RADIATION-INDUCED POLYMERIZATION

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1. INTRODUCTION

Polymers can be synthesized into a variety of topological structures (linear, branched and three-dimensional networks) by two types of polymerization, either of which involves a chain addition process or a step-growth mechanism. Radiation-induced polymerization, for the most part, proceeds by a chain addition mechanism [1].

In principle, step-growth processes can be triggered by the generation of catalysts resulting from the interaction between radiation and the precursors of some acidic or basic species, or between some radiolytic products with acid or base generators. However, this step-growth process has received little attention and is currently limited to few applications of technical relevance. For example, the step-growth addition of the thiol groups on a multifunctional mercaptan derivative to diisocyanates is effectively catalyzed by photobases under ultraviolet (UV) radiation. This results in the formation of hard, flexible materials with interesting uses in microelectronics and as binders for industrial paints and coatings [2].

High energy radiation interacts with organic matter by various physical and chemical mechanisms resulting in the formation of short-lived excited species, and of chemical entities such as thermalized electrons and neutral or ionic free radicals exhibiting longer lifetimes allowing them to undergo bimolecular reactions with various molecular compounds by translational diffusion [3]. The *in-situ* generation of such longer-lived reactive species can be exploited to initiate chain polymerization mechanisms. The resulting process is called radiation-initiated polymerization, the propagation being, in principle, not directly affected by radiolytic events. Propagation essentially proceeds with the same mechanistic and kinetic features of conventional, thermally initiated chain polymerizations. The radiation-induced initiation process makes it possible to trigger polymerization under reaction conditions (temperature, initiation rate, type, location and spatial distribution of the initiating species) that are

unusual, if not specific, compared to the activation with thermally cleavable initiators (such as peroxides) or with redox systems (such as a reductive metal associated with a peroxide). A number of advantages can be found from these peculiarities of radiation-initiated polymerization that benefit processing efficiency or which produce final materials with unique properties [4].

The basic aspects of chain polymerization are discussed in the next section. Then, the specific features of radiation-initiated polymerization carried out by free radical or by cationic propagation will be addressed [5].

2. BASIC ASPECTS OF CHAIN POLYMERIZATION

Chain polymerization is defined as "a chain reaction in which the growth of a polymer chain proceeds exclusively by reaction(s) between monomer(s), (M), and reactive site(s), represented by an asterisk in Eq. (1), on the polymer chain with regeneration of the reactive site(s), at the end of each growth step".

$$\sim\!\sim\!\sim\!\sim (M)_n \sim\!\sim\!\sim\!\sim M^* + M \longrightarrow \sim\!\sim\!\sim\!\sim (M)_{n+1} \sim\!\sim\!\sim\!\sim M^* \tag{1}$$

The chain reaction mechanism includes a sequence of steps forming a chain mechanism, that is a complex reaction path in which one or more reactive intermediates (frequently radicals) are continuously regenerated. This usually happens through a repetitive cycle of steps which propagate the reaction. When the propagation step involves a monomer that is repeatedly bound to an active center, such a process results in the formation of an oligomeric, higher molecular weight entity, which eventually grows further to form a polymeric chain that has an active end group. The most common polymerization processes involve carbon centered free radicals. However, ionic mechanisms, covalent group-transfer and organometallic complexes involved in coordination polymerization have specific features that may offer advantages of technical interest.

Propagation in chain polymerization usually occurs without the formation of small molecules. However, in very specific cases, low-molar-mass molecular by-products are formed, that are not included in the chain undergoing the propagation step. When such molecular extension process occurs, the chain process is a condensation chain polymerization. More commonly, the type of chemical reactions involved in this growth step is specified by using the terms free radical chain polymerization, ring-opening chain polymerization, cationic chain polymerization, *etc*.

The four main steps of the chain mechanism are presented in the following sections for the free radical polymerization of unsaturated compounds such as vinyl, acrylic and styrenic monomers.

## 2.1. KEY STAGES OF THE CHAIN POLYMERIZATION MECHANISM

Step 1 – Chain initiation

Chain initiation can take place as soon as the properly selected initiator starts to decompose into free radicals (In°). Initiation is completed when the initiator radical has added to the first monomer unit, M, to produce the chain initiating species, M_1°. From a kinetic standpoint, the rate of initiation, R_i, is controlled by the initiator decomposition, which is a slower reaction than the subsequent addition of an electron-deficient radical onto the electron rich π bond of the ethylenic monomer. Though directly related to the decomposition rate of the initiator, R_d, the effective initiation rate, R_i, depends on an efficiency factor that takes into account the actual fraction of generated free radicals that effectively add to the monomer for producing M_1°, the chain initiating species. The quenching efficiency of dioxygen for carbon-centered free radicals is extremely high, and, as a result, peroxy radicals are unable to initiate the propagation process. Consequently, free radical polymerizations are preferably conducted with the exclusion of oxygen (*in vacuo* or by deaeration with an inert gas). When a low residual amount of dioxygen is present in the polymerization medium, polymerization starts after an induction period corresponding to the consumption of O_2 *via* the quenching reaction. In some cases, particularly when a photochemical or a radiochemical activation process is used for the initiation, the rate of formation of new free radicals is high enough to overcome the quenching of O_2 that is initially present in the medium and of the amount of O_2 that constantly diffuses from the ambient atmosphere into the reaction medium. This favorable situation can be achieved under intense ultraviolet or light irradiation of properly photosensitized compositions or by processing the radically polymerizable monomers under high dose rate electron beams (EB).
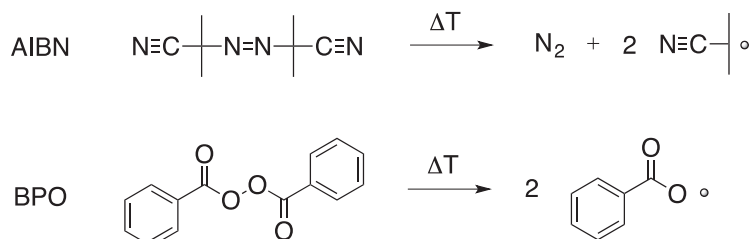
Scheme 1. Examples of thermal initiators with their decomposition products: azo-bis--isobutyronitrile (AIBN) and benzoyl peroxide (BPO).

Typical initiators that are activated by heat include various types of organic compounds with a scissile functional group that is decomposed at reasonable operating temperatures, such as aromatic azo derivatives (–N=N–), disulfides (–S–S–), or peroxides (–O–O–) (Scheme 1). Inorganic and organic redox systems (such as Fenton reagent (FR), peroxide-dimethyl aniline shown
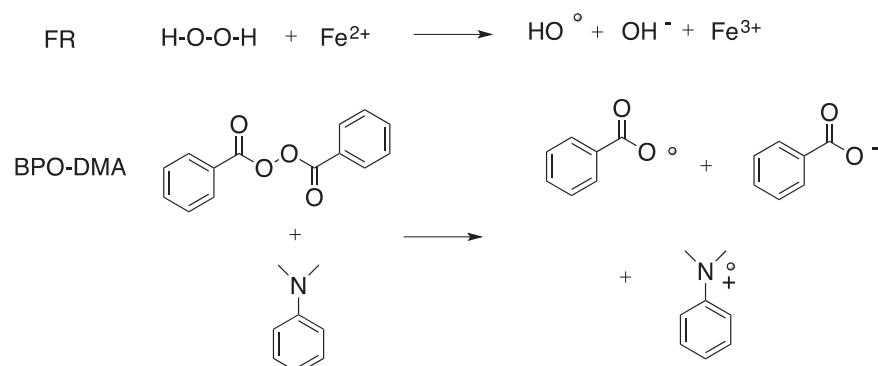
Scheme 2. Examples of redox initiators: Fenton reagent (FR) and benzoyl peroxide–N,N--dimethylaniline system (BPO-DMA).

in Scheme 2) offer the advantage of generating free radicals efficiently at temperatures between 0 and 50°C, without needing to heat the reaction medium in order to induce thermal initiator decomposition.

