



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, etc.) 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, amine functions); (iii) reactions involving activated amines with carbonyl functions (aldehydes, ketones, etc.); (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 higher temperatures (yet 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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1. Introduction

Improvement of the thermal, mechanical, physico-chemical 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 features 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 $2\text{--}3 \cdot 10^3 \text{ g mol}^{-1}$.

According to the category, it 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 crosslinked 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, O_2 , H_2O , etc.),
- (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].

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	hydrogenated 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

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 1960's [5], though deeper investigations started in 1980'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.

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.

Nevertheless, by adapting appropriate catalysis and reaction conditions, the reaction is directed towards the synthesis of N-acyl urea. In this way, Taylor and Basset [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).

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 1970's [19]. Roesler and Danielmeier [20] published a review on the reaction of aziridine with carboxylic acids,

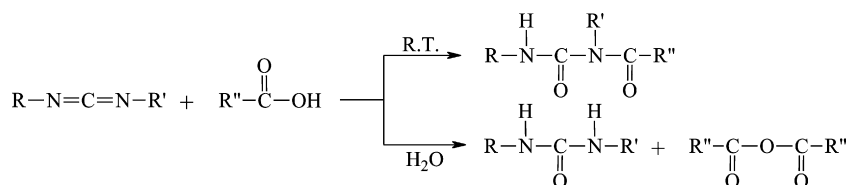


Fig. 1. Formation of acetyl urea compounds by condensation of a carbodiimide with a carboxylic acid and the side reaction in presence of water.

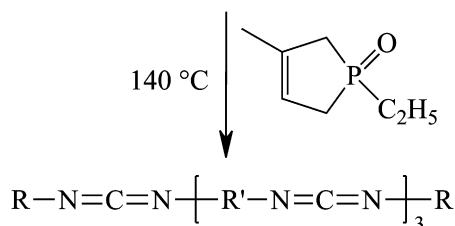
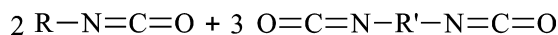


Fig. 2. Synthesis of a carbodiimide from isocyanate.

which spontaneously lead to an amino ester at room temperature, as shown in Fig. 3.

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. 5 shows a triaziridine that is soluble in several polar solvents including water, as described by Pollano and Resins [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. 6 illustrates the crosslinking of carboxylic acid terminated polymer with a triaziridine compounds, reported by Liu et al. [22].

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 1 min in presence of catalyst.

Two drawbacks were observed:

- As for their homologue carbodiimides, their poor water stability led to inactive amino alcohol. Nevertheless, this

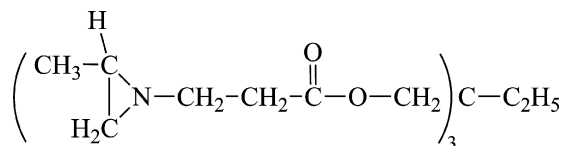


Fig. 5. Structure of trimethylolpropane tris(2-methyl-1-aziridine propionate).

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].

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

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

Aceto acetyl derivatives can react with various groups, such as (i) 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.

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

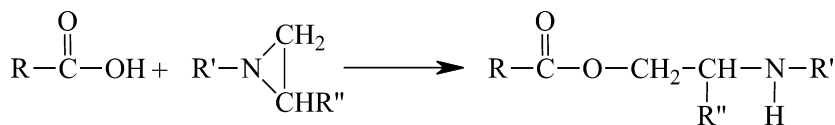


Fig. 3. Reaction between an aziridine and a carboxylic acid leading to an amino ester.

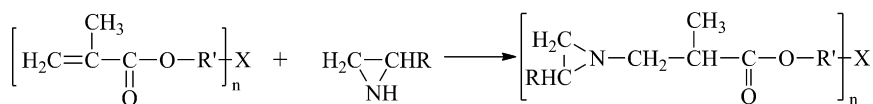


Fig. 4. Synthesis of polyaziridine by “Michael addition” between an amine and an acrylic alkene.

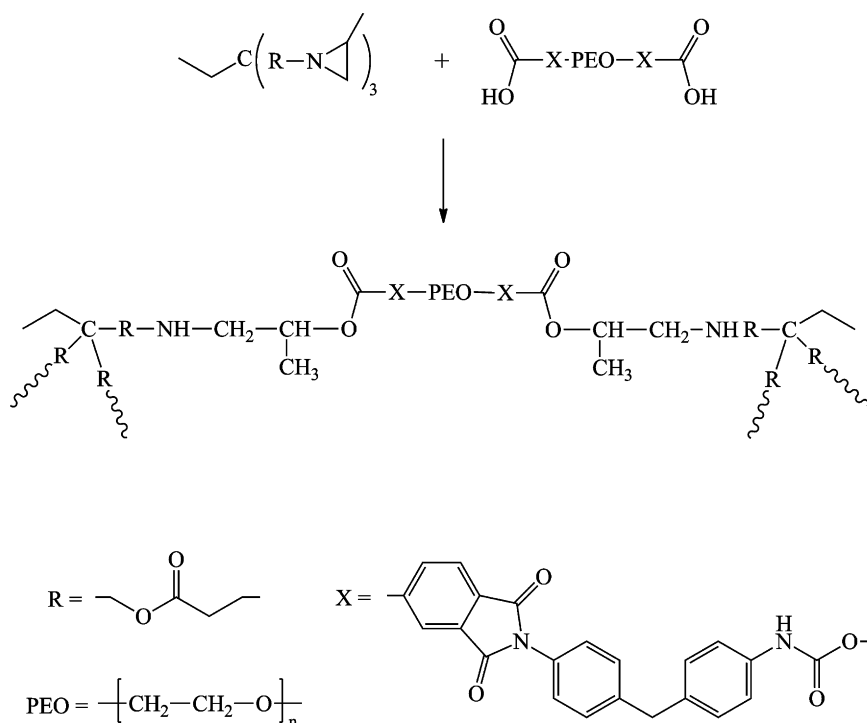


Fig. 6. Crosslinking example of a polymer bearing carboxylic acid functions with a triaziridine.



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

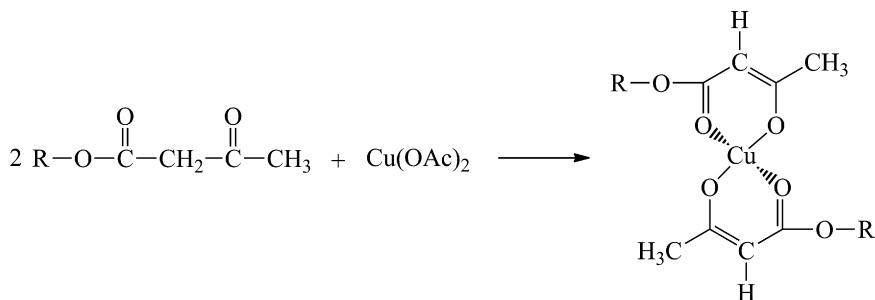


Fig. 8. Chelating of bisketone by copper acetate.

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.

