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Various radical polymerizations of glycerol-based monomers

-Review-

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ABSTRACT

This review aims at making the state of the art of the radical polymerizations of glycerol-based monomers, especially (meth)acrylate and vinylic/allylic derivatives. Acrylate and methacrylate derivatives bearing numerous secondary groups like ester, cyclocarbonate, acetal and urethane were involved in free radical polymerization and radical controlled polymerizations as well as in the photopolymerization. Glycerol-based monomers bearing a vinylic or an allylic polymerizable group polymerize by acceptor-donor process and produce alternating copolymers. From all these monomers, the synthesis of functionalized polymers was possible, leading to various valuable applications.

KEYWORDS

Radical polymerization; glycerol derivatives; acrylate monomers; photopolymerization; acceptor-donor.

1. Introduction

Glycerol is one of the most important feedstock in the modern oleochemical industry [1] obtained as a by-product in saponification of fats, in fatty acid/ester production [2], in microbial fermentation [3] and in biodiesel manufacture by *trans*-esterification of vegetable oils. Due to its competitive cost, worldwide availability, and built-in functionality, the glycerin and its derivatives become useful for numerous commercial applications. As production of glycerin is nowadays exceeding the demand, the valorization of the latter has emerged as a challenging trend [4]. Thus the glycerol is currently used in industry as an intermediate in the synthesis of numerous compounds (glycerin carbonate (GC), solketal (Sol), acrylic acid, *etc.*) [5]. For instance, GC is employed as solvent [6], surfactant [7] or in the synthesis of polyurethane [8], polyether [9] and polycarbonate [10]. More specifically a lot of glycerol derivatives bear a polymerizable unit such as acrylate, methacrylate, allylic or vinylic group as summarized in Figure 1. Among (meth)acrylates, some of them have not a secondary function: glycerol acrylate (GA), glycerol methacrylate (GMA), dihydroxypropylacrylate (DHPA), dihydroxyisopropyl methacrylate (DHIMA) whereas others have a secondary function: i) cyclocarbonate such as glycerol carbonate acrylate (GCA), glycerol carbonate methacrylate (GCMA), carbonate glycerol carbonate acrylate (CGCA) and cyclocarbonate carbamate methacrylate (CCCM), ii) acetal such as solketal methacrylate (SolMA), solketal acrylate (SolA), 5-membered cyclic acetal acrylate (5-CAA) and 6-membered cyclic acetal acrylate (6-CAA), and iii) various pendant chains bearing ether (GM-5), ester (GM-1, GM-2, GM-3, GM-4) or phosphine oxide group (GM-6). Di(meth)acrylates are also described including bis-glycerol methacrylate (Bis-GMA), 1,3-glycerol dimethacrylate (GDM), ethyl α -chloromethylacrylate-glycerol diacrylate (ECMA-GD), methyl α -chloromethylacrylate-glycerol diacrylate (MCMA-GD), urethane

dimethacrylate (UR-1 and UR-2) as well as tri(meth)acrylates: glycerol trimethacrylate (GTM), ethyl α -chloromethylacrylate-glycerol triacrylate (ECMA-GT), methyl α -chloromethylacrylate-glycerol triacrylate (MCMA-GT), and urethane trimethacrylate (UR-3). Several vinylic derivatives based on glycerol are also reported (vinylic solketal (vinylSol), vinylic glycerol carbonate (vinylGC), 1-propenyl glycerol carbonate (1-propenylGC)) as well as allylic one: allylic solketal (allylSol).

Among these monomers, those bearing a cyclocarbonate secondary group are interesting and employed in pharmaceutical or cosmetic fields [11] thanks to their low vapor pressure, flammability, toxicity, good biodegradability and moisturizing ability [12]. The cyclocarbonate function also brings high polarity and coordinating properties [13-16]. Another peculiar type of monomers concerns that bearing acetal group which is hydrolyzable in diol to notably afford polymers bearing hydroxyl functionality leading to hydrophilicity and water-soluble properties. Such derivatives can be used in the pharmaceutical field such as contact lenses, dental materials, optical lenses, drug delivery, encapsulated cells [17-19] for instance, as well as in material field including hydrogels [20,21], chelating agents [22,23] and functionalized polymers [24]. Among all possibilities, some amphiphilic block copolymers bearing hydrophilic block with hydroxyl groups allow applications like thermoresponsive polymers [25,26].