Step 2 – Chain propagation

Propagation consists of the iterative growth of the initiating radical, $M_1°$, that forms, after a sufficient number of additions, a macroradical, as shown in Eq. (2).
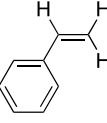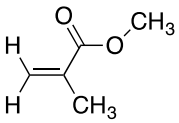
$$\sim\!\sim\!\sim (M)_n \sim\!\sim\!\sim M° + M \longrightarrow \sim\!\sim\!\sim (M)_{n+1} \sim\!\sim\!\sim M° \text{ (rate constant } k_p) \quad (2)$$
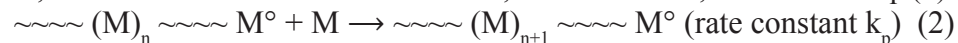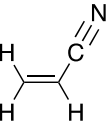
Both for kinetic and thermodynamic reasons, the head-to-tail placement is overwhelmingly predominant for free radical addition of monosubstituted unsaturated monomers 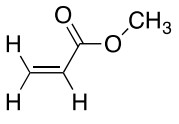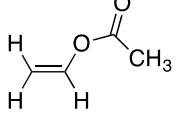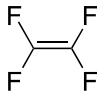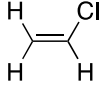(CH_2=CHR) that yield polymer chains where tertiary carbon atoms and methylene groups alternate. Monomers suitable for free radical chain polymerization show varying degrees of reactivity depending on the affinity of the free radical for its monomer. The rate constants for propagation of common unsaturated monomers range between 10^2 and 10^4 $L \cdot mol^{-1} \cdot s^{-1}$ (as shown in Table 1). By comparing the effects of substituents on the stability of the free radical, higher propagation rate constants are observed for less stabilized active centers. However, for achieving the formation of chains with a high degree of polymerization, the reactivity of free radicals has to be mainly directed towards propagation, limiting competing reactions of charge transfer.

Step 3 – Chain termination

Active free radicals in the polymerization of unsaturated monomers are unstable and tend to undergo self-annihilation when on occasion randomly encountering another free radical. This bimolecular process results in the termination of the molecular chains propagated by two encountering macroradicals. Termination occurs either by combination or by disproportionation, which yields a single macromolecule or saturated and unsaturated polymer chains. Combination is the simplest mechanism where the two macroradicals overlap their singly occupied molecular orbital to form a stable σ bond, resulting in the

Table 1. Propagation rate constants k_p for common monomers undergoing free radical polymerization.

Monomer	Structure	k_p [L·mol^{-1}·s^{-1}] at T = 60°C[a]
Butadiene		100
Styrene		165
Ethylene		242
Methyl methacrylate		515
Acrylonitrile		1 960
Methyl acrylate		2 090
Vinyl acetate		2 300
Tetrafluorethylene		9 100 (83°C)
Vinyl chloride		11 000 (50°C)

[a] At T = 60°C, unless otherwise specified. Data were collected from Ref. [5].

formation of a polymer which is the sum of monomer units added by each one of the participating chains (Eq. (3)). Disproportionation is a redox process yielding a hydrogen saturated macromolecule together with its omega unsatu-

rated counterpart (Eq. (4)). This takes place *via* the abstraction of a hydrogen atom at the saturated carbon next to the active center by the other macroradical. The activation energy required for the abstraction process is generally much higher than the straightf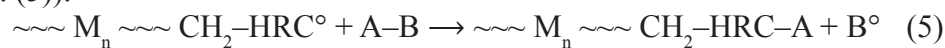orward combination of the two macroradicals. As a consequence, for a number of polymers (*e.g.* poly(methyl acrylate), polyacrylonitrile, polystyrene), disproportionation takes place as a minor mechanistic pathway compared to combination. Disproportionation competes significantly and may become the predominant termination process when the propagating radical is sterically hindered, as in methyl methacrylate polymerization.

$$\sim\sim\sim M_n \sim\sim\sim CH_2-HRC° + °CHR-CH_2 \sim\sim\sim M_p \sim\sim\sim \rightarrow \sim\sim\sim M_{n+p+2} \sim\sim\sim \quad (3)$$

$$\sim\sim\sim M_{nv} \sim\sim\sim CH_2-HRC° + °CHR-CH_2 \sim\sim\sim M_p \sim\sim\sim \rightarrow$$
$$\sim\sim\sim M_n \sim\sim\sim CH_2-CH_2R + RHC=CH \sim\sim\sim M_p \sim\sim\sim \quad (4)$$
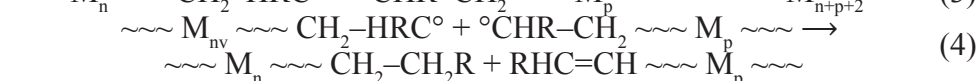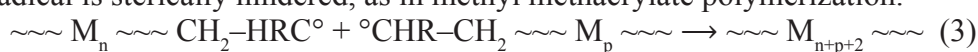
Step 4 – Chain transfer

Chain transfer can be considered as a competing process to propagation. Instead of adding to a monomer, the growing macroradical can react with various types of molecular compounds present in the reaction medium: the initiator, solvent, dead polymer, impurities, or any transfer agent, introduced purposely in the reaction medium to obtain a desired effect on the resulting molecular weight (MW) or on end group functionalization.

The transfer reaction can be depicted by an exchange of an atom by a free radical mechanism, the macroradical abstracting an atom, A, to form a stable polymer molecule fitted with A as an end group, generating the free radical B° (Eq. (5)).

$$\sim\sim\sim M_n \sim\sim\sim CH_2-HRC° + A-B \rightarrow \sim\sim\sim M_n \sim\sim\sim CH_2-HRC-A + B° \quad (5)$$
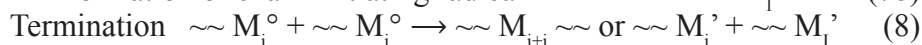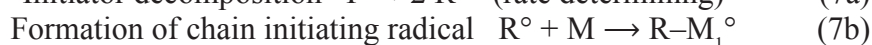
$$B° + n M \rightarrow B-M_n° \quad (6)$$

Chain transfer can compete with propagation in a process where the active center of a growing polymer chain is transferred to various components in the polymerization medium, such as solvent, monomer, initiator, polymer or to a purposely selected additive (a transfer agent). Transfer reactions occur easily with the use of a chlorinated solvent ($CHCl_3$) or with a solvent having an easily abstractable H atom (isopropanol), a monomer, or a polymer. When the molecule subject to the transfer process is a macromolecule formed earlier in the reaction medium, the chain growing from the main polymer backbone will create a side chain. The repetition of this phenomenon leads to multi-branched polymers.

The occurrence of this event terminates the chain involved with the macroradical, but the active site is transferred to another radical, B°, which can restart a new chain polymerization (Eq. (6)). In such a case, the instantaneous number of growing chains is kept constant, with little or no effect on the polymerization rate. The impact of transfer on the average length of the formed polymer chain is discussed below.

2.2. KINETIC ASPECTS OF FREE RADICAL CHAIN POLYMERIZATION

Because of the fast bimolecular combination of free radicals in fluid media, the chain reaction kinetics of free radical polymerization is governed by a steady state that results from the balance between the formation of new growing chains yielded by initiator decomposition and by the addition to the first monomer unit M (Eqs. (7a) and (7b)) and the radical disappearance by termination (Eq. (8)).

$$\text{Initiator decomposition} \quad I \longrightarrow 2\,R° \quad \text{(rate determining)} \tag{7a}$$

$$\text{Formation of chain initiating radical} \quad R° + M \longrightarrow R{-}M_1° \tag{7b}$$

$$\text{Termination} \quad \sim\sim M_i° + \sim\sim M_j° \longrightarrow \sim\sim M_{i+j} \sim\sim \ \text{or} \ \sim\sim M_i' + \sim\sim M_i' \tag{8}$$

The dynamic balance is expressed by equal rates for initiation and for termination yielding

$$2\,f\,k_d\,[I] = 2\,k_t\,[M°]^2 \tag{9}$$

where: f – the efficiency factor of free radicals involved in the chain initiation, k_d – the rate constant for initiator decomposition, k_t – the rate constant for the termination reaction, $[M°]$ – the concentration in propagating free radicals.

