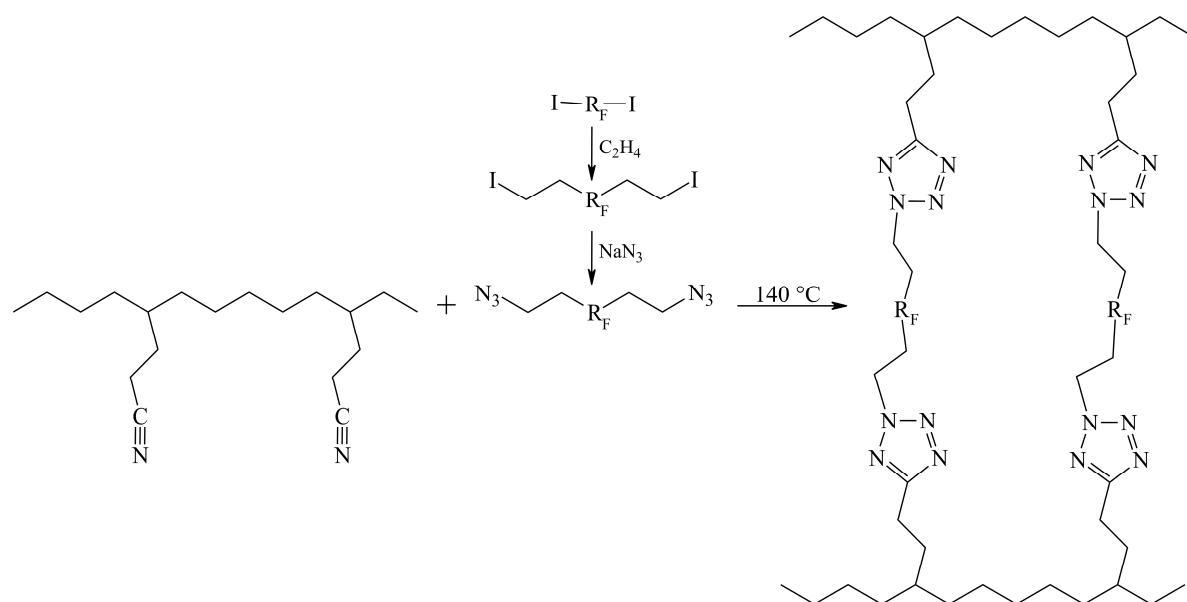


Fig. 61. Crosslinking of a fluorinated polymer with a telechelic bis-azido fluoroalkane by 1,3-dipolar cycloaddition.

Under certain conditions, “Click Chemistry” and the Hay (or Glaser) coupling (see 2.1.6) offer competitive reaction routes [187].

2.2.6 Conclusion

For crosslinking that occurs at intermediate temperatures, various strategies have successfully been used involving key reactions between i) carboxylic acids and various reactive groups such as epoxides (in the presence of specific amino or metallic catalysts) or oxazolines; ii) hydroxyl groups with protected urethanes, azlactones or methylol amide functions; iii) azetidines; iv) Diels Alder type reaction, and finally v) by “Click Chemistry”. All of these reactions require specific conditions and in certain cases (e.g., bisfuran/bismaleimide) they may be reversible as the temperature approaches 150°C . Searched applications are coatings, films, self-healing polymers or textile finishings.

3 – Conclusion:

Crosslinking reactions enable the preparation of materials with improved mechanical, thermal and physico-chemical properties. This review provides a non-exhaustive up-to-date summary

of various strategies of crosslinking. There are no universal systems to carry out crosslinking since it depends on specific groups born by polymers. Considering the influence of temperature, various key functions can be used appropriately to react onto themselves or onto complementary functional groups. For example, at low temperature, specific groups of interest are acetate, isocyanate, water (for sol-gel systems). In fact, the process must be carefully designed since the reactivity plays a great role (e.g., to avoid mixing too reactive components before the processing). At intermediate temperature, various specific functions can lead to crosslinking, such as i) carboxylic acid with epoxides or oxazolines; ii) alcohols with protected urethanes, azlactones or methylol amide function; or other groups, such as azetidines, or key reactions, such as Diels Alder or “Click Chemistry”. However, it can be expected that cleaner processes will also be investigated and depending upon environmental concerns (e.g., regarding EPA or REACH regulations), various reactions will be revisited, improved or banned. In certain conditions, reversible reactions may occur and open to further applications (paints and coatings, membranes, elastomers or self-healing polymers). Moreover, it can be expected that other interesting functions will also be able to produce post-crosslinkable materials under specific conditions not been mentioned in that review (e.g., irradiation by X-Ray, photons, electrons, which are industrial processes,). This should attract industrial or academic researchers' interest and motivation for the next decades.

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CHAPITRE 2

POST-RETICULATION D'UN ELASTOMERE FLUORE

HAUTE PERFORMANCE CONTENANT DES FONCTIONS

NITRILES PAR CYCLOADDITION DE HUISGEN EN

PRESENCE D'UN DIAZIDE TELECHELIQUE

Post-Réticulation d'un élastomère fluoré haute performance contenant des fonctions nitriles par cycloaddition de Huisgen en présence d'un diazide téléchélique

I. Introduction :

Les polymères fluorés sont très utilisés dans l'industrie[1-4] « High Tech » de par leurs remarquables propriétés (résistance thermique, chimique et oxydatives, propriétés optiques, diélectriques, hydrophobes et oléophobes...). Cependant, pour améliorer certaines de leurs propriétés, telles que les propriétés mécaniques et de tenue aux solvants polaires et apolaires, la réticulation[5-7] est alors à envisager.

Dans cette partie nous souhaitons réaliser la réticulation d'un élastomère fluoré et pour cela nous nous intéresserons plus particulièrement à l'utilisation de la réaction de cycloaddition développée par Huisgen[8] à la fin des années 60. Cette réaction appelée cycloaddition 1,3-dipolaire (Schéma 1) se déroule entre un composé dipolarophile et un composé 1,3-dipolaire, et entraîne la formation d'un cycle à cinq atomes.

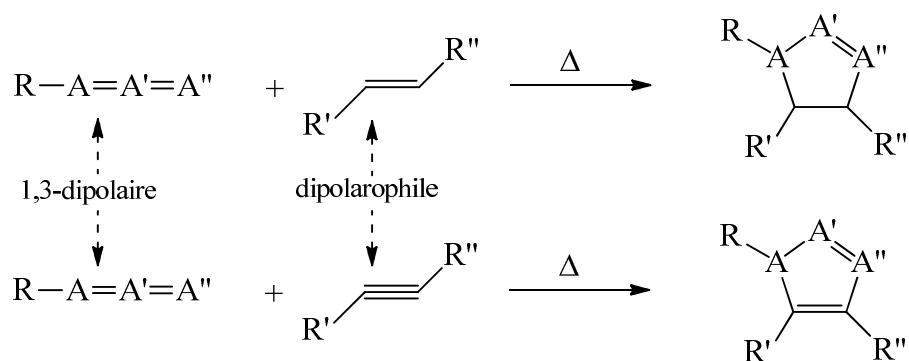


Schéma 1 : Cycloaddition de Huisgen entre un dipolarophile et un composé 1,3-dipolaire.

Les composés 1,3-dipolaires contiennent un ou plusieurs hétéroatomes et doivent posséder au moins une forme mésomère les représentant sous la forme d'un dipôle chargé (Schéma 2).

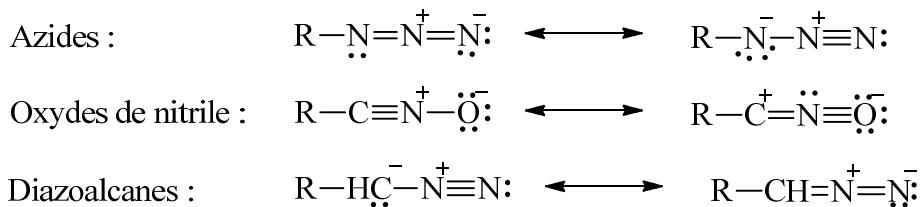


Schéma 2 : Exemples de composés 1,3-dipolaire

Les dipolarophiles sont des molécules possédant des groupes allyle, alcynyle ou des groupes possédant des hétéroatomes tels que nitriles et carbonyles. En 2001, le groupe dirigé par Sharpless[9] a revisité cette réaction en utilisant un catalyseur à base de cuivre afin d'améliorer la régiosélectivité, la vitesse et de diminuer la température de cette réaction. Par ce procédé il a créé le concept de « click chemistry » qui à l'heure actuelle connaît un succès retentissant et a déjà fait l'objet de plusieurs revues[10-12].

L'objectif de ce chapitre concerne la réticulation par cycloaddition de Huisgen d'un élastomère fluoré synthétisé par DuPont Performance Elastomer, le Kalrez® (Schéma 3).

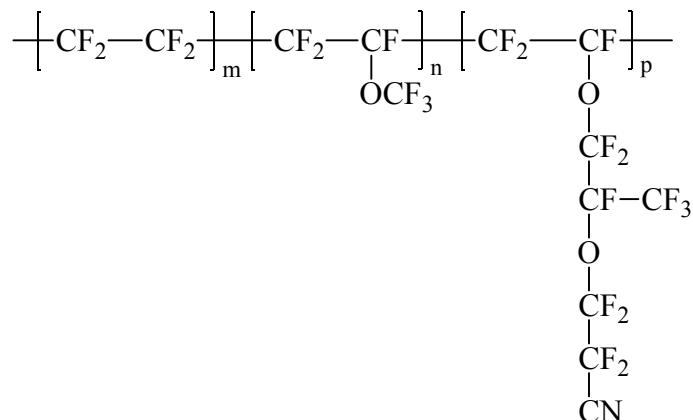


Schéma 3 : Formule chimique du Kalrez®

Celui-ci est un terpolymère à base de tétrafluoroéthylène (TFE), de perfluoro(méthyle vinyl éther) (PMVE) et de perfluoro(8-cyano-5-méthyle-3,6-dioxa-oct-1-ène) (8-CNVE) dont les proportions massiques de chaque monomère sont respectivement comprises dans les intervalles suivants 65-80 %, 20-34 % et 1-3 %. Cet élastomère est utilisé comme joint de haute performance dans des domaines allant des applications aérospatiales, pharmaceutiques[13] et l'électronique. La présence de groupements nitriles pendants, qui sont

des composés dipolarophiles, permet d'envisager la cycloaddition de Huisgen afin de réticuler ce copolymère cyané. Le procédé utilisé par DuPont Performance Elastomer[14] pour mener à bien cette réticulation nécessite beaucoup d'énergie (car la température utilisée est d'environ 300 °C durant deux jours[15]) et les objectifs sont donc ici de réduire le temps et la température de réaction.

Afin de satisfaire ces objectifs nous avons souhaité utiliser la réaction de Huisgen comme voie de réticulation de part ses propriétés précédemment décrites mais également en vu d'un éventuel dépôt de brevet car cela n'avait à notre connaissance pas été utilisé pour la réticulation de polymères fluorés dans la littérature.

Des études modèles ont tout d'abord été réalisées pour deux raisons principales. La première afin d'appréhender la réaction et les conditions s'y rapportant sur des systèmes fluorés moins complexes ce qui est rarement décrit dans la littérature, et la seconde car l'utilisation du Kalrez® est couteuse notamment du fait de l'utilisation de solvant fluoré nécessaire à sa solubilisation.