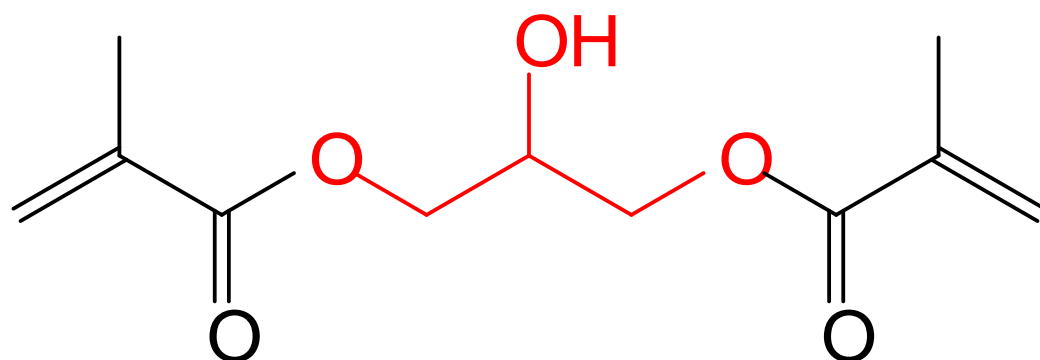


Figure 1. Summary of monomers based on glycerol.

The free radical polymerization (FRP) and the photopolymerization [27,28] are the simplest ways to synthesize polymers with or without radical initiator under thermal or photo conditions (Scheme 1). The second process is appropriate to specific reactive groups such as allylic and vinylic unlike the first one which is employed with acrylic and methacrylic monomers. In some cases, the control of the molecular weight of the polymer with narrow mass distribution, the control of the composition and the architectures (linear diblock, triblock, Y-shaped triblock, 4 arm star copolymers, grafted copolymers) were achieved. Thus, the control/living radical polymerization (CRP) [29,30] using ATRP, and NMP was carried out. Finally, the acceptor-donor polymerization is described for the vinylic, allylic monomers based on glycerol such as allylSol, vinylSol, vinylGC, and 1-propenylGC (Figure 1).

This review aims at providing an overview about the different radical polymerization processes of various monomers based on glycerol such as free radical polymerization, controlled radical polymerization, photo-polymerization and the acceptor-donor polymerization. Applications of the resulting materials will also be discussed.

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Scheme 1. Radical polymerizations of glycerol-based unsaturated monomers.

2. Free radical polymerization

Free radical polymerization (FRP) is a very widespread method of polymerization which has been used for a long time in industry for many reasons: FRP is easy to carry out, can be performed in bulk, in solution in various solvents, and also in dispersed media (suspension, emulsion...). It can be achieved for a large range of reaction temperatures (-100 to +200 °C). Additionally, this polymerization technique can be carried out with a lot of monomers, even functionalized. Monomers can bear “standard” functional groups or heteroatoms such as

phosphorus [31] or silicon [32] for instance. Glycerol-based monomers, often bearing specific functional group(s) (Figure 2) were thus considered using free radical polymerization.

In general, FRP is described by three main steps. In the initiation step, radicals are produced and then add a first monomer molecule. Initiators are typically diazoic compounds such as azobisisobutyronitrile (AIBN), or peroxides, with benzoyl peroxide for instance. Redox systems and energy sources can also produce initiating species. The second step (propagation) corresponds to the growth of the macromolecular chains. Finally, two active chains react together in the termination step to produce macromolecular dead chains.

Figure 2. Glycerol derivatives based-monomers involved in free radical polymerization.

Glycerol-based mono(meth)acrylate monomers were polymerized by free radical polymerization. AIBN is used as initiator in all cases, whereas solvent and temperature vary. Polymerization of acrylates and methacrylates with 2-oxo-1,3-dioxolane (glycerol carbonate) was carried out [33]. Resulting poly(GCA) and poly(GCMA) exhibit a good thermal stability and the glass transition temperature range from 11 to 93 °C, depending on the structure of the glycerol-based monomer. Concerning the application, these polymers showed significant ion conductivity when blended with lithium salts.

In a fundamental study, the solketal methacrylate was polymerized by free radical polymerization [34], and its reactivity ratio was determined using *tert*-butyl methacrylate (*t*BMA), 2-bromoethyl methacrylate (BEMA), or 2-(*N,N*-dimethylamino) ethyl methacrylate (DMAEMA) as co-monomer (Figure 3). This research aims at producing statistical polyampholytes from terpolymers.

Figure 3. Monomers involved in the synthesis of statistical polymer with SolMA.