Considering typical values for the rate of reaction (7b) ($R_i \approx 10^{-4}\text{-}10^{-6}$ mol·L^{-1}·s^{-1}) and for the bimolecular termination rate constant for Eq. (8) ($k_t \approx 10^6\text{-}10^8$ L·mol^{-1}·s^{-1}), a steady state for free radical concentration is reached within a fraction of a second. The steady-state value of a propagating free radical concentration can be introduced in the expression of the polymerization rate, R_p, defined as the rate of monomer consumption in the propagation step,

$$R_p = k_p\,[M]\,[M°] \tag{10}$$

yields

$$R_p = k_p\,(f\,k_d/k_t)^{0.5}\,[M]\,[I]^{0.5} \tag{11}$$

where k_p is the rate constant for propagation. Rate constants k_p are in the range $10^2\text{-}10^4$ L·mol^{-1}·s^{-1}, depending on the structure of the unsaturated monomer. A much higher value of k_t compared to k_p does not prevent propagation because the radical species are present in very low concentrations (typically 10^{-8} mol·L^{-1}) and because R_p is inversely proportional to the square root of k_t.

Besides the polymerization rate, of importance in free radical chain polymerization is the kinetic chain length, λ. In a chain process unaffected by transfer reactions, the kinetic chain length is defined as the average number of propagation steps for each initiation. This quantity corresponds to the ratio of the polymerization rate, R_p, to the initiation rate, R_i, or to the termination rate, R_t, since the latter two quantities are equal. In chain polymerization, it is worth noting that λ represents the average number of monomer molecules added to a growing chain at the moment it is deactivated by termination. Depending on the relative contribution of disproportionation and combination to the overall termination process, the terminated polymer chain will exhibit a number-aver-

age degree of polymerization ($\overline{DP}_n$) between 1 (only disproportionation) and 2 (only combination) times the λ value.

The kinetic data derived from the chain kinetic model are instantaneous values subject to changes in the physical parameters for the reaction, such as temperature and viscosity. Autoacceleration occurs in radical chain polymerization and normally in bulk polymerization. As monomer conversion increases, the gradual formation of polymer in the reaction medium increases the viscosity, essentially reducing the efficiency of chain termination by reducing the diffusion of the macroradicals. This change in viscosity has little effect on initiation and propagation, but it results in a strong increase of the free radical concentration. Autoacceleration, called the Trommsdorff-Norrish effect, is particularly effective when multifunctional monomers are involved in the polymerization.

Chain transfer reactions reduce the average molecular weight of the final polymer while keeping constant the total number of free radicals. Therefore, transfer reactions have no direct effect on polymerization rate, but can be used to control the average degree of polymerization to form chains, acting on the kinetic chain length $\lambda = R_p/(R_i + R_{tr})$, where $R_{tr} = k_{tr}\,[M_i^\circ]\,[TA]$ is the rate of the transfer reaction to the transfer agent TA. Thiols are particularly efficient in this.

2.3. POLYMERIZATION THERMODYNAMICS

As polymerization reactions convert a large number of monomer molecules into a few macromolecular chains, they are generally associated with a strong decrease of entropy ($\Delta S_p < 0$). This situation impacts the free energy state function $\Delta G_p = \Delta H_p - T\Delta S_p$ that governs what happens to the chemical transformations. Polymerization can proceed if the enthalpy variation is exothermal enough ($\Delta H << 0$), so that the net balance appearing in ΔG_p is negative. Monosubstituted unsaturated monomers typically exhibit polymerization enthalpies ranging from 70 to 90 kJ·mol^{-1}. This generally allows for an efficient polymerization to proceed if the monomer concentration is high enough. Taking into account the reversibility of the propagation step of free radical polymerization, the growth of chains is stopped when the free energy $\Delta G_p = \Delta H_p^\circ - T\Delta S_p^\circ - RT \ln\,[M]$ approaches 0. At a given monomer concentration, the temperature increases to a critical value $T_c = \Delta H_p^\circ/(\Delta S_p^\circ + R \ln\,([M]_c)$, called the ceiling temperature. The polymerization of vinyl acetate, methyl acrylate and styrene is not significantly affected by thermodynamic constrains under normal polymerization conditions, but for methyl methacrylate, a monomer exhibiting a lower enthalpy of polymerization due to the presence of a methyl substituent on the double bond, the ceiling temperature is 220°C for pure monomer.

2.4. MICROSTRUCTURE OF POLYMER CHAINS

Chain polymerization of vinyl monomers (CH_2=CHR) yields polymers having stereocenters (–CH_2–C*HR–) which can exhibit either of two different configurations. Free radical propagation is weakly sensitive to the influence of the stereocenter located at the penultimate unit on the macroradical. This results in a weak preference for the formation of a syndiotactic dyad with respect to an isotactic one at each propagation step. The final polymers are therefore essentially atactic in terms of microstructure and are amorphous materials.
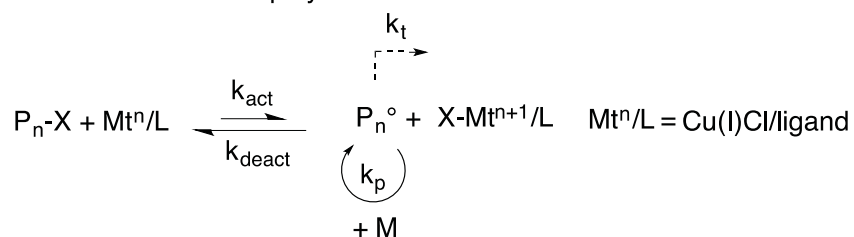
2.5. CONTROLLED FREE RADICAL POLYMERIZATION

The limitations due to the termination reactions taking place during conventional free radical polymerization have been overcome by using various molecules, metal complexes or stable free radicals that convert the growing
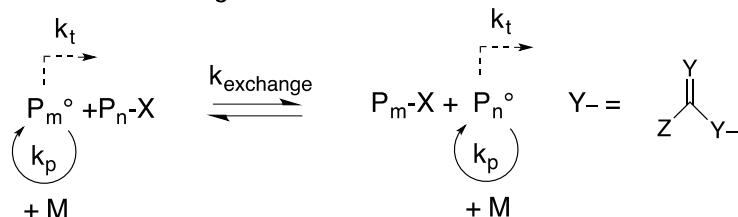
- Nitroxide-mediated polymerization
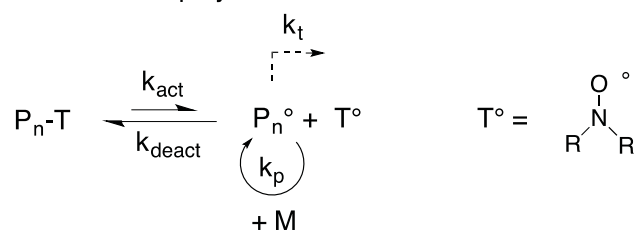
- Atom transfer radical polymerization
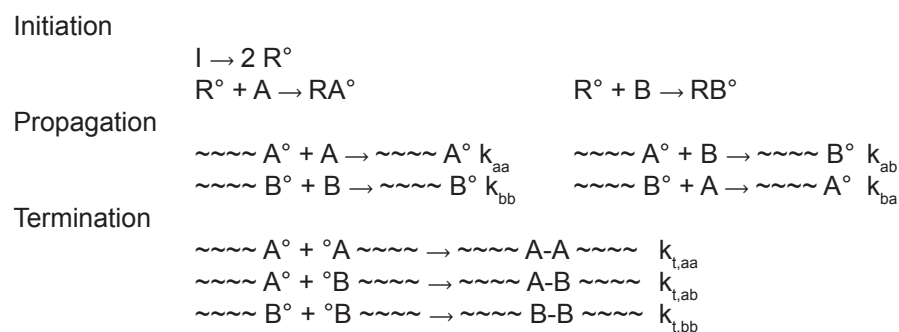