II. Etude modèle mettant en jeu le 8-CNVE :

II-1) Synthèse d'un composé fluoré 1,3-dipolaire :

Afin de réaliser la cycloaddition de Huisgen nous avons tout d'abord envisagée la synthèse d'un composé fluoré 1,3-dipolaire. Cette synthèse se décompose en deux étapes, schéma 4.

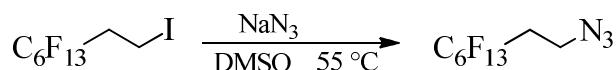
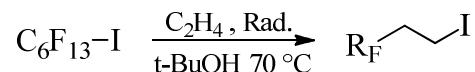


Schéma 4 : Synthèse bi-étape d'un composé mono azidé à partir d'un iodure de perfluorohexyle.

Lors de la première étape, le 1-iodoperfluorohexane est éthyléné dans un autoclave en présence d'éthylène, amorcée par le di(4-tert-butylcyclohexyl)peroxydicarbonate (Perkadox 16) et de tert-butanol (t-BuOH), respectivement réactif, amorceur et solvant. Cette étape est

réalisée à 70°C durant 4 heures et l'éthylène est introduit en fort excès afin que la réaction soit complète (conversion totale du C₆F₁₃I). D'après la littérature[16], nous remarquons que même en fort excès d'éthylène ces conditions réactionnelles ne conduisent pas aux dérivés bis et triéthylénés. Le composé ainsi obtenu (C₆F₁₃C₂H₄I) a ensuite été analysé par spectroscopie RMN (¹H et ¹⁹F) afin de confirmer l'obtention sélective du composé monoéthyléné et le spectre RMN ¹⁹F du composé après ethylénation (Figure 1) permet de prouver que celle-ci est bien complète.

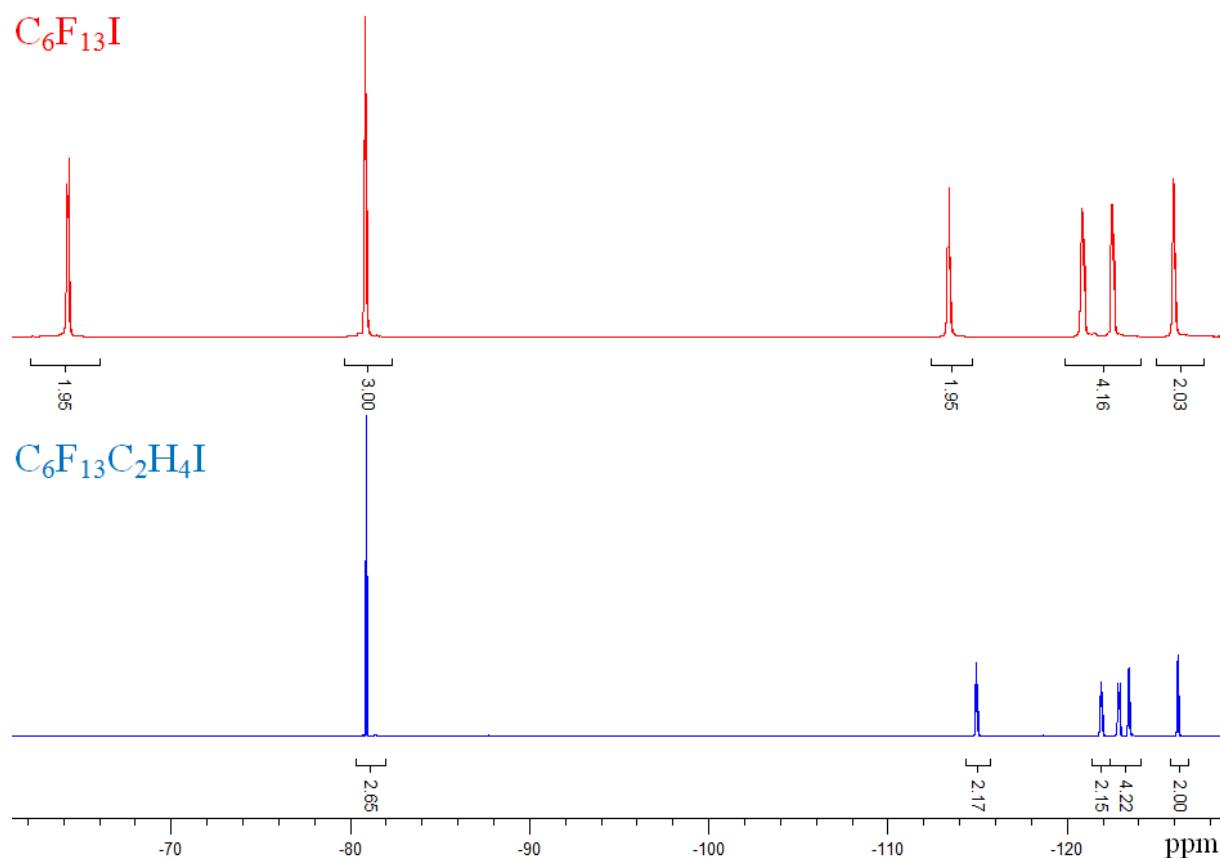


Figure 1 : Spectres RMN ¹⁹F du C₆F₁₃I (haut) et du C₆F₁₃C₂H₄I (bas) dans CDCl₃

En effet le pic caractéristique du motif -CF₂-I situé à -59 ppm disparait après réaction et se blinde à -122,6 ppm correspondant au motif -CF₂-CH₂- . Cette étape a permis d'obtenir le composé éthyléné après purifications avec un rendement molaire compris entre 70 % et 85 % ce qui est satisfaisant par rapport à ceux de la littérature[16,17].

La deuxième étape représentée sur le schéma 3 consiste en une substitution nucléophile de l'iode terminal par un groupement azido (-N₃)[18,19]. Cette étape est réalisée en présence

d'azoture de sodium (NaN_3) et de diméthylsulfoxyde (DMSO), respectivement réactif et solvant. Après purification, le produit obtenu (AzidoC_6) a ensuite été analysé par spectroscopie RMN ^1H et infrarouge. La figure 2 représentant le spectre infrarouge du produit AzidoC_6 et met en évidence la bande caractéristique des azides à 2110 cm^{-1} et des liaisons C-F vers $1200\text{-}1000\text{cm}^{-1}$.

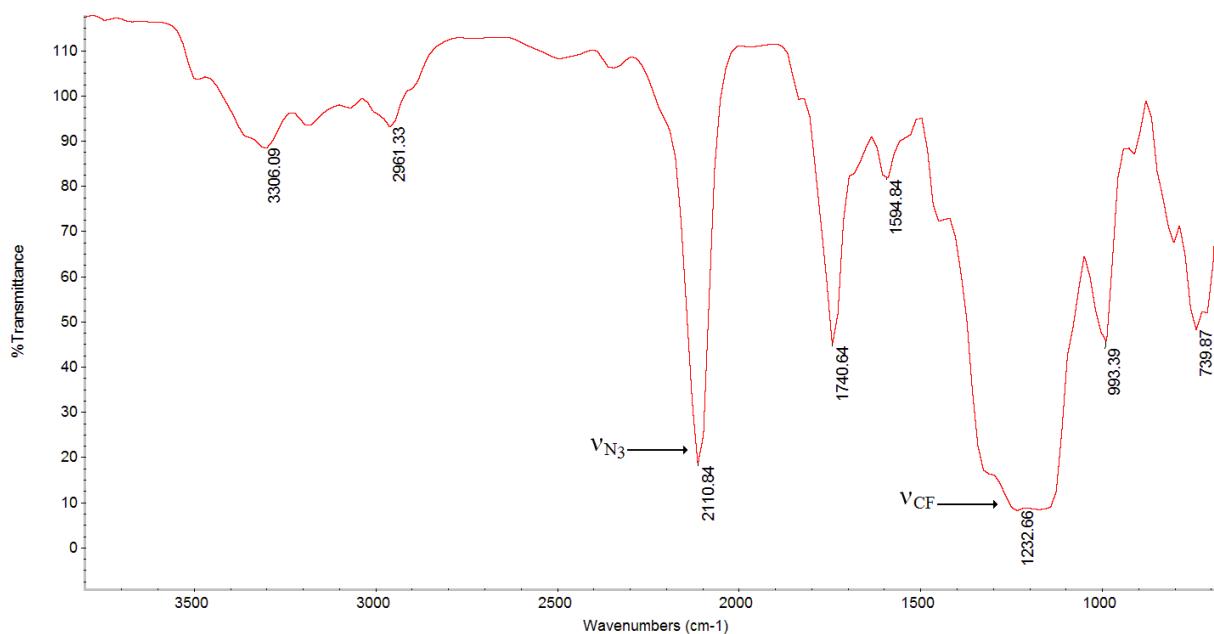


Figure 2 : Spectre infrarouge du produit $\text{C}_6\text{F}_{13}\text{C}_2\text{H}_4\text{N}_3$

Le spectre RMN ^1H du composé après azidation comparé au produit de départ est présenté en Figure 3.

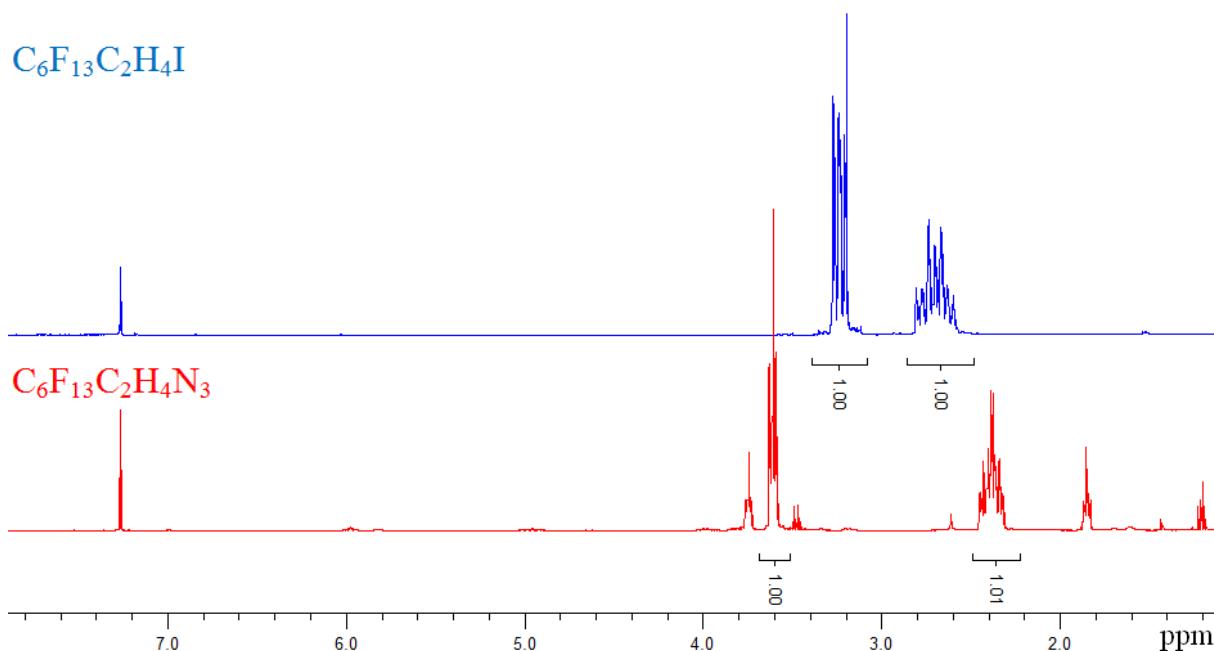


Figure 3 : Superposition des spectres RMN ¹H des composés C₆F₁₃C₂H₄I (haut) et C₆F₁₃C₂H₄N₃ (bas) dans CDCl₃

Après réaction, le spectre montre un déblindage des protons de l'unité -CH₂-CH₂-N₃ adjacents au groupe azido terminal. Cela vient du fait que le groupe azido, qui est un groupe électro-attracteur, est un meilleur accepteur d'électron que le groupe iodo. Les résultats combinés de ces analyses RMN et IR nous démontrent que la réaction de substitution de l'iode par un azide a été réalisée avec succès. A partir des intégrations respectives des signaux attribués aux méthylènes des -CH₂-N₃ vis-à-vis des -CH₂-I, le taux de substitution est estimé à une valeur supérieure à 95 %. Le rendement après purification de cette substitution est de 65 % ce qui est satisfaisant si on se réfère à la littérature[18].