PGMA was prepared *via* FRP from corresponding monomer synthesized by enzymatic way in the presence of lipase catalyst known as *Candida antarctica lipase B* by *trans*-acylation of methyl acrylate [35]. The authors compared the polymers obtained from free radical polymerization and nitroxide mediated polymerization techniques in term of conversions, molecular weights and polydispersity indices.

The glycerol diacrylate (GDA) has also been studied in polymer field and was used as crosslinking agent for solid-phase synthesis. This monomer is introduced into polystyrene [36] or into polyvinyl pyrrol network [37] using free radical aqueous suspension polymerization. The effect of amount of cross-linking agent on the swelling, loading and the mechanical stability of the resin is reported. Interestingly, the presence of hydroxyl groups coming from GDA moiety leads to an optimum hydrophobic-hydrophilic equilibrium of the resin. This permits a high swelling in different polar and non-polar solvents. The structure of

the polymer provided easy diffusion of reagents and solvents through the resin matrix. Poly(styrene-*co*-GDMA) proved to be equally efficient as commercial resins in peptide synthesis.

To conclude, glycerol-based monomers were involved in free radical polymerization and the resulting polymers proved to find interesting applications. Nevertheless, the main drawback of conventional radical polymerization is the lack of control over the molecular weight, and the impossibility to achieve complex polymeric structures. This led to the development of controlled radical polymerization techniques.

3. Controlled/living radical polymerization

The synthesis of well-defined macromolecules with controlled compositions, architectures, and functionalities has emerged as an important aspect of polymer science. The development of controlled/living radical polymerization (CRP) permitted to achieve well-defined polymers using a radical process easy to carry out. In the last twenty years, techniques such as atom transfer radical polymerization (ATRP) [38], nitroxide mediated polymerization (NMP) [39], and reversible addition-fragmentation chain-transfer polymerization (RAFT) [40] led to the synthesis of complex architectures, with control over the molecular weight, low polydispersity indexes and complex architectures notably due to the possible functionalization of terminal end groups [41]. All the CRP is based on a fast equilibrium between active and dormant species. The concentration in active species has to remain low during all the polymerization, minimizing termination and transfer reactions. Kinetics and thus control of the polymerization is easily determined by taking samples throughout the polymerization or using appropriate probes [42].

CRP of many monomers has been carried out and glycerol-based monomers were also considered. Almost all examples described in the literature deal with atom transfer radical polymerization (ATRP) technique. These examples will be discussed as a function of the obtained architecture. Linear diblock and triblock copolymers were prepared using solketal or glycerol carbonate (meth)acrylates. Diblock copolymers combining a biodegradable core and a hydrophilic shell were synthesized [43]. In such case, two polymerization techniques are involved, with the ring opening polymerization (ROP) of the lactic acid (LLA) first followed by the ATRP of the solketal acrylate (SolA). PLLA-*b*-PSolA diblock copolymers are thus obtained (Figure 4).

Figure 4. PLLA-*b*-PSolA diblock copolymers prepared by atom transfer radical polymerization.

These copolymers showed self-assembly property as they form aggregates in aqueous solution. Besides, degradation behavior of latter was also investigated. It was shown that enzymatic degradation proceeds much faster than hydrolytic one, within 4000 minutes. Double hydrophilic block copolymers were also prepared [44]. The SolA was polymerized by ATRP in the presence of a poly(ethylene oxide) (PEO) macroinitiator. Then the hydrolysis of the acetal protecting group of the SolA moiety was carried out in the presence of a chlorhydric acid solution to afford a hydrophilic block (PEO-*b*-PGA). Finally, a reaction

between the glycerol unit of the PEO-*b*-PGA with a fluorescent probe (pyrene derivative) led to an amphiphilic structure (Scheme 2). The micelles, with a PGA-Pyrene core and a PEO shell, self organize in THF/water solution. In acidic medium, acetal groups were deprotected to deliver the pyrene in the core of the micelles. The released ratio of pyrene varied as a function of the pH values. It is equal to 100% at pH 1.0, 80% at pH 5.0 and 9% at pH 7.4. Moreover, the micelles are destroyed after 80% of acetal linkages cleaved. As a result, the hydrophilic PEO-*b*-PGA block copolymer offers a potential application as pH-sensitive drug delivery material for carbonyl bearing hydrophobic drugs.

Scheme 2. Amphiphilic diblock copolymers bearing fluorescent probe from solketal moiety.