- Reversible addition fragmentation chain transfer

Scheme 3. Principles of the three main methods for achieving controlled free radical polymerization.

free radicals into a dormant species, thus dramatically reducing the occurrence of termination [6]. Controlled free radical polymerization (CRP) can be achieved by using stable free radicals as nitroxides (nitroxide-mediated polymerization, NMP), by reversible addition-fragmentation chain transfer (RAFT) to various thiocarbonyl compounds, or by halogen atom transfer from a transition-metal--catalyst subject to a redox exchange (atom transfer radical polymerization, ATRP), as shown in Scheme 3. The active center is capable of reactivation, functionalization, and chain extension to form block copolymers and even more complex polymer architectures. The potential of CRP differs from ionic living polymerization processes because of the tolerance of the selected reversible chemistries to a variety of functional monomers and to unconventional polymerization media.

2.6. FREE RADICAL COPOLYMERIZATION

Chain polymerizations can be carried out with mixtures of two or more monomers to form polymeric products with an almost unlimited composition and structure, hence with new properties. The monomers enter into the copolymer in amounts determined by their relative concentrations and reactivity. Whereas alternating, statistical and random copolymers are produced by simultaneous and competing polymerization of monomer mixtures, graft and block copolymers result from a sequence of separate polymerizations. The instantaneous composition of a copolymer produced by a chain process cannot be determined simply from knowledge of the homopolymerization rates of the two monomers. The relative contribution of cross-propagation with respect to the homopolymerization is described by using the reactivity ratios of each monomer. For a mixture of two monomers, the first order Markov model for copolymerization assumes that the reactivity of the propagating species is dependent only on the monomer unit at the end of the chain, with there being four possible propagation reactions (Scheme 4).

Initiation

$\qquad$ I → 2 R°

$\qquad$ R° + A → RA° $\qquad\qquad$ R° + B → RB°

Propagation

$\qquad$ ~~~~ A° + A → ~~~~ A° k_{aa} $\qquad$ ~~~~ A° + B → ~~~~ B° k_{ab}

$\qquad$ ~~~~ B° + B → ~~~~ B° k_{bb} $\qquad$ ~~~~ B° + A → ~~~~ A° k_{ba}

Termination

$\qquad$ ~~~~ A° + °A ~~~~ → ~~~~ A-A ~~~~ $\ k_{t,aa}$

$\qquad$ ~~~~ A° + °B ~~~~ → ~~~~ A-B ~~~~ $\ k_{t,ab}$

$\qquad$ ~~~~ B° + °B ~~~~ → ~~~~ B-B ~~~~ $\ k_{t,bb}$

Scheme 4. First order Markov model for the free radical copolymerization of monomers A and B.

The reactivity ratios of both monomers with respect to the macroradicals fitted with A° and B° as the propagating end groups, $r_a = k_{aa}/k_{ab}$ and $r_b = k_{bb}/k_{ba}$, respectively, are the main parameters that govern the instantaneous rate of incorporation of both monomers in the growing chains, for a given monomer composition in the reaction medium $f_a = [A]_t/([A]_t + [B]_t)$. The Mayo-Lewis relation (Eq. (10)), derived from the kinetic scheme of the terminal model, states how the instantaneous composition of the formed copolymer, $F_a = d[A]_t/(d[A]_t + d[B]_t)$, is dependent on the variable f_a and on the parameters r_a and r_b.

$$F_a = (r_a f_a^2 + f_a(1 - f_a))/(r_a f_a^2 + 2 f_a(1 - f_a) + r_b(1 - f_a^2)) \qquad (12)$$

An important feature of free radical copolymerization is the composition drift that is expected to take place during a batch process, and the distribution of monomer units along the chain that may ideally take place at random if $r_a \cdot r_b = 1$, or form alternating –A–B– sequences, or eventually produce isolated units of one monomer between blocks of the other.
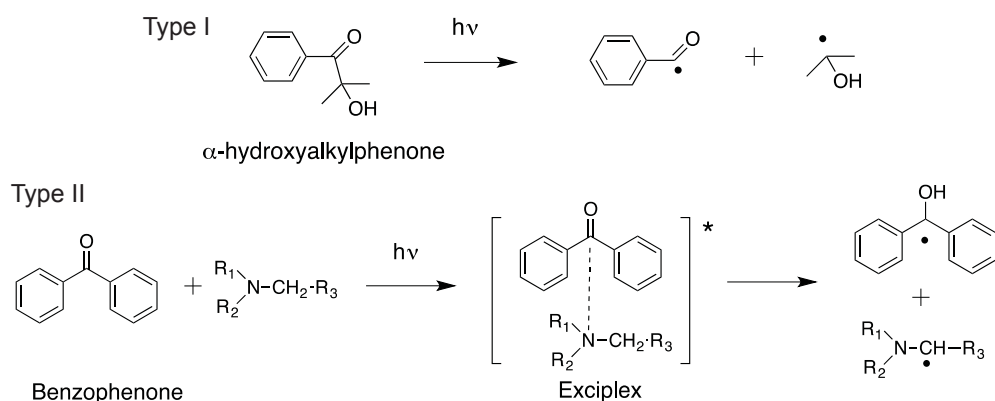
3. RADIATION-INITIATED POLYMERIZATION

Compared to thermal and redox initiation processes, activation methods using radiation exhibit unique features that allow for a time and spatial control of polymerization. Several applications take advantage of these properties: the ultraviolet radiation or electron beam (UV/EB) curing of solvent-free coatings and inks in industry and in graphic arts, the synthesis of vinyl acetate or acrylate latices by emulsion polymerization initiated by using gamma rays, the out-of--autoclave curing of performance composites using EB and/or X-rays, laser or EB micropatterning and nanolithography for microfluidic and electronic devices [7].

Ultraviolet radiation and high energy electron beam radiation can trigger chain polymerization either by direct interaction with monomers or through the intermediacy of some other constituents present in the reaction medium.
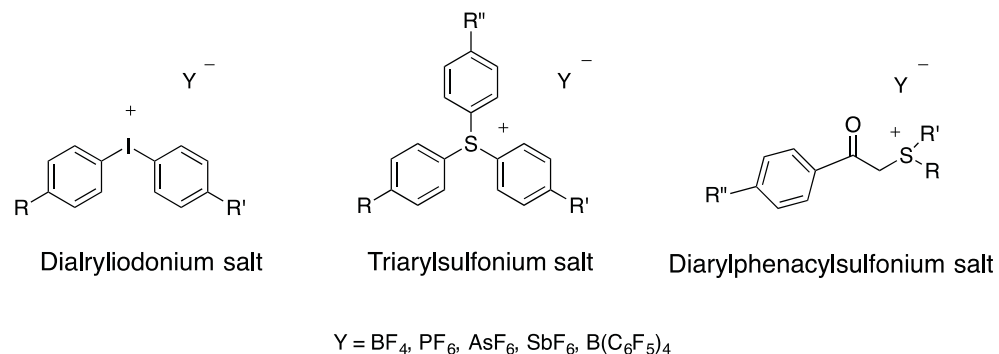
3.1. PHOTOINITIATED POLYMERIZATION

Unsaturated monomers can be activated by short wavelength photons, by specific additives called photoinitiators that generate active centers (free radical or cationic species) upon exposure to an ultraviolet source. Radical initiation mechanisms either involve the direct homolysis of a C–C of the photoexcited initiator (Type I initiation with aromatic carbonyl compounds) or a cascade of reactions (Type II initiation by electron transfer and hydrogen abstraction), as shown in Scheme 5.