II-2) Cycloaddition de Huisgen avec le 8-CNVE et AzidoC₆:

La température de réaction étant supérieure aux températures d'ébullition des solvants utilisés ou du 8-CNVE, les différents essais ont été réalisés dans des tubes de Carius et le schéma réactionnel est donné dans la Schéma 5.

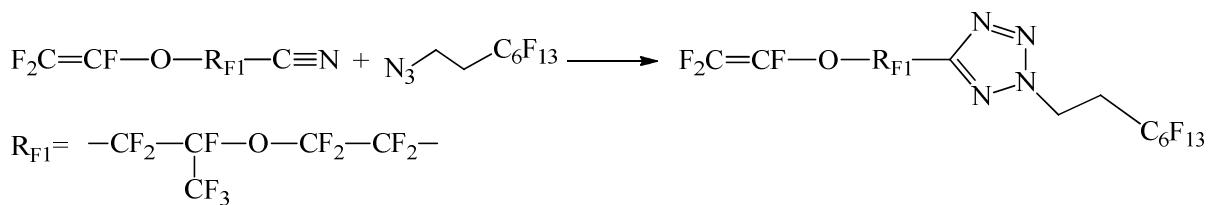


Schéma 5 : Schéma réactionnel de la cycloaddition de Huisgen avec le 8-CNVE et le $\text{C}_6\text{F}_{13}\text{C}_2\text{H}_4\text{N}_3$.

L’AzidoC6 est incorporé en léger excès (rapport molaire de 1,1) de façon à ce que la réaction soit complète sur le 8-CNVE. Le suivi des réactions a été réalisé par RMN ^{19}F afin de vérifier le bon déroulement de la réaction. La figure 4 permet de comparer les spectres RMN ^{19}F du 8-CNVE et celui du produit obtenu après réaction à 150 °C durant 24 heures sans solvant ni catalyseur.

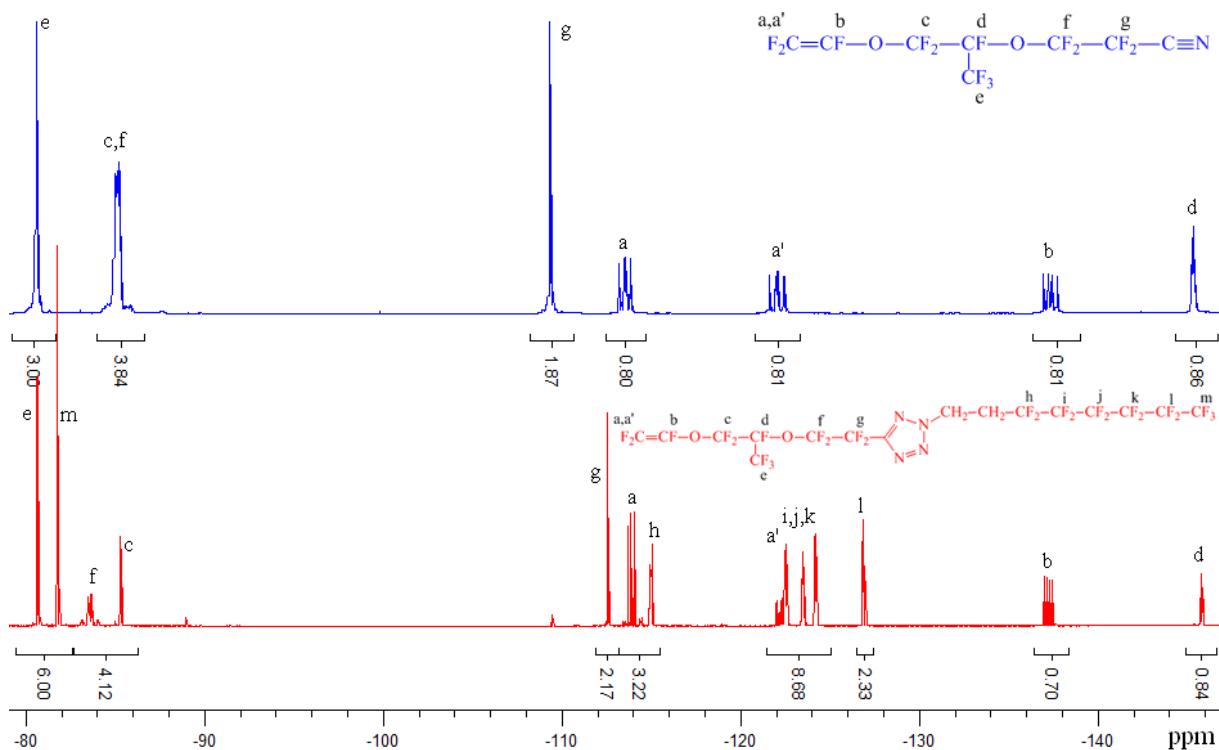


Figure 4 : Superposition des spectres RMN ^{19}F du 8-CNVE (haut) et du produit après cycloaddition (bas).

On remarque un blindage assez important des atomes de fluor adjacents au tétrazole (F_g) et qui étaient précédemment adjacents à la fonction nitrile puisque leur pic caractéristique

présent avant réaction à -109,4 ppm est après réaction à -112,6 ppm. Nous notons également que les signaux caractéristiques des atomes de fluor correspondant au groupe C₆F₁₃ de l'AzidoC₆ sont identifiables. Cela nous démontre que la réaction s'est déroulée avec succès et cela avec un rendement supérieur à 90%.

Le tableau 1 indique que les conditions les plus appropriées dans notre étude sont une température de 150°C, un temps de réaction de 24 heures en absence de catalyseur.

Tableau 1 : Conditions expérimentales et résultats des différents essais de cycloaddition du 8-CNVE avec l'AzidoC₆.

Rapport Molaire AzidoC ₆ / 8-CNVE	Catalyseur	Solvant	Température (°C)	Temps (h)	Rdt molaire (%)
1,1	CuCl/Bipyridine	CH ₂ Cl ₂	80	24	~ 0
1,1	CuCl/Bipyridine	THF	80	24	~ 0
1,1	ZnBr ₂	THF	80	24	~ 0
1,1	/	/	150	20	> 90
1,1	/	/	80	24	~ 0

II-3) Conclusions :

La cycloaddition de Huisgen du C₆F₁₃C₂H₄N₃ sur le 8-CNVE s'est déroulée avec succès. Les conditions expérimentales ainsi que les méthodes de purifications des différentes étapes d'éthylénation, d'azidation et de cycloaddition ont ainsi pu être optimisées en vue de la transposition de cette méthode sur un polymère porteur de fonctions nitriles. On peut également noter que l'absence d'un catalyseur est aussi avantageuse et évite ainsi une purification souvent coûteuse et incomplète après réaction.

III. Réticulation du Kalrez® par cycloaddition 1,3-dipolaire :

Après avoir réalisé dans la partie précédente des études modèles afin d'optimiser les conditions de réaction et la mise en œuvre, nous allons ici utiliser ces données afin d'appliquer ce procédé à la réticulation du Kalrez®. Cette voie a été étudiée parce que la technique de réticulation classiquement utilisée par DuPont[21] est couteuse en énergie comme l'illustre le Schéma 6.

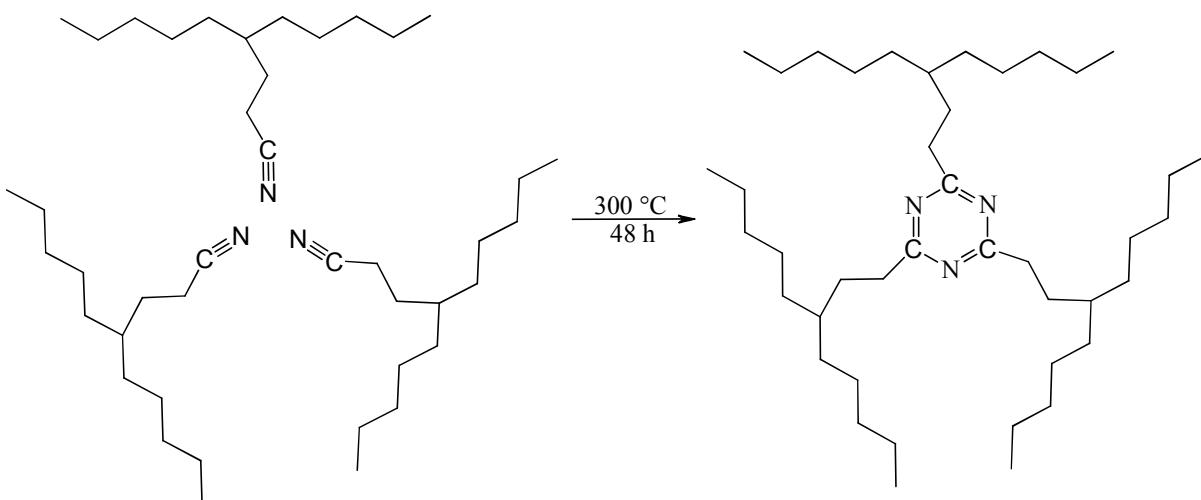


Schéma 6 : Méthode classique de réticulation utilisée par la société DuPont par trimérisation des nitriles du Kalrez® permettant la formation de ponts triazine.

III-1) Synthèses de l'agent réticulant :

La stratégie de synthèse de l'agent réticulant 1,10-diazido-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodécan (BisAzidoC₆) est décrite dans la Schéma 7.

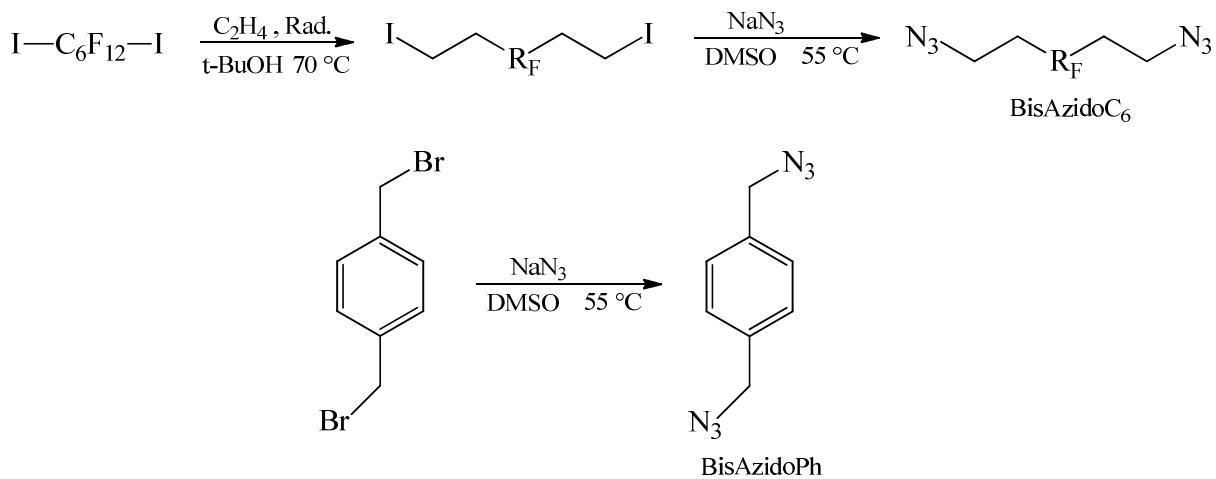


Schéma 7 : Schéma réactionnels pour l'obtention du composé BisAzidoC6.