Fluorescent probe can also be introduced *via* the initiator, as in the case of perylene bis-imide (PBI) [45] which was converted into ATRP initiator for the controlled polymerization of SolA. After hydrolysis of the acetal protecting group of the SolA moiety, resulting polymer (PBIPGA) (Figure 5) becomes water soluble.

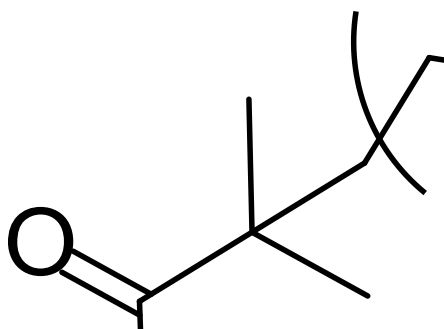


Figure 5. PSolA containing fluorescent segment brought by the difunctional initiator.

Interestingly, the PBIPGA self-assemble onto reduced graphene oxide (RGO) nano-sheets *via* π stacking interactions, resulting in non-covalent functionalization of RGO. Furthermore, the RGO-PBIPGA composites display good dispersity in an aqueous medium and very low cytotoxicity toward mouse 3T3 fibroblasts. As a consequence, this composite is potentially interesting for biomedical applications such as cell imaging and intracellular drug delivery.

Another kind of diblock copolymers results from the copolymerization of SolA and tBA by ATRP using bromine-terminated PSolA to initiate polymerization of tBA and *vice versa* [46]. The SolA units were hydrolyzed using chlorhydric acid without cleaving tBA moiety, whereas SolA and tBA were completely hydrolyzed to give acid acrylic and glycerol unit, respectively, in the presence of trifluoroacetic acid (Scheme 3).

Scheme 3. Hydrolysis of SolA moiety with different experimental conditions, consequently leading to different diblock copolymers.

Glyceryl methacrylate was also directly involved in the synthesis of diblock copolymers, associated with 2-hydroxypropyl methacrylate (HPMA) [47]. Polymerization was achieved at room temperature. In addition, diblock copolymers were successfully synthesized in the presence of different poly(alkylene oxide)s as macroinitiators. For instance, poly(propylene oxide)-*b*-poly(glycerol methacrylate) (PPO-*b*-GMA) diblock copolymers were thermoresponsive, leading to reversible aggregation. The obtained average size of these aggregates is about 150-240 nm, depending on the block composition.

Linear triblock copolymers were also prepared by controlled radical polymerization, involving glycerol-based monomers. GMA was polymerized from a poly(propylene oxide) difunctional macroinitiator to afford water-soluble PGMA-*b*-PPO-*b*-PGMA triblock copolymers (Figure 6) [48].

Figure 6. PGMA-*b*-PPO-*b*-PGMA triblock copolymers from the ATRP of GMA.

The polymers exhibit monomodal molar mass distribution and relatively low polydispersities for different lengths of the PGMA block. The self organization in aqueous solution was also studied. It was proved that the micelles are formed when the degree of polymerization of PGMA block is half the one of the PPO block. Hydrodynamic radius (R_H) was measured around 10-15 nm in the temperature range of 15-40 °C and the critical micellization temperature (CMT) is about 8 °C. When the degree of polymerization of PGMA is equal to the one of the PPO blocks, the CMT is about 19 °C. At temperatures below the CMT, the aggregates with sizes in the range of $R_H \sim 175$ -215 nm are formed. Copolymers with much longer PGMA blocks are unimers in the aqueous solution.

SolA was also used to produce triblock copolymers. Synthesis is accomplished with copper mediated living radical polymerization using a difunctional poly(vinyl acetate) as macroinitiator preliminary synthesized (Figure 7) [49].



Figure 7. PSolA-*b*-PVA-*b*-PSolA triblock copolymers prepared by ATRP.

The triblock was obtained with predictable molecular weight and low polydispersities. The surfactant properties of the resulting amphiphilic copolymers were also investigated and can be tuned by varying the percentage of the hydrophilic part in order to obtain different amphiphilic properties.

Finally, GCMA was involved in the synthesis of (PGCMA-*b*-PEG-*b*-GCMA) ABA triblock or (AC)B(AC) (PGCMA-*stat*-PMMA-*b*-PEG-*b*-PMMA-*stat*-PGCMA) terblock copolymers *via* ATRP [50] (Scheme 4) using PEG as macroinitiator.