These authors used strong bases ($\text{p}K_a > 12$), 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 $\text{p}K_a$ of

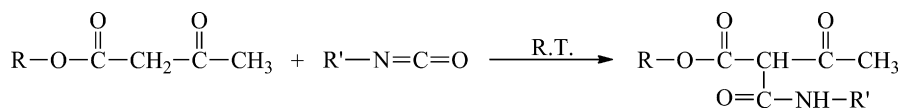


Fig. 9. Reaction between an isocyanate and an acetoacetyl compounds.

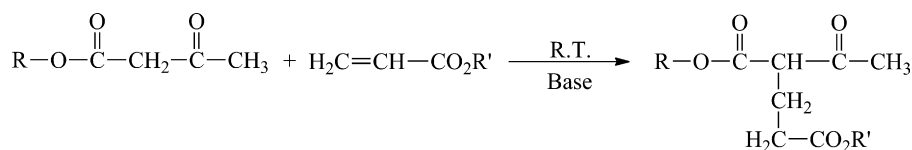


Fig. 10. “Michael addition” between an aceto acetyl compounds and an activated alkene.

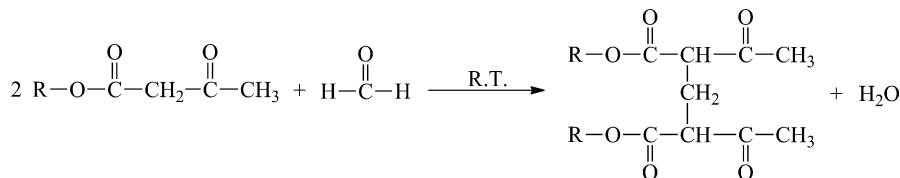


Fig. 11. Formation of a linkage between two acetylacetonate groups by reaction with formaldehyde.

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

such an acetylacetonate 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.

(iii) Aldehydes and more especially formaldehyde.

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

(iv) Amines

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

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.

Other reactions may occur when acetyl acetonates 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, the structure of which is given in Fig. 14, has been marketed and is used in many fields, such as with acrylic latexes.

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 acetonates reported in Fig. 15, aldehydes and ketones [32] are also featured reactants, and imine groups are also produced in this way.

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

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

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.

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

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

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

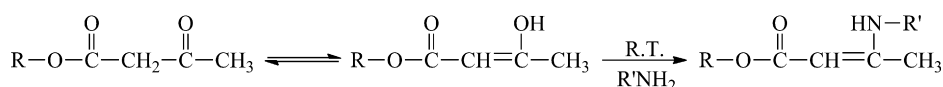


Fig. 12. Reactions between enolic form of aceto acetyl with an amine.

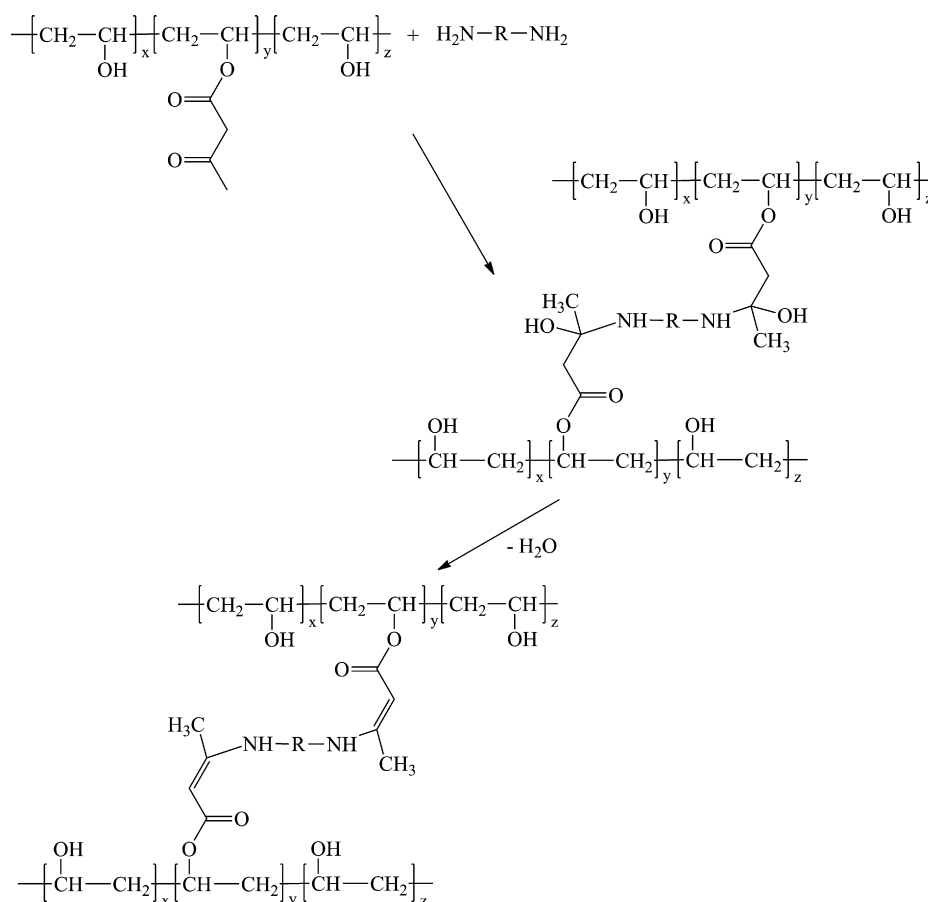


Fig. 13. Crosslinking of poly(vinyl alcohol) bearing acetoacetylated groups with a diamine.

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 pre-crosslinking) 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, hence limiting pre-crosslinking.

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 min at 65 °C. However, storage stability is not much improved. 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

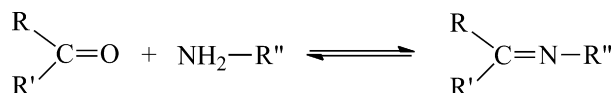


Fig. 15. Preparation of imines by reaction between an amine and a carboxylic group.

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 so high surfactant properties 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.

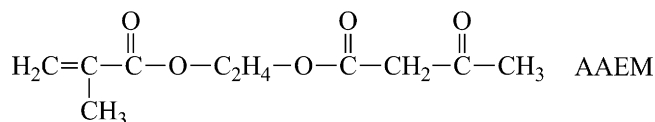


Fig. 14. Acetoacetoxyethyl methacrylate (AAEM) monomer bearing acetylacetonate group.

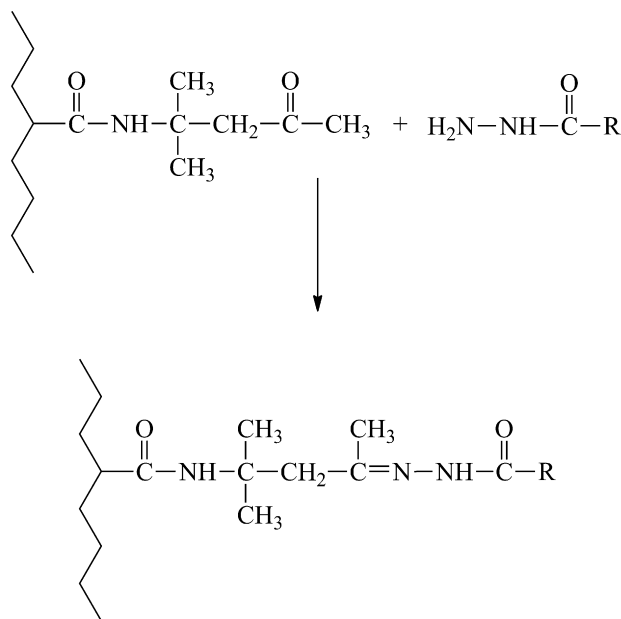


Fig. 16. Reaction of a hydrazine derivative with a polymer bearing ketones groups.