La synthèse du BisAzidoC₆ nécessite la même stratégie que celle utilisée pour l'obtention du composé AzidoC₆ c'est-à-dire une éthylénation suivie d'une azidation. Les suivis de réaction ont été réalisés par RMN ¹⁹F et ¹H comme le montrent les figures 5a et 5b.

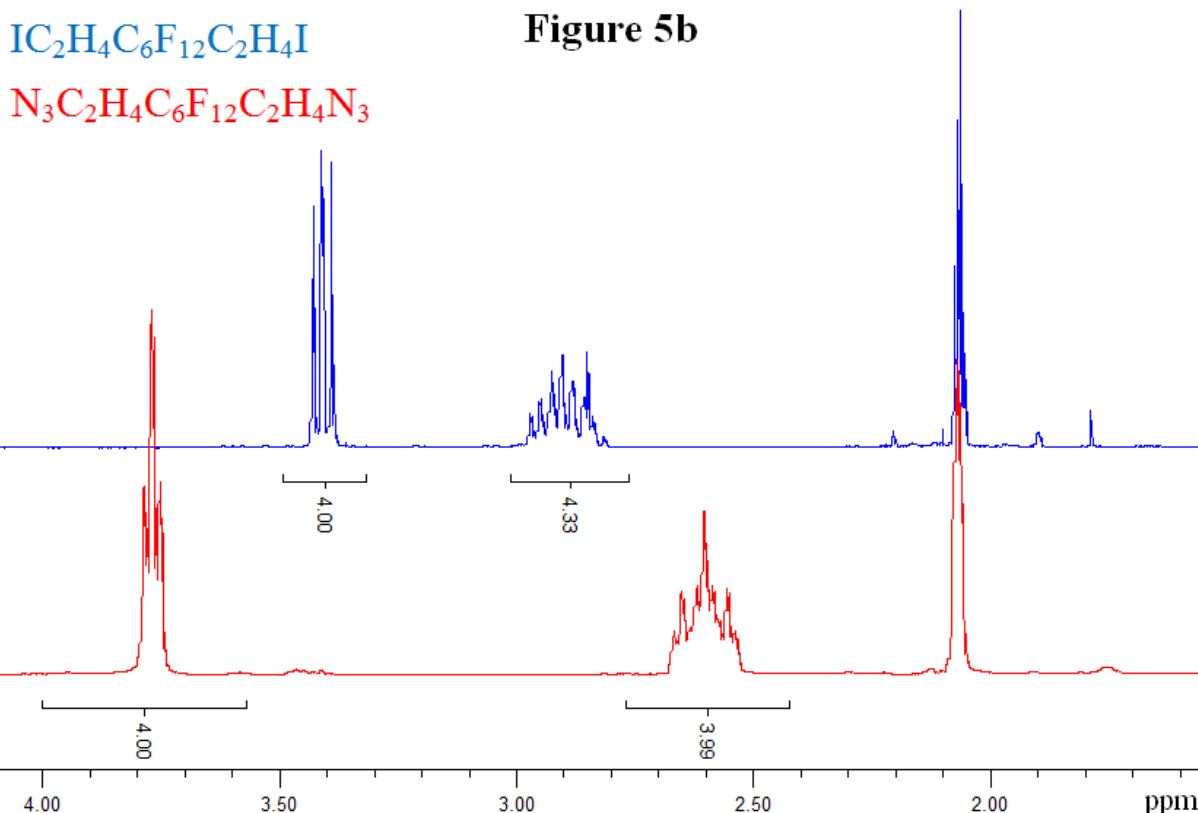
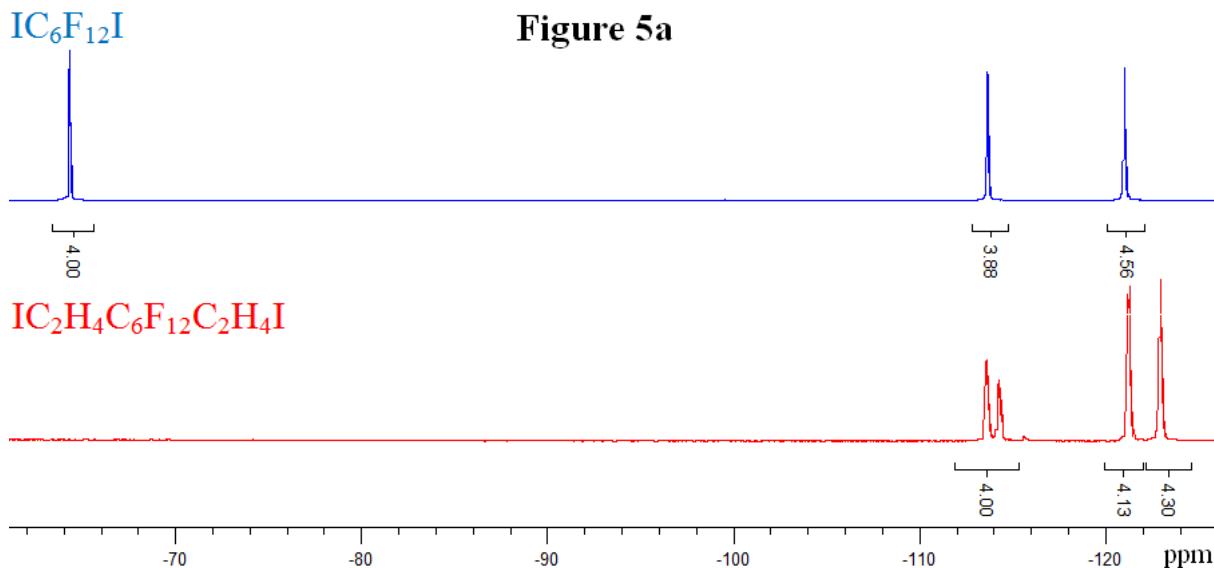


Figure 5 : a) Superposition des spectres RMN ^{19}F de l' $\text{IC}_6\text{F}_{12}\text{I}$ (haut) et de l' $\text{IC}_2\text{H}_4\text{C}_6\text{F}_{12}\text{C}_2\text{H}_4\text{I}$ (bas) après éthylénation, b) Superposition des spectres RMN ^1H dans l'acétone d_6 des composés *avant* (haut) et *après azidation* (bas).

Comme pour le $\text{C}_6\text{F}_{13}\text{I}$ éthyléné précédemment la réaction est ici complète de part la disparition totale du pic à -64,4 ppm. De même l'azidation est quasi-complète car nous

remarquons clairement les pics des protons des méthylènes « shifter » et ne notons pas la présence de pics correspondant aux méthylènes de produit non azidé.

Pour les différentes étapes de cette réaction, nous obtenons des rendements similaires (~65%) à ceux décrits dans la partie précédente pour le même type de synthèse.

III-2) Formation de films de Kalrez® réticulés :

Nous avons utilisé l'agent réticulant BisAzidoC6 dont la synthèse a été décrite dans la partie précédente. Selon les données fournies par DuPont sur les échantillons de Kalrez® utilisés le taux massique de 8-CNVE dans l'élastomère est inférieur à 3 %. La figure 6 illustre les différentes étapes de la mise en œuvre utilisée pour l'obtention de film de Kalrez® réticulés.

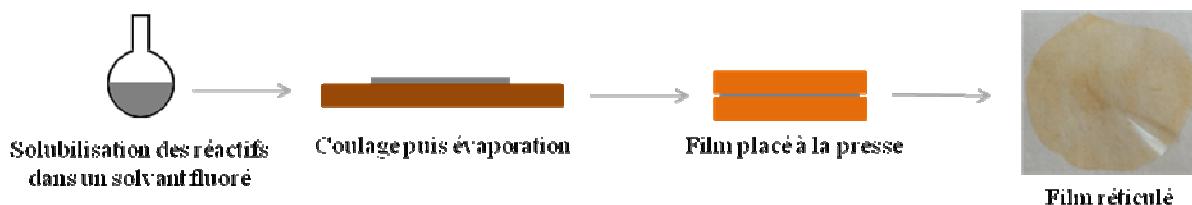


Figure 6 : Illustration des étapes nécessaires pour l'obtention d'un film de Kalrez® réticulé via un composé bisazido.

Le Kalrez® et le BisAzidoC6 sont solubilisés dans le perfluoro(butyltetrahydrofurane) (FC75), puis la solution est coulée afin d'obtenir un film après évaporation du solvant. Cette méthode présente l'avantage d'être simple à mettre en œuvre et l'étape cruciale pour l'obtention d'un film homogène est l'étape d'évaporation du solvant. En effet, cette évaporation ne doit pas être trop rapide afin d'éviter la formation de bulle à l'intérieur du film et pour cela une pré-évaporation est préalablement réalisée à froid (cf Partie expérimentale). La réaction quant se produit dans une presse à 150 °C durant 24 heures. Après réactions, des analyses thermiques (ATG et DSC) et spectroscopique (Infrarouge) ont été réalisées sur les films ainsi obtenus.

III-3) Analyses thermogravimétriques des films de Kalrez® réticulés :

Les films de Kalrez® réticulés ont été analysés par ATG afin de comparer leurs thermostabilités à celle du Kalrez® de départ mais également à un film ayant suivi une mise en œuvre identique à celle du film réticulé à l'exception de l'ajout du BisAzidoC6. La figure 8 présente la superposition des thermogrammes réalisés sous air de différents films de Kalrez® après réaction avec celui du Kalrez® de départ.