Scheme 5. Examples of Type I and Type II photoinitiators for free radical polymerization.

Aromatic onium salts can generate cationic active centers (Brønsted acids or carbenium ions) upon absorption of ultraviolet radiation [8]. There are two basic classes of cationic initiators grouped by dependence on the mechanisms of photolysis. The first group includes diaryliodonium and triarylsulfonium salts, which undergo fragmentation to yield aryl radicals and/or arylionium cation radicals. Dialkylphenacylsulfonium and dialkyl-4-hydroxyphenylsulfonium salts form the second group that generates yields and Brønsted acids by a reversible photolysis (Scheme 6).

$Y = BF_4, PF_6, AsF_6, SbF_6, B(C_6F_5)_4$

Scheme 6. Examples of onium salts used for radiation-initiated cationic polymerization.

Both classes of onium salts can be photosensitized in order to extend their response to long wavelength ultraviolet and to light. This can be achieved by energy transfer, electron transfer or through the intermediary of free radicals. A simplified description of the direct and sensitized pathways for the generation of cationic species from a diaryliodonium salt is represented in Scheme 7. Structural variations within the cations of onium salts have a marked influence on the photolytic efficiency, whereas the nature of anion mainly affects the course of the resulting cationic polymerization.
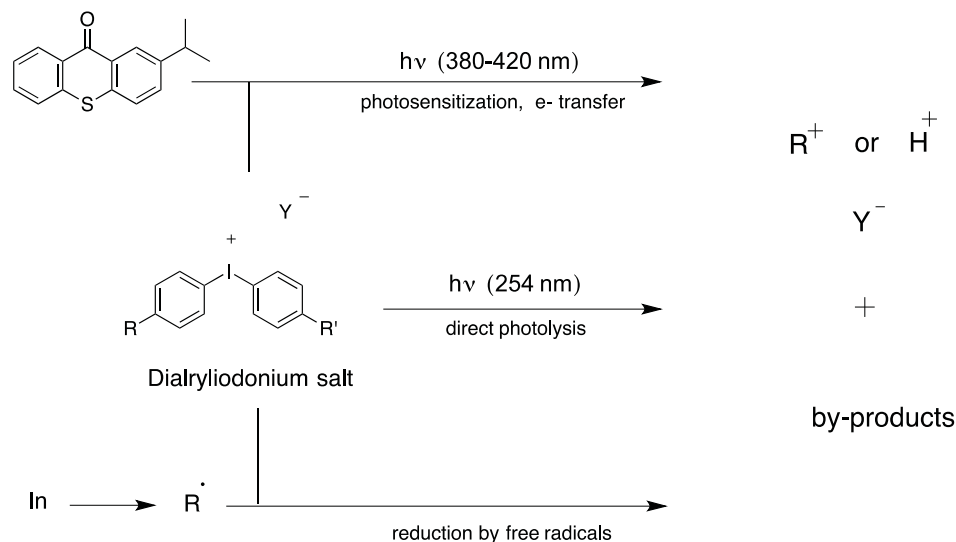
Scheme 7. Examples of onium salts used for radiation-initiated cationic polymerization ("In" is a source of free radicals generated by any type of mechanism).
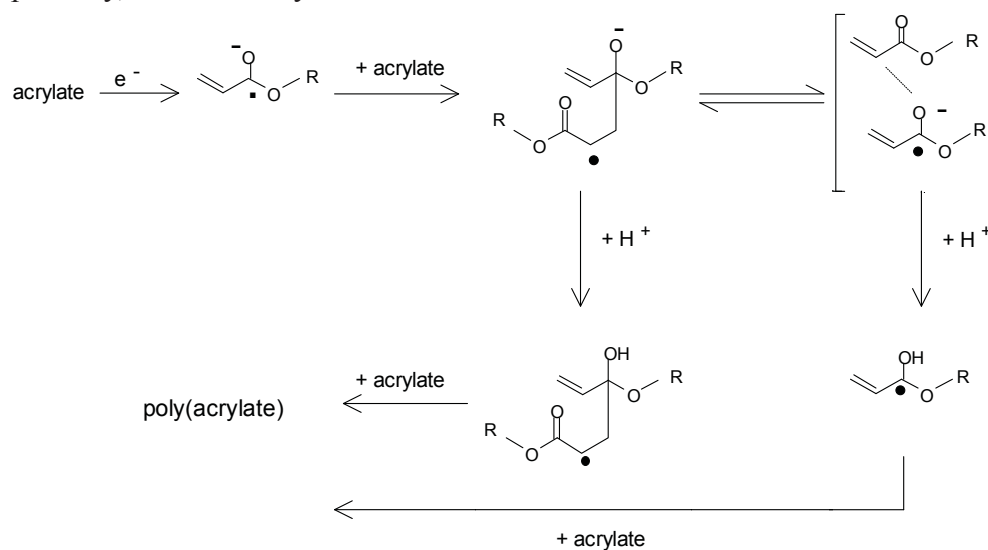
3.2. POLYMERIZATION INDUCED BY HIGH ENERGY RADIATION

Despite the high intrinsic efficiency of commercial photoinitiators for free radical or for cationic polymerization, the effectiveness of photochemically triggered initiation is limited by the low penetration depth of ultraviolet radiation into opaque compositions. This is why accelerated electrons as well as photonic ionizing radiations (gamma and X-rays) have a significant advantage over ultraviolet radiation and light. Light is the visible range of the electromagnetic spectrum. The depth of penetration is much greater with less attenuation for ionizing radiation than for ultraviolet radiation and light. Pigmented coatings, printing inks but also adhesives and sealants sandwiched between non--transparent materials as well as fiber-reinforced composites can be cured by crosslinking polymerization of multifunctional monomer compositions.

The radiolysis of olefinic monomers produces cations, anions, and free radicals. Such species are capable of initiating chain polymerization. The cationic polymerization of isobutylene, of vinyl ethers, of epoxies, and of styrene and the anionic polymerization of acrylonitrile have been observed in the absence of additional initiators under controlled laboratory conditions. Long-lived cationic chain reactions involving carbenium or oxonium intermediates are unlikely because of the high reactivity of active centers that make transfers and deactivation reactions very fast unless special conditions (purity of involved chemicals, low temperature) are maintained throughout the process. For that reason, onium salts are used in the monomer composition.

From a practical perspective, most radiation polymerizations are mediated by free radicals, since at temperatures of technical relevance ionic species are not stable and dissociate to yield radicals.

Pulse radiolysis experiments on various mono- or multiacrylate monomers monitored by time-resolved spectroscopy have permitted a better understanding of the various pathways that lead to initiation. The mechanism [9] involves the attachment of a thermalized electron to an acrylate carbonyl group, and the subsequent formation of a radical anion dimer under the form of a charge transfer complex, or of a covalent adduct (Scheme 8). Protonation of the radical-anions yields the effective initiators for propagation. On the basis of experimental data, this model considers the direct formation of free radicals by homolytic dissociation of electronically excited molecular segments as a minor pathway, based on acrylates that were studied.


Scheme 8. Initiation mechanism for acrylate polymerization under high energy radiation [9].