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.

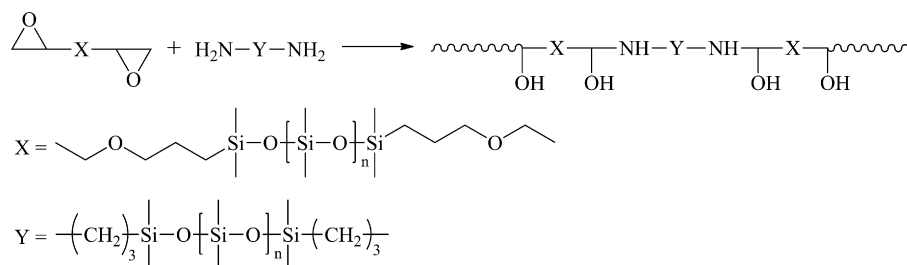


Fig. 18. Reaction between an epoxy and an amine often used to crosslink epoxy resins.

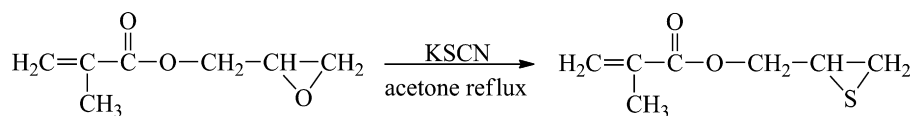


Fig. 19. Synthesis of thiirane from an epoxy.

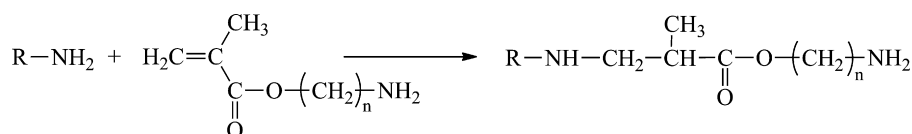


Fig. 20. "Michael reaction" between an amine and a methacrylate amino monomer.

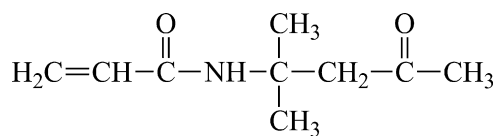


Fig. 17. Structure of N-(1,1-dimethyl-3-oxobutyl)acrylamide.

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.

Pichot's group [41] was one of the first team that used this concept involving 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).

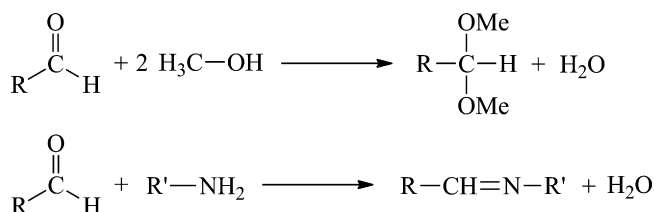


Fig. 21. Protection reaction of an aldehyde by alcohol, reaction between an aldehyde and an amine.

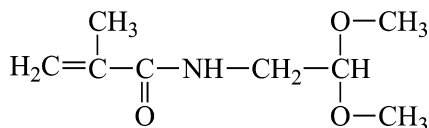


Fig. 22. Structure of N-(2,2-dimethoxyethyl)methacrylamide (MAAMA).

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.

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 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.

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.

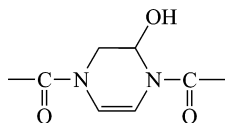


Fig. 23. Cyclic structure after the dimerization of an amido group with an aldehyde.

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].

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 photochemical effects). Typically, the use of oxygen and water are reported below.

2.1.6.1. Water [51–100].

2.1.6.1.1. 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 $\text{Si}(\text{OR})_4$, $\text{Ti}(\text{OR})_4$, $\text{Zr}(\text{OR})_4$, $\text{Al}(\text{OR})_3$] and a polymer. For example, Blanchard et al. [54] reported an extensive study on the hydrolysis and condensation reaction of different metal alkoxides $\text{M}(\text{OR})_n$ (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.

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,

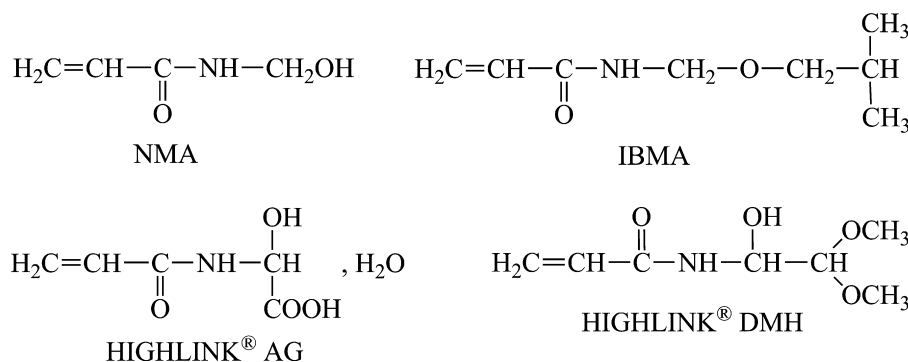


Fig. 24. Structure of some acrylamide monomers.

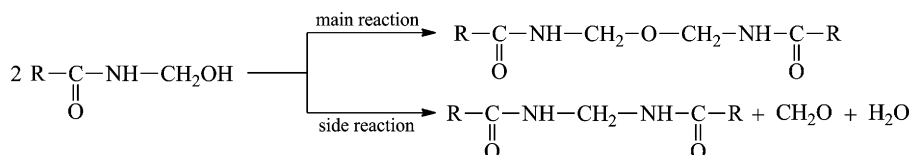


Fig. 25. Self-reactions of acrylamide compounds.

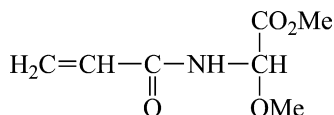


Fig. 26. Structure of N-(methoxymethyl acetate)acrylamide monomer.

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 10-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.

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 Laboratory [89] used such a method that employed fluorinated model compounds, as shown in Fig. 28.

A similar strategy involving longer fluorinated compounds (C_8F_{17} , $\text{C}_{10}\text{F}_{20}$) was also claimed by the

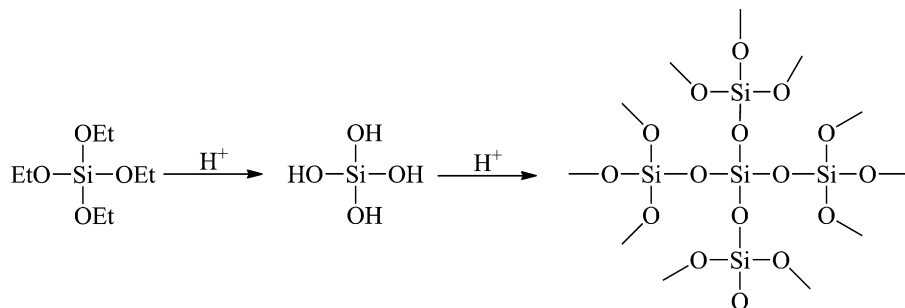


Fig. 27. Hydrolysis and polycondensation of tetraethoxysilane.