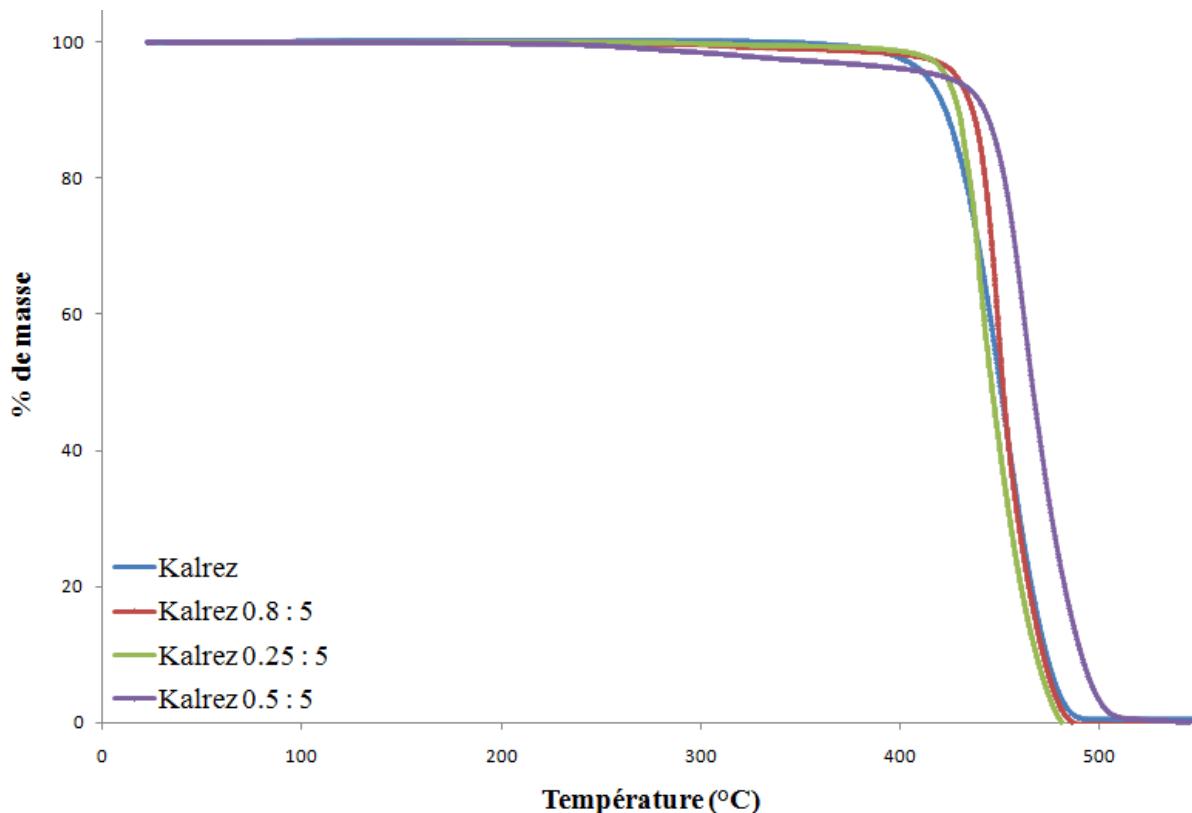


Figure 7 : Superposition des thermogrammes réalisés sous air de Kalrez® et de différents films de Kalrez® réticulés où Kalrez x : y représente le rapport massique de BisAzidoC6 :

Kalrez

Après réaction nous remarquons que la plupart des films présentent sensiblement le même thermogramme que celui du Kalrez® original. Cependant on note que les thermogrammes montrent une légère perte de masse dès 150 °C qui semblerait correspondre à l'évaporation de l'agent réticulant résiduel. Nous constatons également que l'échantillon présentant un rapport massique en BisAzidoC6 : Kalrez® de 0,5 : 5 avant réaction présente

une température de décomposition à 10% (T_{d10}) supérieure d'environ 20 °C au Kalrez® non réticulé.

III-4) Analyses infrarouge des films de Kalrez® réticulés :

Le film réticulé obtenu avec un rapport massique BisAzidoC6 : Kalrez® de 0,5 : 5 a été analysé par infrarouge et comparé au polymère de départ, le spectrogramme est présenté en Figure 14.

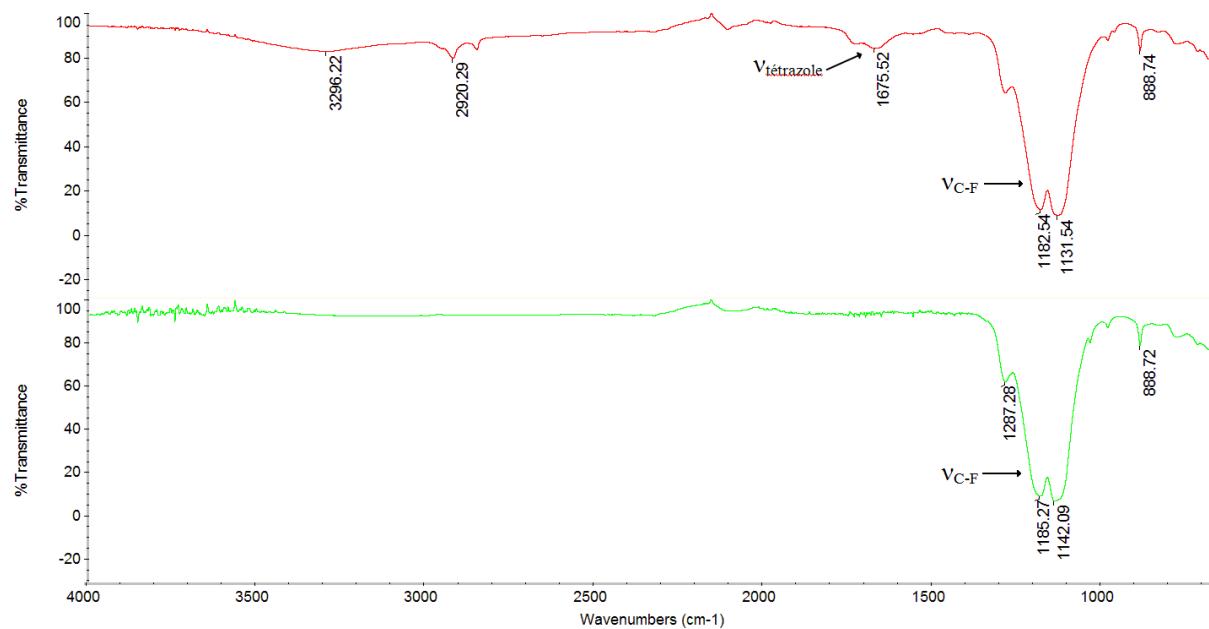


Figure 8 : Comparaison des spectrogrammes IR du Kalrez Pur et du Kalrez Réticulé.

On peut remarquer que les spectres du Kalrez pur et réticulés sont très proches. On remarque cependant une bande à 1675 cm^{-1} qui n'est pas présente sur le spectrogramme du Kalrez pur et qui correspond à la bande caractéristique des tétrazoles.

III-5) Analyses des taux de gonflement et d'extractible du Kalrez® réticulés :

Des analyses des taux de gonflements et d'extractibles ont été réalisées sur différents échantillons de Kalrez® réticulé. Les résultats obtenus sont regroupés dans le tableau 2.

Tableau 2 : Valeurs minimales, maximales et moyennes du taux de gonflement et d'extractible d'échantillons de Kalrez® réticulé.

	Valeur Minimale % massique	Valeur Maximale % massique	Valeur Moyenne % massique
Taux de gonflement	400	650	550
Taux d'extractible	10,5	13,9	12,6

On remarque que les valeurs des taux de gonflement et d'extractible sont élevées ce qui indique un faible nombre de nœud de réticulation. Le faible taux du monomère 8-CNVE dans le Kalrez® avant réticulation peut expliquer des valeurs aussi élevées. Il serait intéressant de synthétiser un Kalrez® contenant une proportion plus élevée de 8-CNVE afin de vérifier que sa réticulation par notre méthode entraînerait de plus faibles valeur des taux de gonflement et d'extractibles que celles obtenues avec les échantillons utilisés.

IV. Conclusions :

Des films de Kalrez® ont été réticulés grâce à la réaction dite de Huisgen à partir de copolymère pur et d'agents réticulant bis-azidés synthétisés avec un bon rendement (~ 65 %) après avoir déterminé les conditions de réaction sur des dérivés fluorés modèles. Les films réticulés ont ainsi été analysés par spectroscopie infrarouge et par analyse thermogravimétrique afin de confirmer la réticulation. Les températures de dégradation sous air des films réticulés ont été améliorées de plus de 10 °C après 10 % de perte de masse. Les mesures des taux de gonflement ont montré que le polymère réticulé présentait un gonflement très élevé ce qui indique le faible nombre de nœuds de réticulation. L'optimisation de cette réaction et de sa mise en œuvre permettra certainement d'améliorer encore les résultats dans le futur.

V. Partie expérimentale :

V-1) Réactifs :

Le télogène fluoré $C_6F_{13}I$ nous a été offert par la société Atofina tandis que l' IC_6F12I a été fourni par la société Apollo (Angleterre). Les produits suivants nous ont été fournis par Aldrich et leur pureté est donnée entre parenthèse : CuCl (99 %), Bipyridine (99 %), ZnBr₂ (98 %), 1,4-Bis(bromomethyl)benzene (98 %) et polystyrene-co-acrylonitrile ($M_n = 165000$ g.mol⁻¹ et de composition massique 25% en acrylonitrile). Le monomère 8-CNVE et les échantillons de Kalrez® ont été gracieusement fournis par la société DuPont Performance Elastomer (Willmington,USA). L'azidure de sodium de pureté 99% a été fourni par Acros Organics. Le perfluoro(butyltetrahydrofurane) nous a été offert par la société 3M. Enfin le di(4-tert-butylcyclohexyl) peroxydicarbonate (nommé Perkadox 16S, 99 %) a été gracieusement offert par Akzo Nobel (Compiegne).

V-2) Ethylénation d'un télogène fluoré de type R_FI ou IR_FI :

Les réactions d'éthylénation ont été réalisées dans un autoclave du fait de l'utilisation de l'éthylène qui est gazeux. L'autoclave a tout d'abord subi un test de mise sous pression afin de s'assurer de son étanchéité suivi d'un dégazage, ensuite l'autoclave a subi trois cycles consécutifs constitués d'une mise sous vide suivie d'un remplissage d'argon. Enfin le réacteur a été placé 25 minutes sous vide poussé afin de s'assurer une élimination aussi complète que possible de l'oxygène (celui-ci étant un inhibiteur de radicaux). Le télogène et le Perkadox 16S (2 % molaire par rapport à l'éthylène) préalablement dissous dans du tert-butanol sont ensuite introduits dans le réacteur. En dernier lieu l'éthylène (3 fois la quantité stoechiométrique par rapport à l'iode) est injecté dans l'autoclave en refroidissant ce dernier par un mélange d'azote liquide et d'acétone afin de faciliter l'injection. L'autoclave est ensuite progressivement chauffé jusqu'à 70 °C, en veillant à n'enclencher l'agitation qu'une fois la température suffisamment élevée (> 25 °C) pour que le tert-butanol soit liquide, et est ainsi chauffée durant 4h. Au cours de l'éthylénation on observe un fort exotherme dû aux réactions combinées de la décomposition de l'amorceur et de l'attaque des radicaux télogènes sur l'éthylène. Une fois la réaction terminée le réacteur est refroidi puis dégazé afin d'éliminer

l'éthylène en excès. Le contenu de l'autoclave est ensuite récupéré, le tert-butanol est évaporé puis le produit est solubilisé dans le THF et précipité dans l'eau. Le télogène fluoré éthyléné est ensuite lavé, puis séché sous vide pendant 24 heures. Le rendement de la réaction est compris entre 70 et 85%.

A titre d'exemple, dans un autoclave de 160 mL, après un test de pression suivi de cycles vide/argon on introduit 1,71g de perkadox 16S et 19,78 g de C₆F₁₂I₂ dissous dans 80 mL de tert-butanol puis 6 g d'éthylène. On chauffe ensuite progressivement jusqu'à 70 °C, température à laquelle il est maintenu pendant 4 heures. Une fois revenu à température ambiante on dégaze l'excès d'éthylène et on purifie le produit obtenu par évaporation, précipitation, lavages puis séchage. Une fois séché on obtient un solide blanc.

RMN ¹⁹F (400 MHz; Acetone-d₆) : δ (ppm) -114,1 (4 F, m), -121,6 (4 F, m), -123,2 (4 F, m).