The subsequent steps of the free radical polymerization follow the same pathway as that of conventional crosslinking polymerization initiated by thermal or redox processes. The specific aspects of the cationic polymerization of epoxies are discussed below. Contrary to the mechanism of onium salt photolysis upon selective absorption of ultraviolet radiation, the dominant pathway under ionizing radiation in a medium rich in monomers is the production of free radicals which can reduce the onium salt, and generate in a second stage carbenium cations (Scheme 9). Reduction of the onium salt can also occur from its interaction with solvated electrons (reduction pathway). This mechanism was confirmed by pulse radiolysis experiments on diglycidyl ether of bisphenol A (DGEBA) in the presence of an iodonium salt [7].
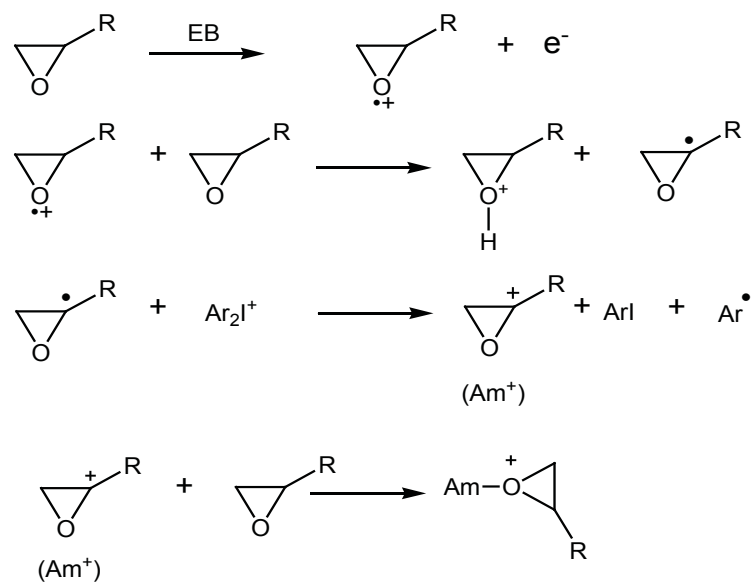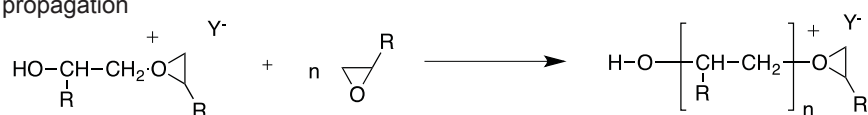
Scheme 9. Initiation mechanism for epoxy polymerization under high energy radiation.
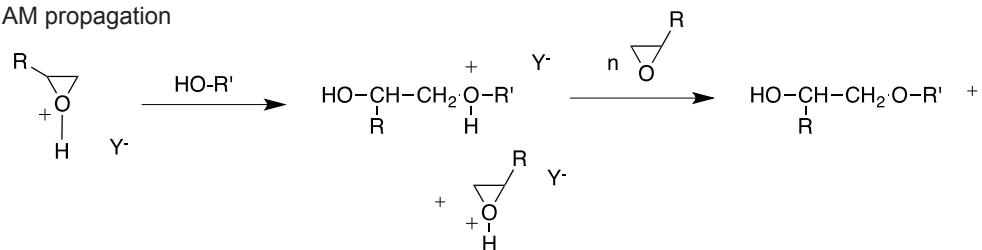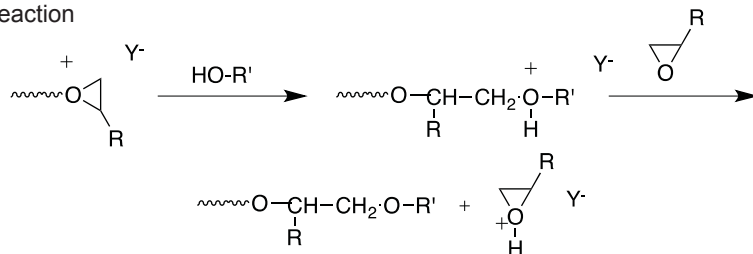
Initiation
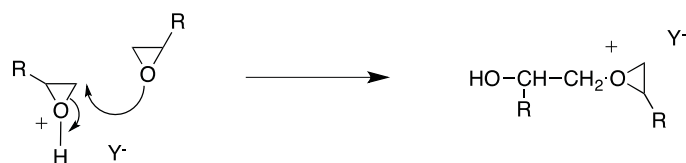
ACE propagation

AM propagation

Transfer reaction

Scheme 10. Propagation and transfer reactions during the cationic polymerization of epoxides.

Cationic chain propagation results from the reaction of oxonium ions with epoxy monomers by activated chain end (ACE) or activated monomer (AM) mechanisms. The ACE mechanism consists of the repeated addition of the monomer on the growing chain by the nucleophilic attack of the oxygen from the epoxy monomer on the carbon atom adjacent to the oxonium ion (Scheme 10). The AM mechanism takes place in presence of hydroxyl containing species and involves their addition to the protonated monomer followed by a charge transfer. The activated monomer is then regenerated and can react again with a hydroxylic compound. As the epoxy ring opens, hydroxyl groups are formed which favor the AM mechanism. Other transfer reactions can take place between an active chain and nucleophilic species such as water, alcohol or any other hydroxylic compounds resulting in the liberation of a proton and an inactive oligomer.

Two cationic species cannot react together. Thus, no termination reaction occurs by self-quenching of the active centers, as in the case of free radical processes. Once irradiation has ceased, cationic polymerization will continue to propagate without new initiation, by the so-called dark cure phenomenon, until the active centers are trapped in a glassy network or quenched by some inhibitor entering the material. This behavior enables further thermal activation giving rise to some benefits of post-curing.

3.3. GENERAL AND SPECIFIC FEATURES OF RADIATION-INDUCED POLYMERIZATION

One of the attributes of radiation as an alternative mode for activating chemical reactions is the immediacy and the control of the spatial distribution for generating active centres. The ability to trigger polymerization reactions independent of temperature is of interest for decoupling the influence of thermal activation on the various steps of the chain polymerization mechanism that follow initiation. This last feature can be exploited both from a fundamental perspective (mechanistic studies, determination of activation energies, pulse laser polymerization) and for technical reasons (design of low cost molding equipment, use of temperature sensitive substrates, design of thermal post--treatments).

The crosslinking polymerization of multifunctional monomers and pre--polymers is by far the largest use of this technology. Various analytic methods can be used for monitoring the kinetic behavior of polymerizable compositions exposed to ultraviolet radiation, to light and to ionizing radiation [7] and for studying the influence of the processing conditions on the properties of the materials produced. A selection of results illustrates some of the important aspects of polymerization kinetics and of network formation.
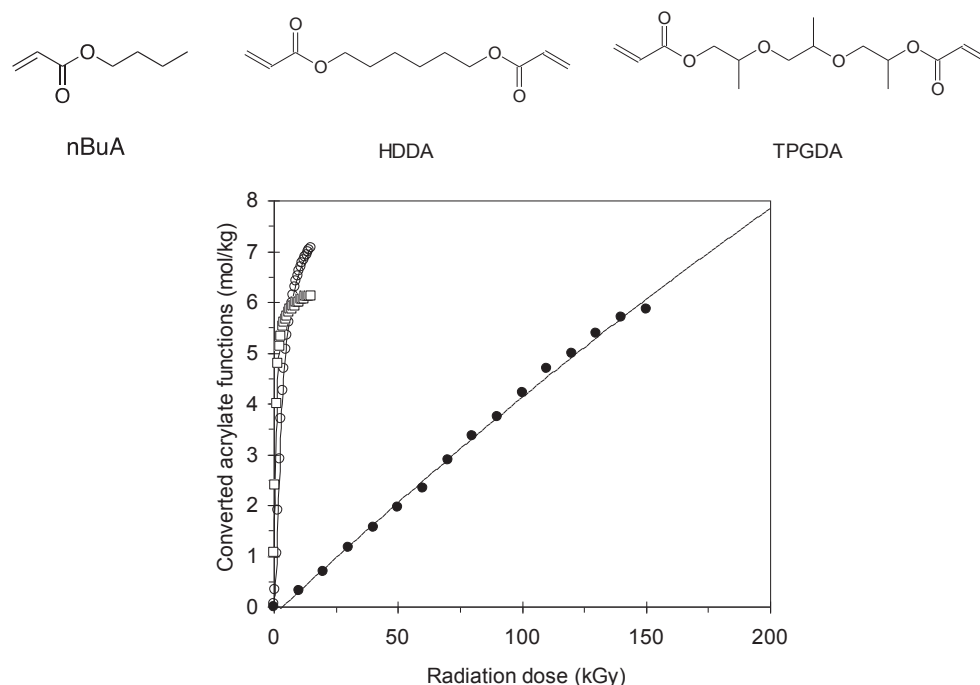
Fig.1. Kinetic profiles of acrylate consumption in monomer films as a function of EB radiation dose: nBuA (●), TPGDA (□) and HDDA (○).