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).

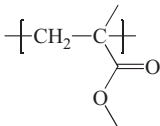
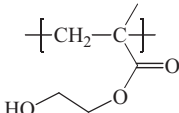
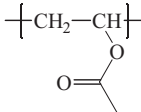
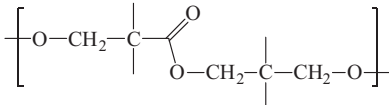
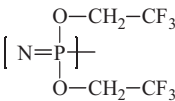
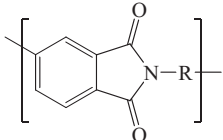
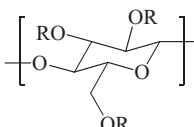
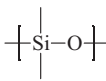
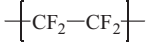
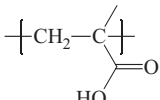
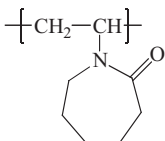
Polymer	Base unit	References
PMMA		Landry et al. [56]
PHEMA		Kaddami et al. [62]
PVAc		Girard-Reydet et al. [63], Landry et al. [64] Yano et al. [65]
Polyester		Frings et al. [66]
Polyphosphazene		Coltrain et al. [67]
Polyimide		Kaddami et al. [68], Morikawa et al. [69,70]
Hydroxypropyl cellulose		Yano [71]
PDMS		Pinto et al. [72]
PTFE		Chen et al. [57]
R _F (AA) _n R _F		Sawada et al. [73]
Poly(N-vinylcaprolactam)		Loos et al. [74]

Table 3

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

Polymer	Base unit	References
PEO		Kweon and Noh [75,76]
PTMO		Huang and Wilkes [77], Trossaert and Goethals [78]
PCL		Kaddami et al. [79], Cuney et al. [80], Messori et al. [81]
PDMS		Surivet et al. [82]
H-PBd		Surivet et al. [82], Kaddami et al. [83]
PMMA		Coltrain et al. [84]
Polyoxazoline		Chujo et al. [85]
PAEK		Wang et al. [86]
PS		Mourey et al. [87]
Ar-PFCB-Ar		Rizzo and Harris [88]
R-R _F -R		Ameduri et al. [89], Zhao et al. [90], Michalczyk [91]
Poly(VDF-co-PMVE)		Hung et al. [92]

DuPont de Nemours Company [91]. This process was recently investigated using telechelic bis(triethoxysilane), bis(dimethylethoxysilane) or bis(dimethylethoxysilane) with poly(VDF-co-PMVE) elastomers (where VDF and PMVE stand for vinylidene fluoride and perfluoromethyl vinyl ether, 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

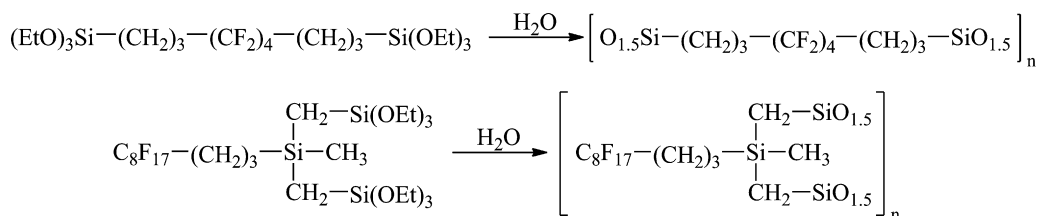


Fig. 28. Sol-gel model reaction of fluorinated compounds.

available: (i) triethoxyvinylsilane is not very reactive during the polymerization, but it has sufficient reactivity for use in material crosslinking (such as polyolefins), and (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:

trimethoxy (\sim dimethoxy) > triethoxy \approx triisopropoxy
> diethoxy

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 -SO₂F side group (i.e., Nafion[®] monomer) have been synthesized and chemically modified to obtain crosslinked membranes for fuel cell applications [95]. Interestingly, the conductivity of the membrane reached 43 mS cm⁻¹ at 65 °C at 100% relative humidity.

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.

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

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 the 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.

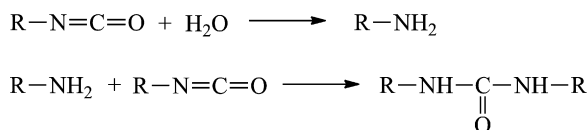


Fig. 29. Self-reaction of an isocyanate in presence of water.

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.

2.1.6.2.1. 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 enables 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 though 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.

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 of type of reactions, as presented in Fig. 33.

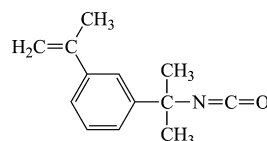


Fig. 30. Structure of *m*-isopropenyl- α,α -dimethylbenzyl isocyanate.

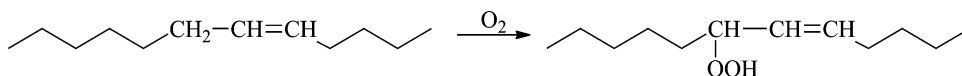


Fig. 31. Formation of an allylhydroperoxide by reaction of a non-conjugated double bond with dioxygen.

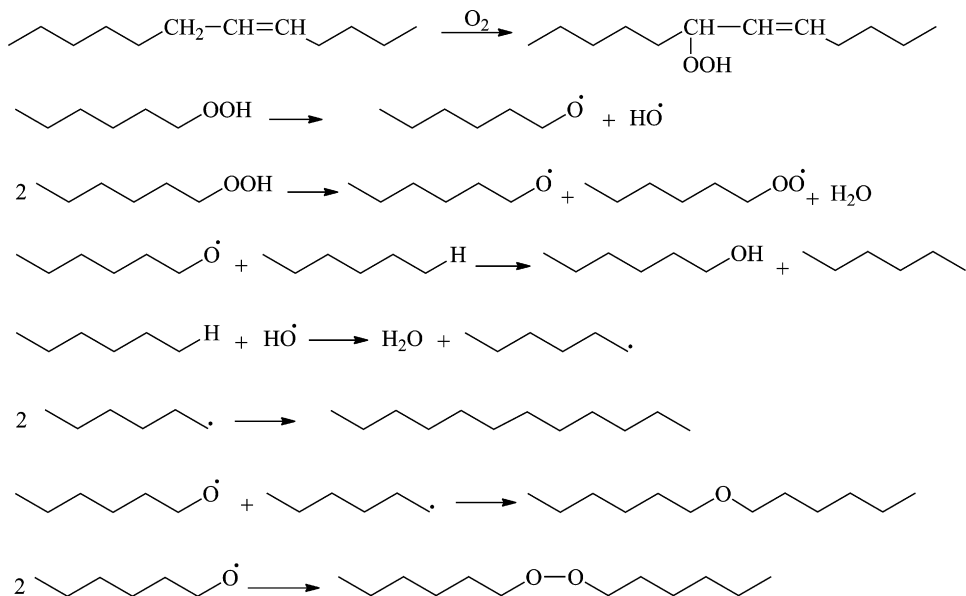


Fig. 32. Different reactions after decomposition of hydroperoxides.