RMN ¹H (400 MHz, Acetone-d₆) : δ (ppm) 3,4 (4 H, t), 2,8 (4 H, m).

V-3) Azidation d'un composé contenant un ou plusieurs atomes d'iode ou de brome terminaux :

Les réactions d'azidation ont été réalisées dans des ballons de 50 ou 100 mL. Une solution d'azoture de sodium à 0,5 M dans le DMSO est tout d'abord réalisée (car selon la littérature[20] une solution supérieure à 0,5 M conduit à une mauvaise dissolution de l'azoture) par dissolution de la quantité d'azoture de sodium souhaitée (1,1 fois la quantité stoechiométrique) avec le volume de DMSO correspondant et agitation durant 24 heures à température ambiante. Une fois la solution d'azoture terminée, on y ajoute par un septum le composé halogéné, préalablement dissous dans du DMSO et placé dans une seringue, et on chauffe ensuite à 55 °C durant 48 heures sous agitation. Une fois la réaction terminée, on stoppe la réaction en versant le contenu réactionnel dans 500 mL d'eau (cet ajout déclenche une légère exothermie) puis on extrait par deux fois à l'éther diéthylique. La phase éthérée est ensuite lavée par deux fois à l'eau, puis deux fois à la saumure et enfin une nouvelle fois à l'eau avant d'être séchée sur MgSO₄. L'éther est ensuite évaporé sous pression réduite afin d'obtenir le produit azidé.

A titre d'exemple, dans un ballon de 100 mL, on introduit 1,51 g d'azoture de sodium et 47 mL de DMSO et on agite durant 24 heures à température ambiante. On ajoute ensuite 10 g

de $C_6F_{13}C_2H_4I$ préalablement dissous dans 10 mL de DMSO et on chauffe à 55 °C sous agitation durant 48 heures. La solution récupérée est alors versée dans 500 mL d'eau puis extraite deux fois avec 100 mL d'éther diéthylique. La phase éthérée subit ensuite deux lavages à l'eau suivis de deux lavages à la saumure et d'un autre à l'eau avant d'être séchée sur $MgSO_4$. L'éther est ensuite évaporé sous pression réduite afin de récupérer le $C_6F_{13}C_2H_4N_3$ qui se présente sous la forme d'un liquide jaunâtre.

RMN ^{19}F (400 MHz; $CDCl_3$) : δ (ppm) -80,9 (3 F, t), -115,0 (2 F, t), -122,0 (2 F, s), -122,9 (2 F, t), -123,5 (2 F, s), -126,2 (2 F, s).

RMN 1H (400 MHz; $CDCl_3$) : δ (ppm) 3,6 (2 H, t), 2,4 (2 H, m).

V-4) Cycloaddition de Huisgen entre le monomère 8-CNVE et l'AzidoC₆ :

Les essais de cycloaddition de Huisgen entre le monomère 8-CNVE et l'AzidoC₆ ont été réalisés en tube de Carius (Figure 5b) du fait de la température d'ébullition des solvants utilisés et du 8-CNVE. On insère tout d'abord les réactifs 8-CNVE et AzidoC₆ accompagnés ou non de catalyseur et solvant dans le tube. Le tube est ensuite bouché avec un take off puis est placé dans un mélange azote liquide/acétone afin de geler le mélange réactionnel. Une fois gelé le tube est laissé dans l'azote ce mélange froid puis placé sous vide poussé durant 15 minutes. Le tube est scellé en utilisant un chalumeau à oxygène/propane puis est placé dans un four à agitation à la température désirée durant 24 heures. Une fois la chauffe terminée le tube est refroidit puis ouvert en coupant l'extrémité du tube à l'aide d'un couteau à verre. Le mélange récupéré est ensuite filtré en cas d'utilisation de catalyseur et évaporé. Le produit de la cycloaddition se présente sous la forme d'un liquide brun.

A titre d'exemple on introduit dans un tube de Carius 1g d'AzidoC₆ et 1,1 g de 8-CNVE puis on referme à l'aide d'un take off. On place le tube dans un bain d'azote liquide/acétone et une fois le milieu réactionnel gelé le tube est placé sous vide poussé durant 15 minutes, puis scellé et placé dans un four à agitation à 150 °C durant 24 heures. Une fois le tube débarrassé de son extrémité le produit liquide de couleur brune est récupéré.

RMN ^{19}F (400 MHz; CDCl_3): δ (ppm) -80,9 (3 F, t), -81,9 (3 F, t), -83,6 (2 F, m), -85,0 (2 F, m), -112,5 (2 F, m), -114,0 (1 F, m), -115,0 (2 F, m), -122,1 (1 F, m), -122,5 (2 F, m), -123,5 (2 F, m), -124,2 (2 F, m), -126,9 (2 F, m), -137,5 (1 F, m), -146,1 (1 F, m).

V-5) Réticulation du Kalrez par cycloaddition 1,3-dipolaire :

La réticulation du Kalrez par cycloaddition de Huisgen se déroule en plusieurs étapes :

- solubilisation du Kalrez dans le THF fluoré FC75,
- ajout de l'agent réticulant dans la solution de Kalrez,
- coulage du mélange dans une coupelle en aluminium,
- évaporation du solvant.

Pour obtenir un film homogène et ne présentant pas de bulle plusieurs points importants sont à respecter. En effet, lors de la solubilisation et du mélange l'agitation avec l'agent réticulant doit être contrôlée afin de ne pas incorporer de bulles dans la solution qui de part sa viscosité seraient difficiles à éliminer. De même, l'évaporation doit être bien contrôlée car une évaporation trop rapide provoquerait l'apparition de bulles au sein du film. Pour cela une fois le mélange coulé, l'évaporation est effectuée dans un premier temps en chambre froide à 5°C durant 24 heures avant de l'être à 35 °C dans une étuve. Après évaporation le film obtenu est ensuite placé à la presse comme montré dans la figure 9.



Figure 8 : Dispositif utilisé lors de la réticulation dans la presse hydraulique.

Après 24 heures de pressage à 150 °C, le film de Kalrez réticulé est récupéré.

A titre d'exemple, dans un ballon de 250 mL 5 g de Kalrez et 50 mL de FC75 sont introduits puis agités lentement à l'aide d'un turbulent à température ambiante. Une fois le Kalrez® dissous 0,25 g de BisAzidoC₆ est ajouté à la solution puis après agitation durant 1 heure le mélange est coulé dans des coupelles en aluminium. Ces coupelles sont ensuite placées dans une chambre froide afin que l'évaporation soit bien contrôlée durant 24 heures. Ensuite l'évaporation est achevée dans une étuve à 35 °C durant plusieurs heures. Le film ainsi obtenu est ensuite placé à la presse hydraulique durant 24 heures à 150 °C.

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CHAPITRE 3

NOVEL FLUORINATED COPOLYMERS BEARING PHTHALOCYANINE SIDE GROUPS AS POTENTIAL ORGANIC PHOTOVOLTAICS

Novel Fluorinated Copolymers Bearing Phthalocyanine side groups as Potential Organic Photovoltaics

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Abstract:

The design of novel alternated copolymers based on fluoromonomers and vinyl ethers bearing phthalocyanine side groups is presented: alternating poly(CTFE-alt-CEVE) copolymers were successfully synthesized by conventional radical copolymerization of chlorotrifluoroethylene (CTFE) with 2-chloroethyl vinyl ether (CEVE) and subsequently modified in poly(CTFE-alt-2-iodoethyl vinyl ether). Further, the iodine side groups were converted into azido functions in the presence of sodium azide without affecting the polymeric backbone, then the phthalocyanine bearing CF₃ groups were finally grafted by a copper catalyzed Huisgen dipolar 1,3-addition achieving fluorinated copolymers with different degrees of grafting of phthalocyanine side groups. IR and NMR spectroscopy were exploited to assess the grafting of the phthalocyanine over the fluorinated copolymer and to evaluate the degree of grafting. Thermal degradation of such original fluorinated copolymers bearing phthalocyanine and first attempt of photovoltaic properties were assessed.

Introduction:

Fluoropolymers exhibit remarkable properties [1-5] which open up high technology applications: fuel cell membranes, paints and coatings resistant to U.V., lubricants for electronics, and thermal stable coatings for cookware applications, gaskets and O-rings for aerospace applications, elastomers for transmission in automotive industries. However, few fluoropolymers have already found applications as solar cells [6-9]. Indeed, UV treated PTFE

thin layer improves open circuit voltage, short circuit voltage and power conversion efficiency [10].

In addition, phthalocyanine can be candidate of choice to increase power conversion efficiency since inorganic photovoltaic cells are chiefly attributable to the introduction of donor-acceptor heterojunctions as dissociation sites for strongly bound photogenerated excitons [11-13].

However, to the best of our knowledge, the literature does not report any survey on fluorinated (co)polymers bearing phthalocyanine groups. It was thus of interest to synthesize such fluoropolymers since interesting photovoltaic properties could be anticipated. Actually, poly(fluoroalkenes) are usually inert to be suitable chemically modified through atom transfer radical polymerization of various monomers (methacrylates and styrene) from PVDF [14] or irradiation (via electron beam [15], gamma rays [16], ozone [17]) followed by grafting led to graft copolymers. The approach that is presented in this article is different since alternated copolymers based on fluoromonomers (regarded as electron acceptors) and vinyl ethers (that are electron donors) contain 50% of both co-monomers that bear the expected properties. The vinyl ether units were chemically modified to insert the phthalocyanine counterpart moiety through Huisgen 1,3-cyclo polar reaction or "click chemistry" [18]. That last strategy has been used only once to achieve original fluoropolymers [19].

The objective of this study is to improve performance of solar cell by grafting a phthalocyanine compounds onto a fluorinated copolymer.

Experimental:

Reactants: Dimethylsulfoxide (DMSO) and tetrahydrofuran (THF), (Acros Organics, 98%) were distilled prior to use. Copper (I) bromide (Acros Organics, 95%) was washed with glacial acetic acid to remove any soluble oxidized species and then filtered, washed with ethanol, and dried. Sodium azide was purchased from Aldrich.

Analyses and characterizations: ^1H , and ^{19}F NMR spectra were recorded on a Bruker 400 MHz FT NMR spectrometer with either deuterated chloroform or acetone as the solvents. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) for ^1H and to CFCl_3 for ^{19}F NMR spectra. Letters s, d, t, q stand for singlet, doublet, triplet and quintet, and the

coupling constants are in Hz. Fourier transformed IR spectra were performed on a Nicolet 510P Fourier spectrometer with an accuracy of $\pm 2 \text{ cm}^{-1}$ using OMNIC® software.

Thermogravimetric analyses were performed under air and nitrogen on a TGA Q50 apparatus from TA Instruments at a heating rate of 20 °C/min from room temperature to 600 °C.

1) Synthesis of poly(CTFE-alt-IEVE) copolymer

This reaction was already reported in a previous work [20]

2) Synthesis of azido poly(CTFE-alt-IEVE) copolymer:

A mixture composed of 2.01 g (10 mmol) of poly(CTFE-alt-IEVE) copolymer and 0.50 g (7.7 mmol) of sodium azide dissolved in DMSO (20 mL) and water (1 mL) was stirred at 50 °C for 48 hrs. Then, the reaction mixture was precipitated in water. This procedure was repeated twice. The organic layer was washed with water twice, 10% sodium sulfite solution twice, water (3 times), brine, then dried over MgSO₄, and filtered. The solvent was evaporated under reduced pressure to give 1.2 g of a pale green oil. The yield of the azido copolymer was 60 %.