The gel effect associated with crosslinking polymerization is shown by comparing the kinetic profiles under exposure to increasing EB doses of a monoacrylate (n-butylacrylate, nBuA) with those of diacrylates (hexanediol diacrylate, HDDA and tripropyleneglycol diacrylate, TPGDA). All three monomers exhibit similar initial acrylate functionality content (7-8 mol·kg^{-1}). The plots of Fig.1 clearly show that diacrylates polymerize much faster than nBuA, as a result of the Trommsdorff effect. The extremely fast polymerization of compositions including multiacrylates is used in ink formulations for graphic arts and for coatings for optical fibers, with curing speeds under high energy radiation as high as 1000 m·min^{-1} on high-performance industrial lines.

The viscosity of solvent-free radiation-curable compositions typically ranges from 0.5 to 5 Pa·s at application temperatures which facilitates the spreading of the composition onto a substrate or the impregnation of the composition as the matrix in a composite material. Since polymerization is aimed at converting the monomer and prepolymer blend into a hard material, curing proceeds with a dramatic evolution of the mobility of monomer functions in the medium, from the initially fluid state, to a gel, and eventually to a vitreous network. The viscosity gradually increases by several orders of magnitude until solidification, being influenced by polymerization kinetics.

An instructive result was obtained by comparing the polymerization profile of an aliphatic polyurethane triacrylate (APU3), which has an initial acrylate
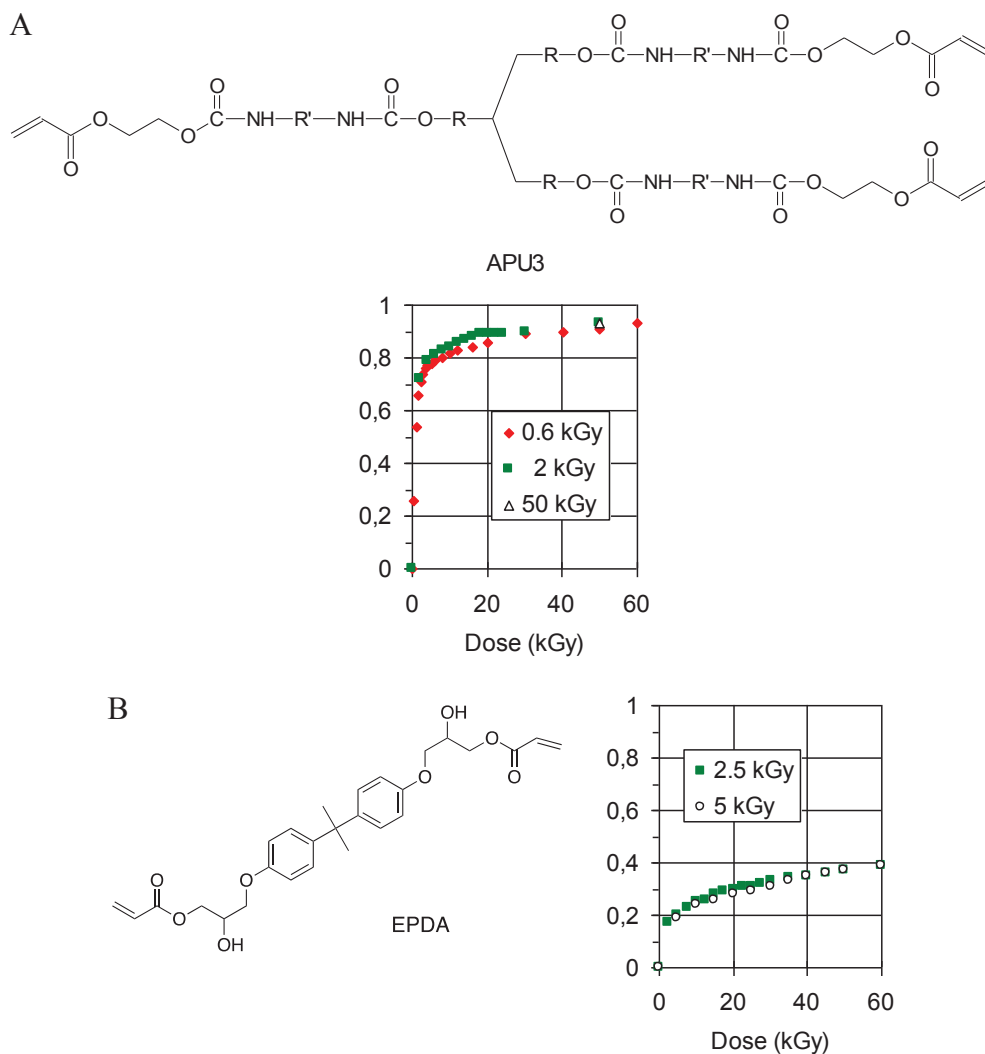
A

B

Fig.2. Kinetic profiles of acrylate consumption in pre-polymer films as a function of EB radiation dose: APU3 (A) and EPDA (B).

content of 3.5 mol·kg^{-1}, with those observed for an aromatic epoxydiacrylate (bisphenol A epoxy diacrylate, EPDA) with an initial acrylate content of about 6 mol·kg^{-1}, being subjected to various EB dose increments (as shown in Fig.2). The polyurethane pre-polymer possesses a flexible backbone that forms a soft material upon curing. Its kinetic profile shows a steep increase in acrylate fractional conversion, up to 0.75 for a dose lower than 10 kGy, regardless of the dose increment (Fig.2A). The profile then gently levels off to reach a conversion level higher than 0.9. The corresponding plot recorded for the aromatic epoxy diacrylate shows an initial fast polymerization to a conversion level of 0.2 for a dose of 2.5 kGy, followed by a weak reactivity with a rather small increase of conversion up to 0.4 at 60 kGy (Fig.2B). At this point, the concen-
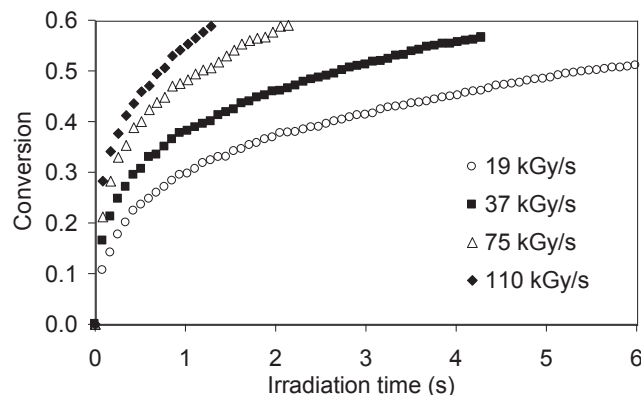
Fig.3. Kinetic profiles of acrylate consumption in EPAD pre-polymer as a function of EB radiation dose rate.

tration of unreacted acrylate functionality is about 3.6 mol·kg^{-1}, a value that is even higher than the acrylate concentration in the unreacted APU3 sample. This shows the influence of incipient vitrification that limits the propagation step, in spite of there being a still large concentration of monomer in the partially cured EPAD samples. These experiments were conducted at room temperature with small increments of dose using thin films of the curable compositions which limited any increase in temperature. Under these quasi-isothermal conditions, vitrification took place in the PUA3 material at conversion levels slightly above 0.7, the critical value at which the kinetics started to level off. The vitrification phenomenon took place at much lower conversion levels (typically 0.2) in the more rigid EPAD pre-polymer when cured at room temperature. These observations stress the importance of the relation between the effective curing temperature and the conversion dependence of the glass transition on the material networks.