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].

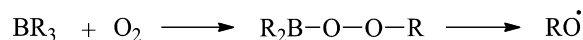


Fig. 34. Formation of peroxide borinated derivatives.

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.

2.1.6.2.2. *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] provide an extensive overview of acetylenic coupling used in the field of material chemistry.

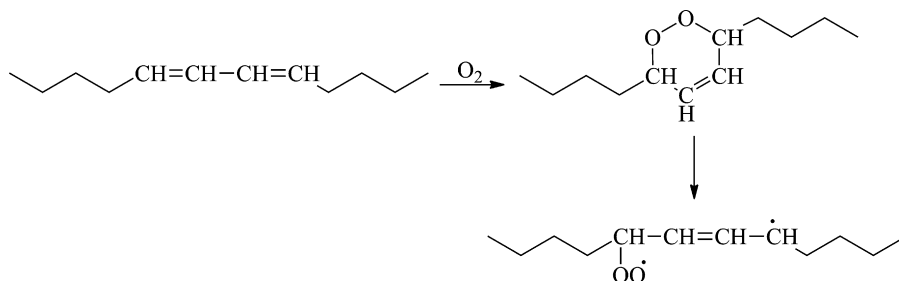


Fig. 33. (a) Formation of cyclic peroxide by reaction of dioxygen with conjugated double bonds and (b) decomposition of cyclic peroxide.

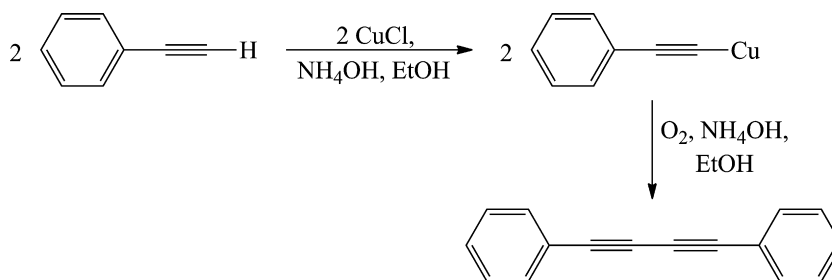


Fig. 35. Mechanism of “Glaser coupling” reaction with an acetylenic compound in presence of O_2 and Cu(I).

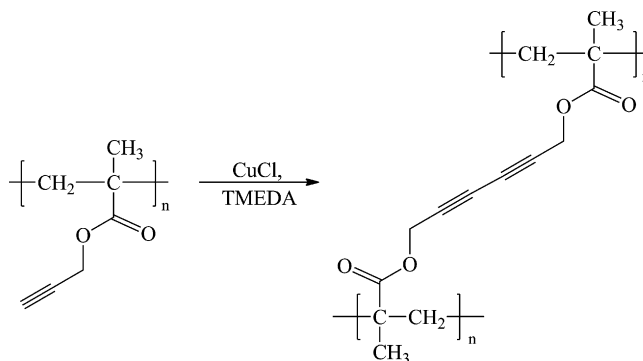


Fig. 36. Crosslinking of poly(propargyl methacrylate) by “Hay coupling” reaction.

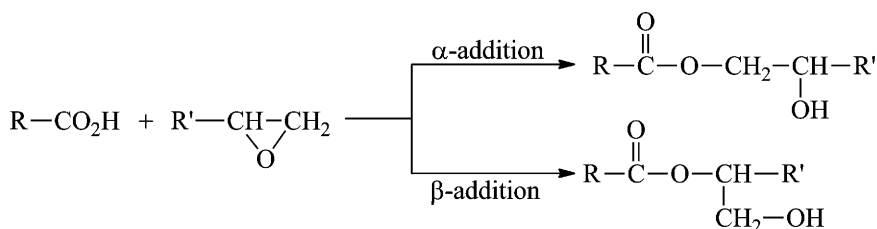


Fig. 37. α - and β -Addition between a carboxylic acid and an epoxy.

In the 1960s, Hay [111,112] improved this coupling by addition of a tertiary amine, which complexes the copper salts. Dirlikov and Chen [113] subsequently claimed the crosslinking of poly(propargyl methacrylate) in the presence of copper(I) and tetramethylethylenediamine as displayed in Fig. 36.

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 150–300 °C. As in the previous sec-

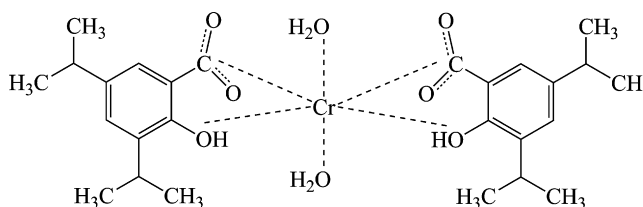


Fig. 38. Structure of diisopropyl salicylate chromium complex.

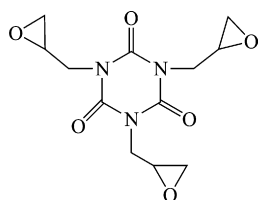


Fig. 39. Structure of triglycidyl isocyanate (TGIC).

tion, 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.

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 salicylate chromium is the best known [128]; its structure is shown in Fig. 38.

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].

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 epichlorohydrine to an isocyanurate [131] derivative. These strategies are illustrated in Fig. 40.

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.

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

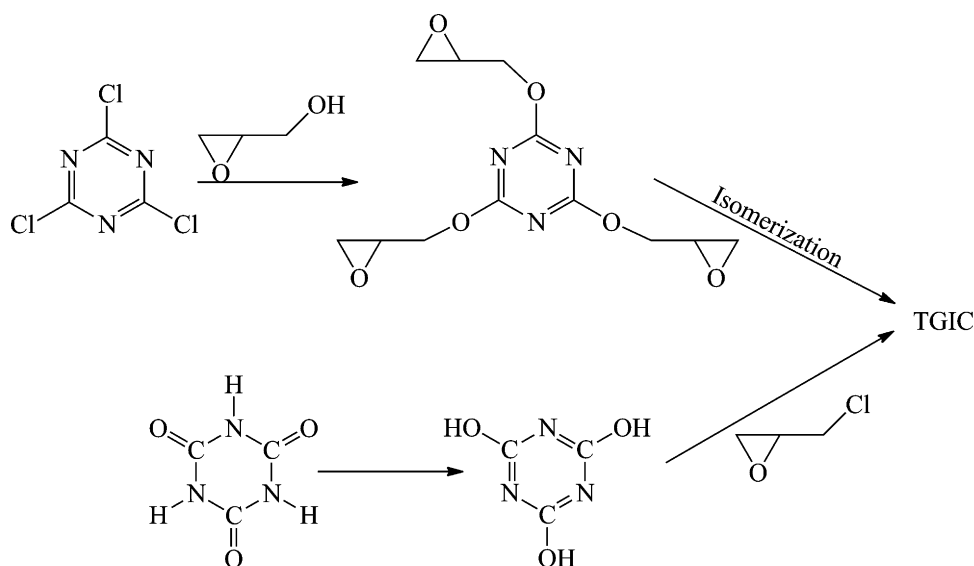


Fig. 40. Synthesis of TGIC from 1,3,5-trichlorotriazine and from an isocyanurate derivative.