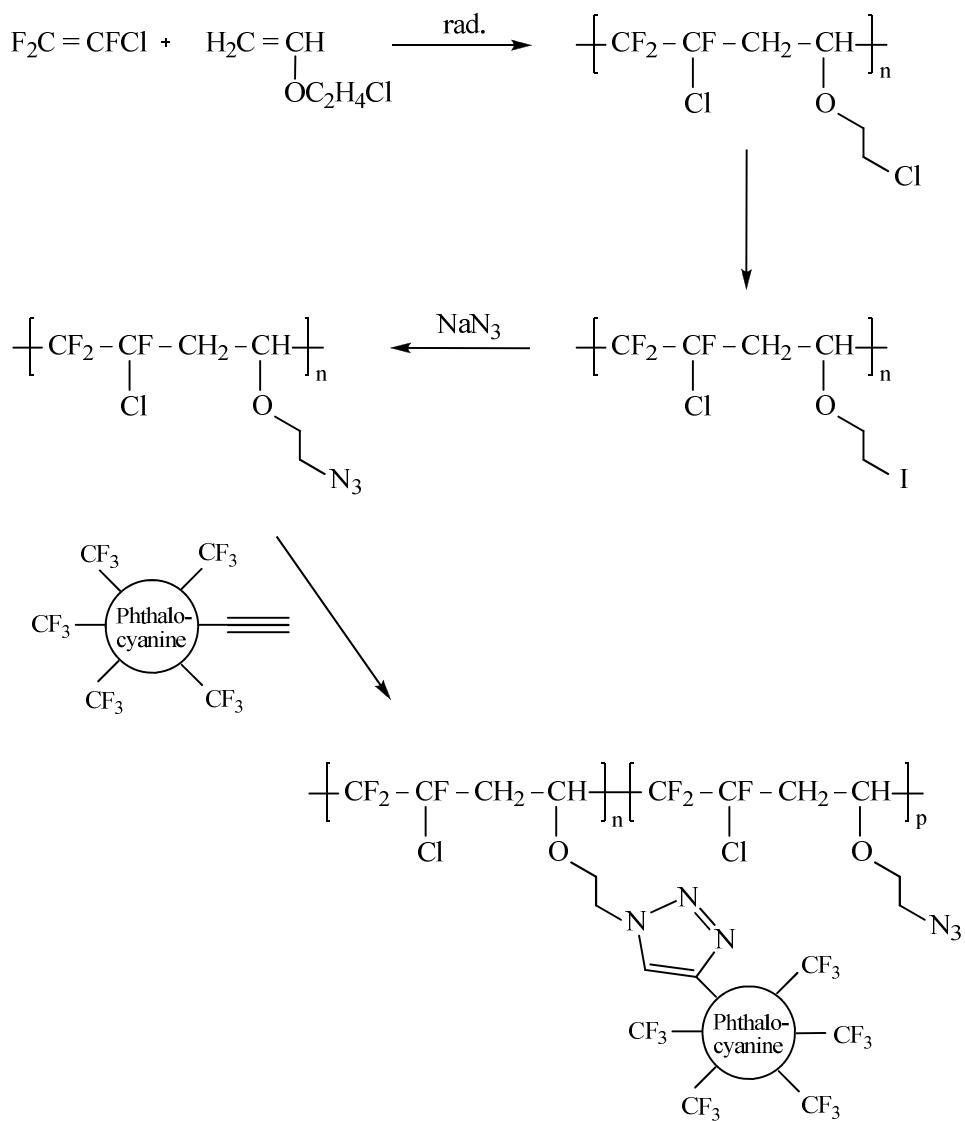
3) Synthesis of phthalocyanine bearing trifluoroethoxy groups and en alkyne end-group:

The synthesis of the corresponding phthalocyanine was already reported in a previous work by palladium-catalyzed Sonogashira cross-coupling followed by Glaser coupling as key reactions [21].

4) Grafting of CF₃ containing Zn phthalocyanine onto azidated poly(CTFE-alt-IEVE) copolymers: copper bromide (20 mg, 0.2 mmol) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (47 mg, 0.2 mmol) were added to a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer. The flask was sealed with three septa and the suspension was purged with dry nitrogen for 30 min. A solution of azidated poly(CTFE-alt-IEVE) copolymers (0.39 g, 0.03 mmol) and the CF₃ containing phthalocyanine (0.3 g, 0.17 mmol) in 20 mL of THF were transferred via a syringe through a septum. The resulting mixture was stirred at room temperature for 48 hrs. The final mixture was passed through a short silica column to remove the copper catalyst. The mixture was precipitated from cold water (500 mL). After filtration, the precipitate was dried under vacuum to give 0.4 g of a green product (Yield= 58 %).

Results and discussion:

The synthesis of original fluorinated poly(CTFE-alt-vinyl ether)s copolymers bearing phthalocyanine side groups was achieved by a four step-procedure involving Huisgen 1,3-cycloaddition between an alkyne phthalocyanine bearing trifluoroethoxy groups and an alternated poly(CTFE-alt-vinyl ether) copolymer bearing azido side groups, as follows:



First, the radical copolymerization of chlorotrifluoroethylene (CTFE), regarded as an electron withdrawing monomer with 2-chloroethyl vinyl ether (CEVE), considered as electron donating monomer, leads to alternating poly(CTFE-alt-CEVE) copolymers as already reported [22-26]. A further step concerns the nucleophilic substitution of chlorine atoms in iodine atoms of the alternating copolymers in the presence of sodium iodide in order to obtain

a poly(CTFE-alt-2-iodoethyl vinyl ether). Third, another nucleophilic substitution occurs on the copolymers in the presence of sodium azide followed by a copper catalyzed Huisgen dipolar 1,3-addition (or “click chemistry”) of these modified fluorinated copolymers bearing azido function with a phthalocyanine bearing CF_3 groups containing an alkyne end group.

1) Synthesis of poly(CTFE-alt-vinyl ether) copolymers containing azido side groups:

Several attempts to achieve the nucleophilic substitution of poly(CTFE-alt-CEVE) or poly(CTFE-alt-IEVE) copolymers into original copolymers bearing azido dangling groups were investigated and the results are listed in Table 1.

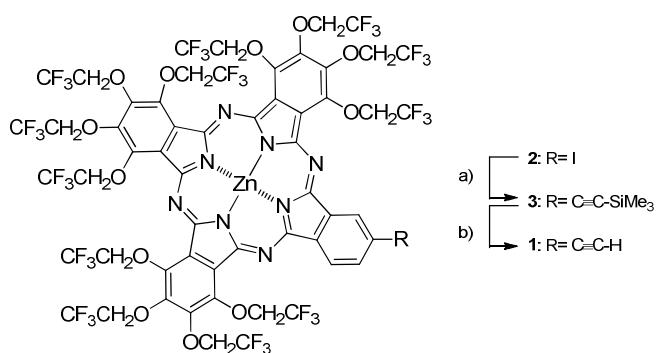
Starting copolymer	$\frac{[\text{NaN}_3]_0}{[\text{CH}_2 - X]_0}$	T (°C)	T (hrs)	Yield (%)	d.o.g. (%)
poly(CTFE-alt-CEVE)	1.1	55	24	0	~ 0
	1.1	55	24	0	~ 0
poly(CTFE-alt-IEVE)	0.55	55	24	28	40
	1.1	55	24	65	> 90

Table 1: Nucleophilic substitution of poly(CTFE-alt-XEVE) by sodium azide in DMSO, XEVE: 2-chloroethylvinyl ether (CEVE) or 2-iodoethylvinyl ether (IEVE); $[\text{CH}_2 - \text{X}]$ represents the concentration of CEVE or IEVE in the starting polymer; d.o.g. stands for degree of grafting.

These results indicate that it is necessary to perform the azidation onto poly(CTFE-alt-IEVE) copolymers to obtain an azido copolymers because the iodine is a better leaving group than chlorine atom. The nucleophilic substitution provides high yields and a degree of grafting easy to tune.

2) Synthesis of phthalocyanine bearing trifluoroethoxy groups and en alkyne end-group:

The suppression and control of the aggregation properties of phthalocyanines, both in solvents and in solid films, by only their inherent specificity without any external assistance is a challenge in materials science, especially for solar cells, optical filters, and sensors. Phthalocyanine derivatives offer a very wide choice of molecular physicochemical properties, including color, photodynamics and catalytic activity by changing the nature of their aggregation states: monomer, dimer or highly aggregated [27],[28],[29]. The outstanding optical and photosensitizing properties of Pcs with both a wide absorbing spectral range and high luminescence quantum yields are often perturbed in a randomly aggregated state. Freedom from molecular aggregation is particularly desirable for solar cells, because self-association reduces the efficiency of solar cells and quenches fluorescence. Recently, we discovered the unique non-aggregation property of trifluoroethoxy-coated phthalocyanines and noted their prominent avoidance of intermolecular aggregation [21, 30-34]. We were therefore interested in the synthesis of fluorinated polymers containing trifluoroethoxy-coated phthalocyanines. The trifluoroethoxy-coated phthalocyanines can be incorporated into polymer by the use of “click chemistry” between azide containing polymers and A₃B-type alkynyl-trifluoroethoxy-coated phthalocyanines. The synthesis of A₃B-type alkynyl-trifluoroethoxy-coated phthalocyanine **1** was achieved from iodo-phthalocyanine **2** by the reported procedure using palladium-catalyzed Sonogashira cross-coupling followed by Glaser coupling as key reactions as indicated below [21].



(a) trimethylsilylacetylene, Pd(PPh₃)₄Cl₂, CuI, Et₃N, THF, 40 °C, 24 h, 97%;
(b) K₂CO₃, MeOH, RT, 4 h, 99%

3) Huisgen 1,3-dipolar cycloaddition of azido-containing fluoropolymers with alkyne phthalocyanine bearing CF₃ groups:

The concept of “click chemistry” based on a 1,3-dipolar cycloaddition was first pioneered by Huisgen et al. [35] in 1967 and then revisited and developed by the Sharpless group [18]. The principle of “click chemistry” which can be explained by the condensation reaction between an azido group and a triple bond in the presence of catalyst. This method possesses several benefits because the reactions occur at low temperatures (< 100 °C), give high yields and are tolerant to the media since they can be carried out in the presence of oxygen and even in water. The reaction needs a catalytic system, such as Cu(I) / pentamethyldiethylene triamine (PMDETA) or Cu(II)/Ascorbic acid. Reviews by many authors [36-39] have been published on the use of “click chemistry” in the field of polymers.

The chemical modification of poly(CTFE-alt-CEVE) copolymers with phthalocyanine derivative was performed according to Huisgen 1,3-dipolar cycloaddition (or “click chemistry”) in the presence of CuCl and 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) at 35 °C for 10 hours. Two experiments were carried out at different [Phthalocyanine] / [poly(CTFE-alt-CEVE_{N3})] initial molar ratio.

After reaction and purification, the fluorinated copolymers bearing phthalocyanine side groups were characterized by IR and NMR spectroscopy.