The influence of dose rate on polymerization kinetics can be examined, provided that isothermal conditions are maintained within the sample. The results of a series of EB curing experiments conducted with EPAD at different dose rates ranging from 19 to 110 kGy·s^{-1} are plotted in Fig.3.

The rate of polymerization measured in the initial regime (steep increase) was shown to be proportional to the square root of the dose rate $\dot{D}$, as would be expected from the bimolecular termination kinetics in a fluid medium (Eq. (13)).

$$R_p = \frac{k_p R_{init}}{2\sqrt{k_t}}[C = C] \propto \frac{k_p}{2\sqrt{k_t}}[C = C]\left(\dot{D}\right)^{0.5} \tag{13}$$

Deviations from this law were observed as soon as the initial slope weakened as a consequence of mobility being restricted. From the lines drawn in the final regime, a first order dependence of the polymerization rate on $\dot{D}$ was observed. This situation corresponds to a chain process with monomolecular termination by occlusion of the growing free radicals in a vitrified matrix.

From a practical viewpoint, careful attention must be paid to the thermal effects within a sample subjected to radiation-induced polymerization. There should be a finely-tuned interplay between the control of the polymerization exotherm (typically 80 and 100 kJ·mol^{-1}, for acrylates and epoxy functionality, respectively), the energy conversion from the deposited radiation dose, the heat and radiative exchanges with the surrounding environment and the conversion dependence of vitrification.

3.4. APPLICATIONS OF RADIATION-INDUCED POLYMERIZATION

High energy radiation can be used to synthetize linear polymers by emulsion free radical polymerization, but is rarely done. The process consists of irradiating an oil-in-water dispersion of one or several hydrophobic monomers in the presence of a surfactant. Hydroxyl radicals are produced by water radiolysis and are the main species responsible for the polymerization initiation after entering the monomer micelles. This process results in the formation of latex particles with the typical dimension of about 100 nm. The particles grow in size during the reaction since monomers continue to diffuse from reservoir droplets and to swell the polymer particle. Since initiation occurs at a slow rate in the aqueous phase, the kinetic chain length inside a single particle is extremely long producing polymer chains of high molecular weight. Emulsion polymerization is used to manufacture several commercially important polymers that find use in adhesives, coatings, paper coatings and textile coatings. Low dose rate ^{60}Co gamma radiation can be used as an efficient initiating process which can be used as alternative to thermal initiation of peroxides under modest heating conditions. The radiation process makes it possible to decouple the thermal activation of the polymerization from the initiation step and thus avoids affecting the chain length of the formed polymers. This is likely to receive increasing interest for commercial developments in the coming years.

Solvent-free formulations of adhesives, inks and coatings can be cured by radiation-induced crosslinking polymerization. This important use is expanding as a an alternative to solvent-based and/or heat-curing processes which are being restricted because of their detrimental impact on the environment. Radiation processing brings several important benefits in terms of ecoconception (energy saving, limitation of volatile organic compound (VOC) emission). *In-situ* polymerization of restorative resins infused into damaged archeological objects made of wood or into weak artistic pieces of porous structure is another illustration of the unique in-depth chemical effects that can be created using the mild ambient conditions of high energy radiation processing.

Compared to ultraviolet-initiated polymerization, a well-established technology for the curing of various coatings and inks, high energy radiation processing proves to be more efficient than intense ultraviolet for initiating in depth

the crosslinking polymerization of solvent-free compositions, including unsaturated monomers and reactive pre-polymers to yield mechanically functional and chemically resistant materials. Printed labels and materials produced by the packaging industry are fully cured using high energy EB and do not need initiators for free radical polymerization. This results in lower amounts of unreacted monomers and other extractable compounds. Adhesion to substrates can also be improved by grafting reactions that take place at the substrate-coating interface. Advances in improved formulations and in process control spur on developments in food packaging and in industrial coatings (flooring, building parts with long resistance to long outdoor environment).

Fiber-reinforced polymer composites can also be efficiently cured by high energy electron beams and offer significant advantages for the manufacture of a variety of aerospace, ship and ground vehicle components. The EB curing process is shorter than for conventional thermosets and yields materials with reduced residual internal stress. Innovative formulation concepts based on polymerization-induced phase separation achieve higher mechanical performance than state-of-the-art thermally cured materials. Advanced studies on network formation provide an understanding of structure-properties relationships.

Finally, the spatial control of radiation-induced polymerization is used in making photomasks. These are used in the microelectronics industry for producing opaque plates with holes or transparencies for patterning a photopolymerizable composition in the domains that are exposed to the frontal beam of ultraviolet radiation. After development in an appropriate solvent a negative
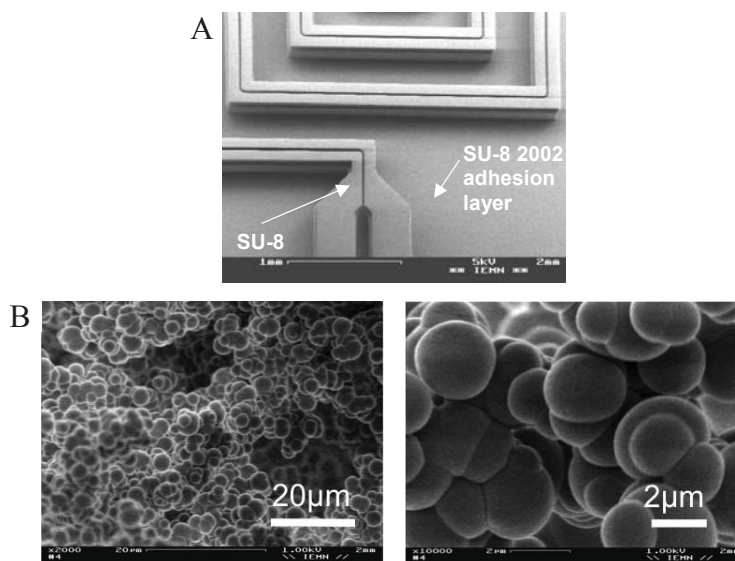

Fig.4. Scanning electron micrographs of a microchannel made by cationic photolithography (A), and porous polymer monoliths synthetized within a closed microsystem by EB-initiated polymerization (B).

photoresist is obtained. Micro- and nanowriting with a laser and/or an electron beam scanned across the radiation sensitive composition avoids using an optical mask and produces much finer patterns and lower resolutions.

Figure 4A shows the scanning electron micrograph of a channel fabricated on a chip by the photomasking process using the cationic photopolymerization of an aromatic epoxide. In a subsequent step, the channels were covered by a lid and a porous polymer monolith was polymerized *in situ* using EB radiation using an acrylate composition dissolved in a mixture of porogenic and precipitating solvents (Fig. 4B). The interconnected polymer-sphere morphology obtained by this technique can be used for producing microreactors and separation microcolumns for lab-on-a-chip applications [10].

4. CONCLUSIONS

Ultraviolet radiation and high energy electron beam radiation efficiently initiate free radical or ionic polymerization depending on the experimental conditions, on the type monomer being used and on the presence of initiators that may be needed. Besides the specific features of radiation-triggered initiation, the basic mechanisms and kinetic models of conventional chain polymerization presented above can be used. However, the specific conditions of radiation processing, dose deposition, dose rate effects as well as thermal effects should be carefully considered. Many end uses can benefit from the numerous advantages offered by radiation processing. Some areas of considerable technical relevance are addressed in specific chapters, such as the radiation synthesis of nanoparticles, radiation grafting, and composite materials.

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