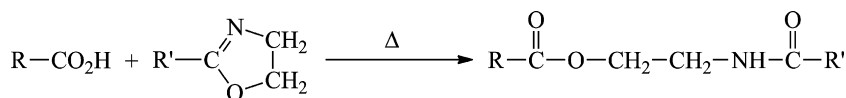


Fig. 41. Reaction of an oxazoline with a carboxylic acid.

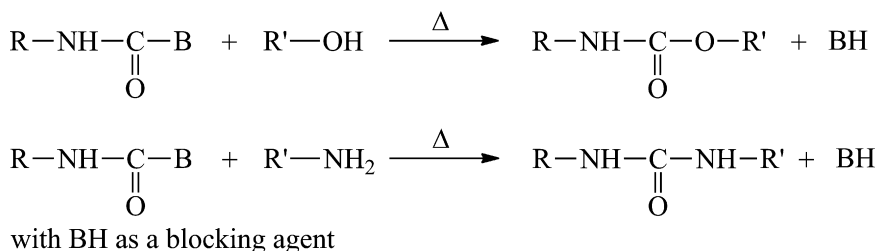


Fig. 42. Reactions of protected urethane with alcohol or amine.

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.

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 lactams). 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

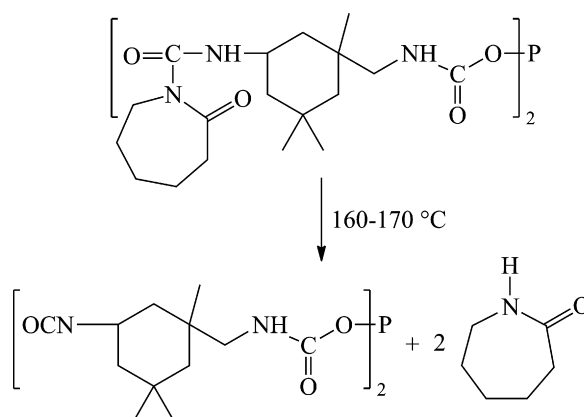


Fig. 43. Deprotection mechanism of a polymer bearing isocyanate functions blocked by caprolactame (where P stands for a polymeric structure).

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, lactams 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 and the temperature of deprotection varies from 130 to 165 °C. The deblocking mechanism is described in Fig. 43.

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.

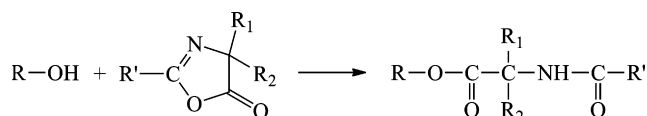


Fig. 44. Reaction between an azlactone and an alcohol.

[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.

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 and Engle [155,156] in their 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 derivatives (methyl 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.

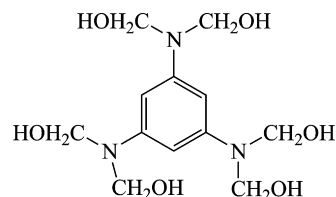


Fig. 45. Structure of hexamethylol melamine (HMM).

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 Chemical Company [162,163] and Subrayan and Jones [164] is shown in Fig. 47.

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.

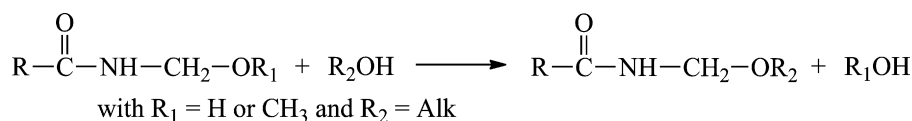


Fig. 46. Reaction between an amide and an alcohol.

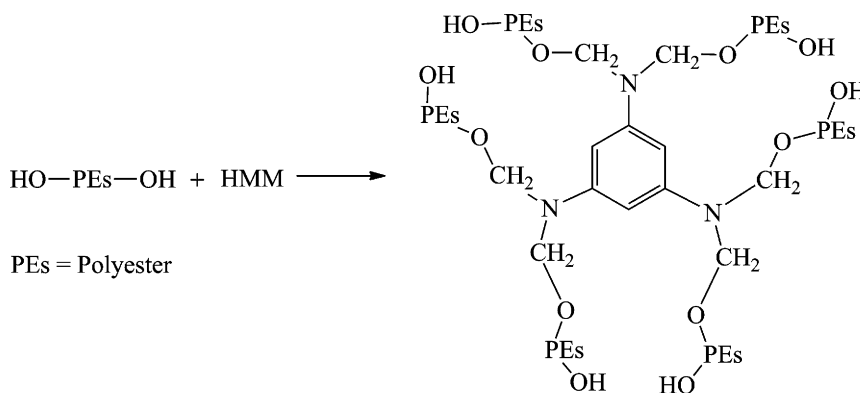


Fig. 47. Crosslinking reaction, developed by Exxon, between HMM and alcohol terminated polyester (PEs).

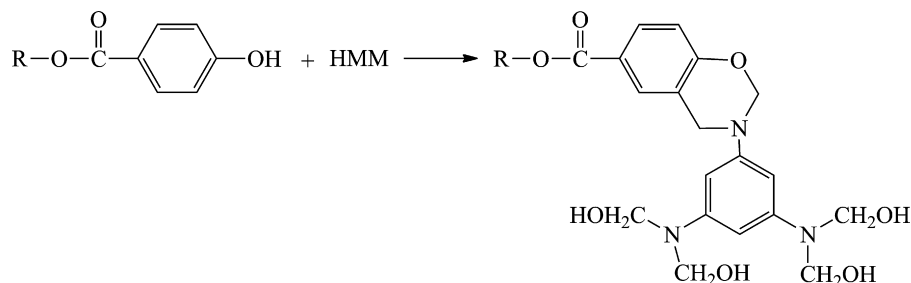


Fig. 48. Reaction between HMM and a parahydroxybenzoic acid derivative.

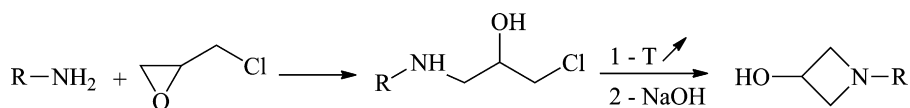


Fig. 49. Reaction of a primary amine with epichlorohydrin to obtain azetidinol.

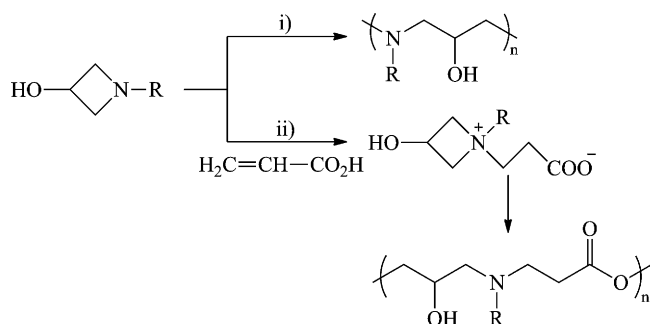


Fig. 50. Azetidinol involved in (i) cationic homopolymerization or in (ii) copolymerization with an acrylic acid.