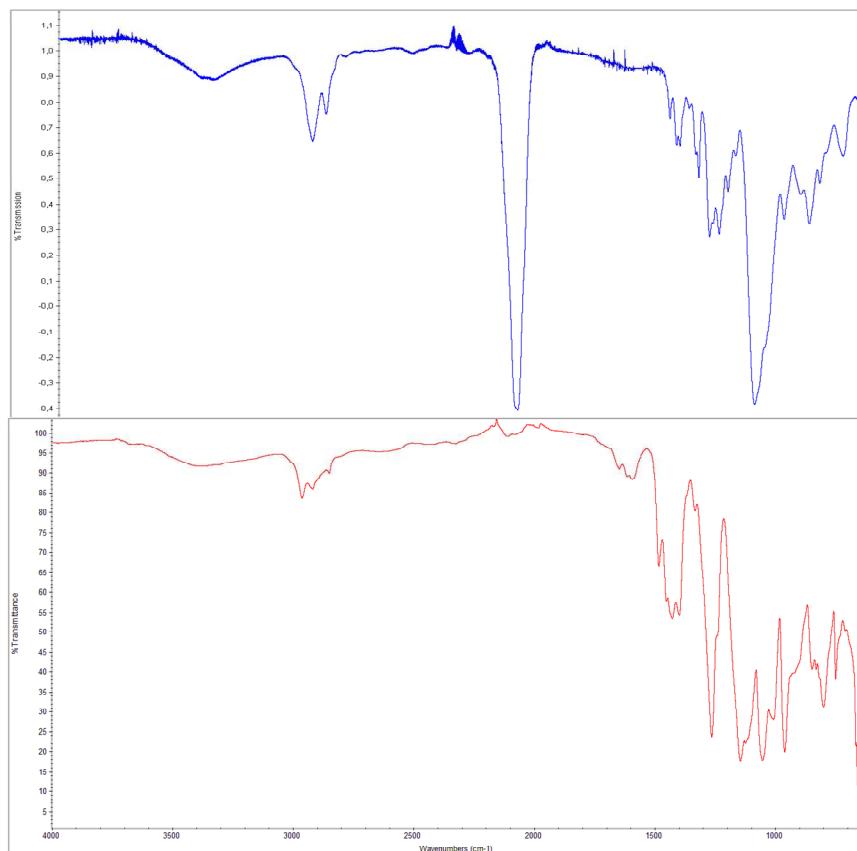


Figure 1. IR spectra of azido-containing poly(CTFE-alt-vinyl ether)s copolymer (upper graph) and poly(CTFE-alt-vinyl ether)s copolymer bearing phthalocyanine side groups (lower graph).

IR spectra of azido-containing poly(CTFE-alt-vinyl ether)s copolymer exhibits expected frequency at 2100, 1000-1200 cm^{-1} assigned to ν_{N_3} and $\nu_{\text{C}-\text{F}}$ respectively (Figure 1, upper spectrum). After “click” reaction it is noted a sharp decrease of ν_{N_3} frequency (Figure 1, lower spectrum).

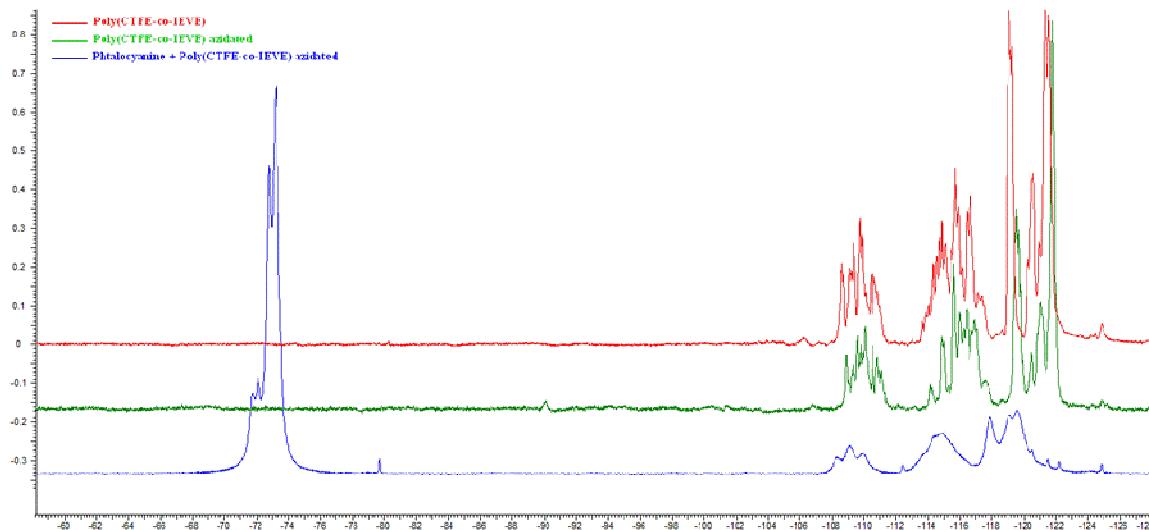


Figure 2a. ^{19}F NMR spectra of fluorinated poly(CTFE-alt-vinyl ether)s copolymer (red graph), azido-containing poly(CTFE-alt-vinyl ether)s copolymer (green graph) and poly(CTFE-alt-vinyl ether)s copolymer bearing phthalocyanine side groups (blue graph) dissolved in d-acetone.

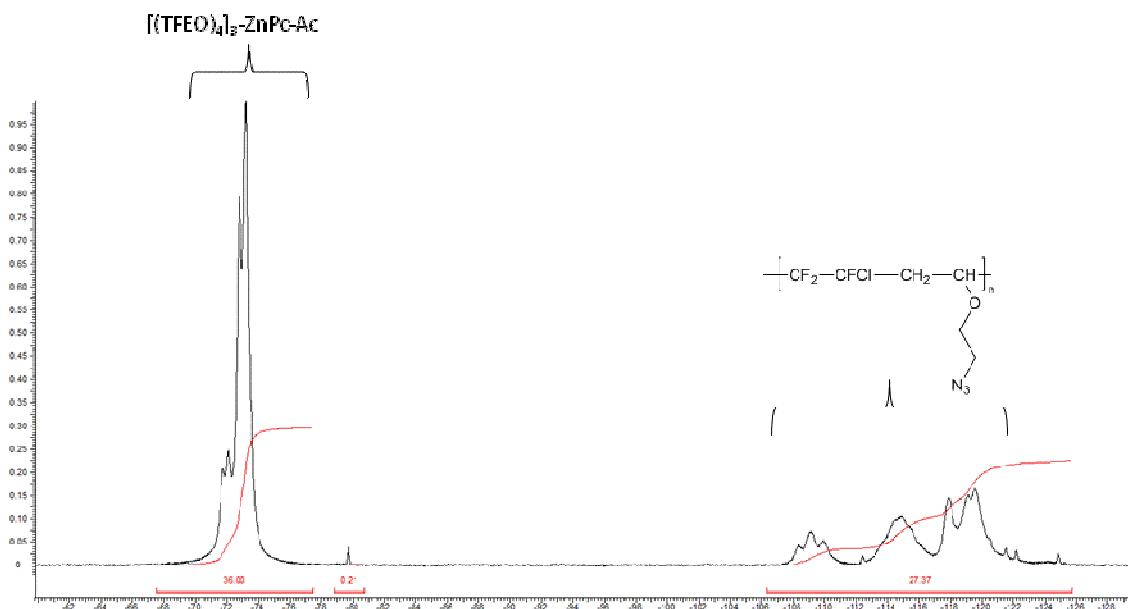


Figure 2b. ^{19}F NMR spectrum of poly(CTFE-alt-vinyl ether)s copolymer bearing phthalocyanine side groups dissolved in d-acetone.

^{19}F NMR spectrum of “clicked” poly(CTFE-alt-CEVE) (figure 2b) shows the presence of both the signals centered at -73 ppm assigned to CF_3 groups in phthalocyanine and those centered at -109, -114 and -119 ppm attributed to the CF_2CFCl units of the copolymer. The ratio of integrals of these above signals enables to assess the degree of grafting (d.o.g.) of the phthalocyanine over the fluorinated copolymer:

$$\text{d.o.g.} = \frac{\int_{-73} \frac{\text{CF}_3}{36}}{\int_{-73} \frac{\text{CF}_3}{36} + \int_{-109}^{-119} \frac{\text{CF}_2\text{CFCl}}{3}}$$

The degree of grafting were from 10% to 80%.

	[Ph-CF ₃] ₀ / [CTFE-CEVE] ₀	[CuCl] ₀	[Ligand] ₀	Yield (%)	d.o.g. (%)
1	3	2 10 ⁻³	2 10 ⁻³	58	10
2	10	10 10 ⁻³	10 10 ⁻³	65	40
3	15	20 10 ⁻³	20 10 ⁻³	Under progress	80

Conclusion (underwriting)

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CONCLUSION GENERALE

CONCLUSION GENERALE

L'objectif de cette thèse consistait à développer, à partir de télamères fluorés de tétrafluoroéthylène et de polymères fluorés à base de chlorotrifluoroéthylène fonctionnalisés azido, des méthodes originales de modifications chimiques ou de réticulation basées sur la réaction de cycloaddition de Huisgen afin d'améliorer les propriétés de polymères fluorés.

Dans le premier chapitre, une revue quasi-exhaustive sur la réticulation et la post-réticulation de polymères via des réactions clés, à des températures comprises entre la température ambiante et 150 °C.

Dans le second chapitre, nous avons utilisé la réaction de cycloaddition d'Huisgen pour réticuler un élastomère fluoré commercial, composé de motifs tétrafluoroéthylène (TFE), de perfluoro(méthyle vinyl éther) (PMVE) et de perfluoro(8-cyano-5-méthyle-3,6-dioxa-oct-1-ène) (8-CNVE), le Kalrez® par réaction entre les fonctions azides du 1,10-diazido-1H,1H,2H,2H,9H,9H,10H,10H-perfluorodecane et les fonctions nitriles pendantes du Kalrez®. L'étude modèle de la réaction sur le monomère fluoré 8-CNVE, porteur de groupe nitrile, a permis par sélection progressive des conditions opératoires d'optimiser la réaction de cycloaddition entre un groupement azido et un nitrile. La transposition de ces conditions sur le Kalrez® a été réalisée et les différentes analyses des échantillons réticulés ont permis de confirmer la validité de cette méthode. Les polymères réticulés ainsi obtenus montrent une amélioration notable de la thermostabilité ainsi qu'une insolubilité dans un solvant perfluoré (le THF fluoré FC-75, solvant du Kalrez® non réticulé). Les valeurs des taux de gonflement et d'extractible montrent cependant que le nombre de nœuds de réticulation est faible. Afin d'augmenter ces taux il faudrait utiliser des échantillons de Kalrez® ayant une proportion de 8-CNVE plus élevée.

Dans le troisième chapitre, nous avons utilisé la réaction de cycloaddition d'Huisgen organocatalysée afin de greffer sur un copolymère fluoré alterné, à base de chlorotrifluoroéthylène azidé et d'un éther vinylique porteur d'un groupement $\text{CH}_2\text{-N}_3$, une phthalocyanine porteuse d'une fonction alcyne. Ce greffage réalisé par « click chemistry » a pour but d'obtenir un composé possédant des propriétés photovoltaïques.

Conclusion générale

Les perspectives à envisager pour ces travaux sont d'une part, pour la réticulation du Kalrez®, l'utilisation d'un polymère de départ contenant une quantité plus importante de fonction nitrile mais aussi la recherche et l'utilisation d'un système catalytique permettant d'améliorer la cinétique de réaction de réticulation, et d'autre part, pour la synthèse de composés possédant des propriétés photovoltaïques, d'optimiser la réaction afin de contrôler parfaitement le taux de greffage et d'améliorer la mise en œuvre de la purification des produits de réaction afin d'en optimiser le rendement.