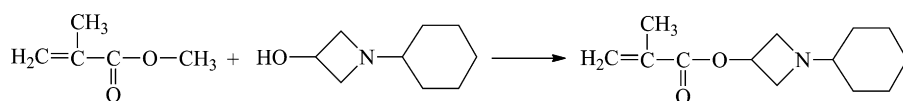


Fig. 51. Formation of a methacrylate monomer bearing an azetidine function by reaction between a methacrylate and an azetidinol.

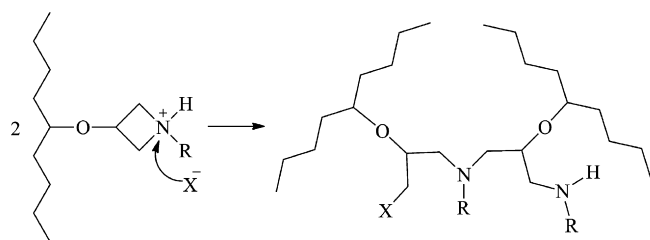


Fig. 52. Crosslinking of a polymethacrylate polymer bearing quaternized azetidine.

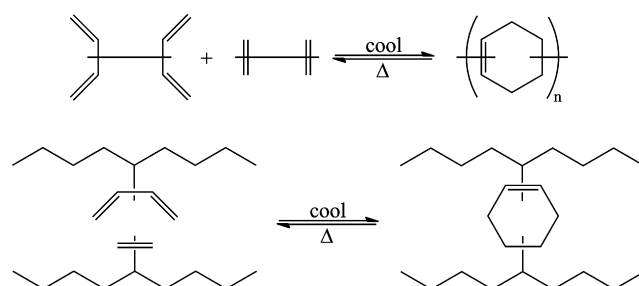


Fig. 53. Example of Diels–Alder [4 + 2] reaction in polymer chemistry.

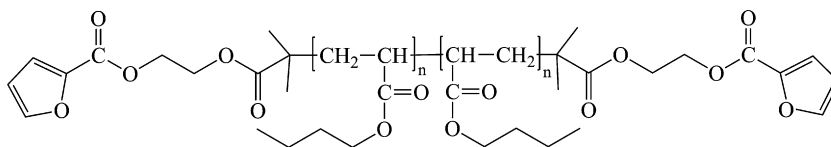


Fig. 54. Structure of telechelic difuranic poly(butylacrylate).

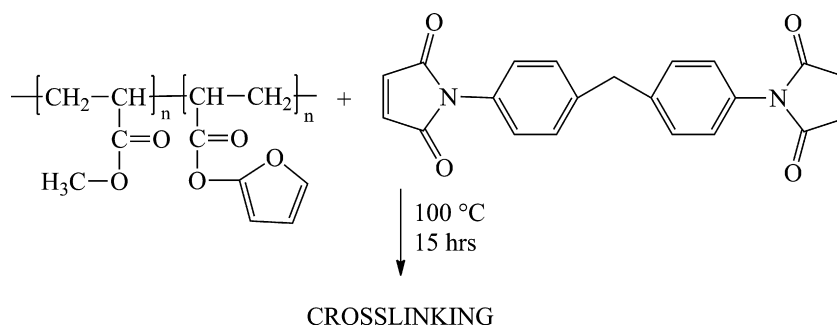


Fig. 55. Crosslinking of polyacrylic bearing furan group with maleimides telechelic compounds.

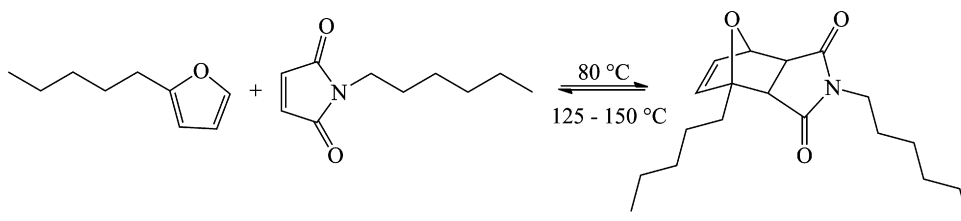


Fig. 56. Reversible Diels–Alder reaction between furan and maleimide compounds.

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 epichlorhydrine, as illustrated in Fig. 49.

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.

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

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 azetidiny 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].

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.

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

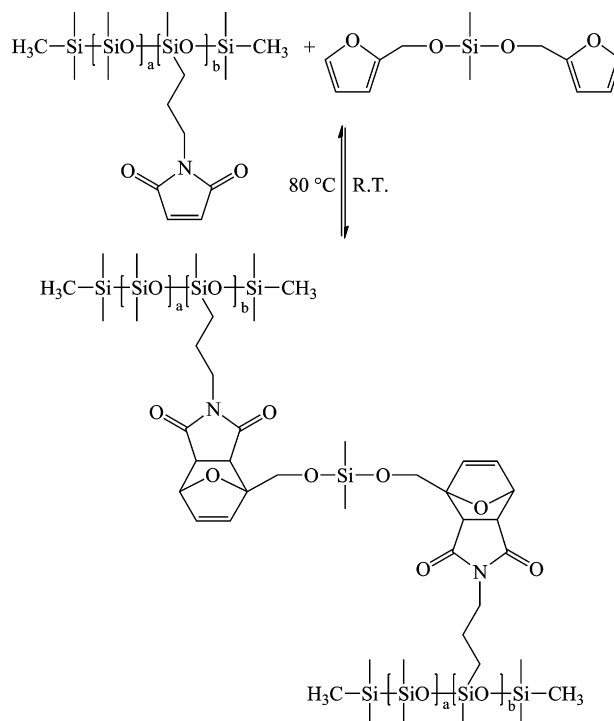


Fig. 57. Crosslinking of a silicone polymer bearing furan side groups by Diels–Alder reaction.

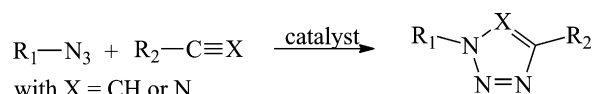


Fig. 58. General reaction illustrated the principle of “click chemistry”.

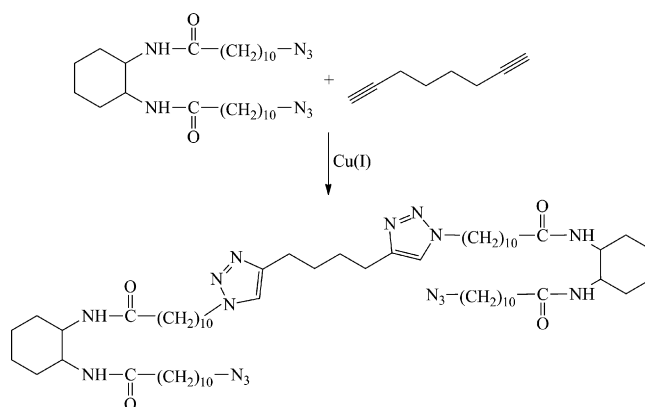


Fig. 59. Synthesis of organogel by click chemistry.

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.

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 shown in Fig. 56.

The crosslinking obtained is thermally reversibility, but this reversibility is not quantitative. After 15 min at 150 °C, 25% of the linkages were lost, returning to the initial state on cooling to 80 °C.

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 °C) was very close to that of its linear precursor (T_g = −112 °C), indicating that PDMS soft segments were preserved.

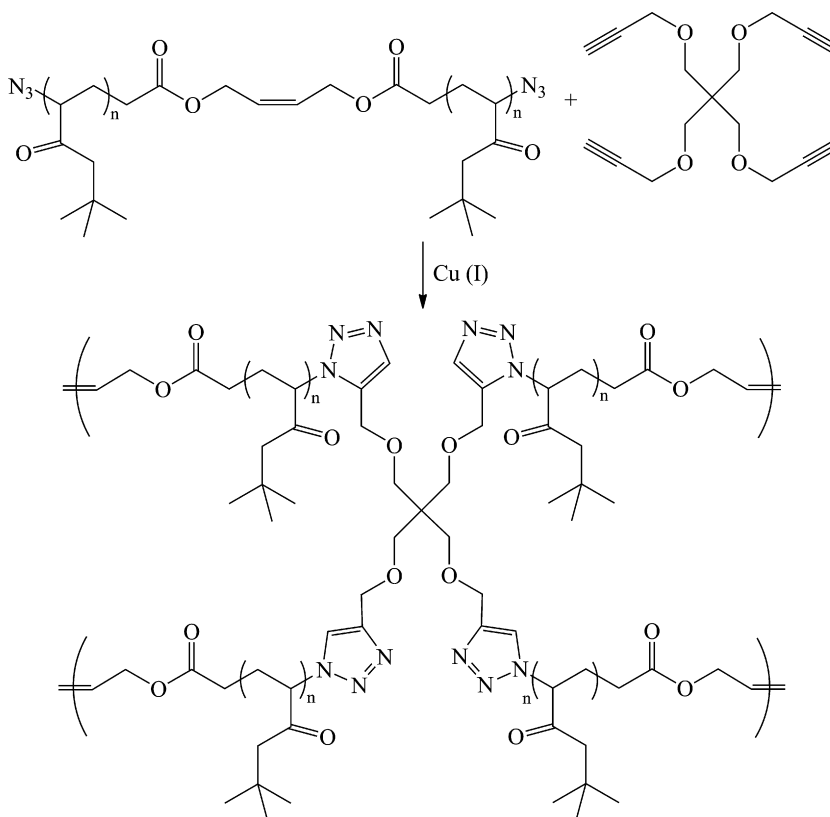


Fig. 60. Crosslinking of end-azido polyacrylate with an acetylenic crosslinker agent.

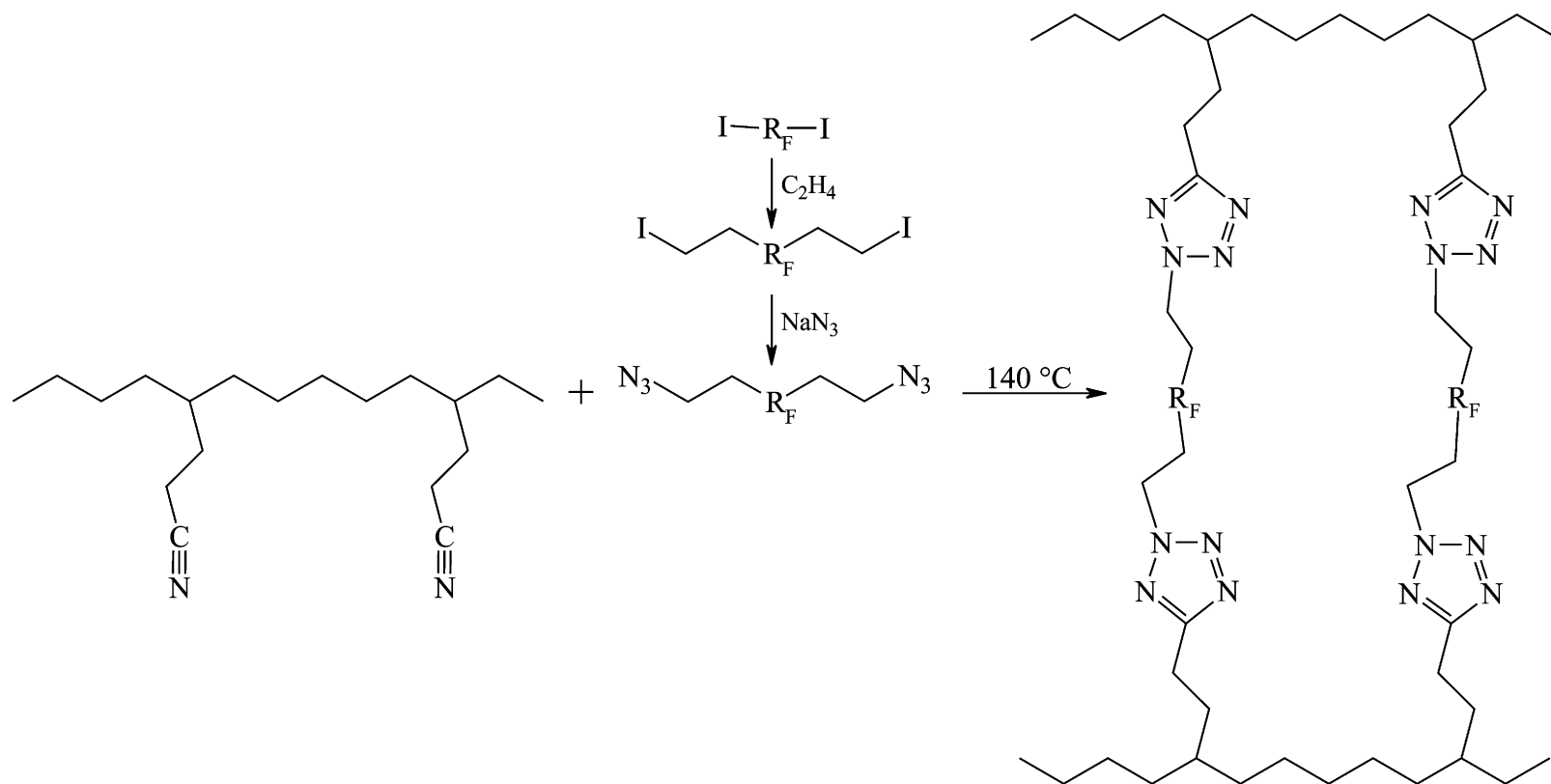


Fig. 61. Crosslinking of a fluorinated polymer with a telechelic bis-azido fluoroalkane by 1,3-dipolar cycloaddition.

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.

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 (PMDTA) 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. Johnson et al. [185] crosslinked polyacrylates, synthesized by atom transfer radical polymerization (ATRP), via the “click chemistry” concept to obtain a star polymer (Fig. 60).

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 and a telechelic bis-azido perfluoroalkane [186] is in progress in order to decrease the crosslinking temperature (see Fig. 61).

Under certain conditions, “click chemistry” and the Hay (or Glaser) coupling (see Section 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 physicochemical 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 that have 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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