Scheme 4. Block copolymer synthesis involving GCMA.

Solubility, film forming property, wettability, and thermal stability were investigated. (AC)B(AC) type terpolymers reveal an enhanced solubility, film-forming property, and thermal stability thanks to the presence of additional methyl methacrylate repeat units. The

lithium ion conductivity of all polymers bearing cyclocarbonate was determined when mixed with lithium bis(trifluoromethane) sulfonamide. In addition, ring-opening reaction of cyclocarbonate by mono- and diamine was achieved. Treatment with monoamine afforded polymer bearing hydroxyurethane whereas the reaction with diamine gave an insoluble and crosslinked polymers. Y-shaped triblock copolymers (PSolA-*b*-PEG-*b*-PSolA) (Figure 8) were designed from a dibromine-PEG macroinitiator on which ATRP of SolA was carried out [51].

Figure 8. Y-shaped PSolA-*b*-PEG-*b*-PSolA triblock copolymers prepared by ATRP.

The Y-shaped triblock polymers exhibit micelles composed of PEG and PSolA as hydrophilic and hydrophobic block, respectively. The amphiphilic polymers self assemble, forming a core-corona type spherical micellar aggregate. The particle sizes depend on hydrophobic block length of the amphiphilic polymers and on the temperature. Furthermore, the encapsulation and release of Nile red were also investigated and proved to be temperature

dependent. As the biocompatibility of these copolymers to cells was revealed by MTT assay, these thermoresponsive polymer micelles can be potentially useful to produce nano-vehicles for biomaterial applications in the near future.

Star copolymers also represent architecture achievable by controlled radical polymerization. Well-defined linear and star homo- and diblock- copolymers of PMA, PSolA, and P(MA-*b*-GA)_n (with n, number of arms, ranging from 1 to 4) (Figure 9) were prepared by the Single-Electron Transfer Living Radical Polymerization (SET-LRP) using Cu(0) powder [52].

Figure 9. PSolA-based star copolymers prepared by ATRP.

All SET-LRP reveal first order kinetic and reach high conversions in a short time. Besides, the copper residue is easily removed, resulting in the obtaining of pure polymer. The molecular weight distribution is well controlled using the Cu(II)Br₂/Me₆-TREN catalytic complex. The hydrolysis of linear and star block copolymers afforded biocompatible

amphiphilic P(MA-*b*-GA)_n polymers. In aqueous solution, they form core-shell micelles and vesicles for the linear and star blocks, respectively, in which the hydrophilic block comes from the glyceryl side-groups. Consequently, the vesicle structure can be potentially used for drug delivery applications.

ATRP method has been broadly used for glycerol-based monomers, in particular for solketal acrylate, in order to obtain well-defined compositions, architectures, and molecular weights. Many applications have been envisaged thanks to the architecture diversity. Nitroxide mediated polymerization (NMP) has been reported in the literature only for dihydroxypropyl acrylate (DHPA), and GMA. The kinetic studies of these hydroxyl functional monomers were investigated [35]. On the reverse, RAFT polymerization has not been considered.

To conclude, polymers based on glycerol derivatives have been well investigated in the literature using ATRP and NMP controlled radical polymerization. Different complex architectures were synthesized and polymers were obtained with a predictable molecular weight, and relatively narrow mass distribution indexes. In term of applications, the polymers bearing solketal pendant functionality exhibited amphiphilic and thermoresponsive behaviors. They could be potentially applied in the biomedical field. Polymers bearing cyclocarbonate rings were used as low molecular weight polymer solvent for lithium ion conductivity.

4. Photopolymerization

The UV radiation is a simple and convenient energy which does not require expensive devices and requires low temperature and energy efficient processes [27,28]. Thanks to its high output this special polymer processing is enjoying a new expansion and is applied at industrial scale for coating industry, paints or printing inks, adhesives, composite materials and dental

restorative formulations and many others. Liquid resins can be converted into solid resins in a few tenths of a second making this process very attractive for the scientist community since almost three decades. The photopolymerization mechanism can be achieved either by polyaddition of double bonds under radical or cationic initiation. Glycerol (meth)acrylate-based monomers were involved in photopolymerization (Scheme 5). According to the target applications, these (meth)acrylate monomers bear one, two or three unsaturated groups for developing thermoplastic or thermoset materials. The impact of the polymer structure on the material properties is investigated as well as the effect of monomer structure on the polymerization kinetic. In order to explain the difference of reactivity of these glycerol derivatives in photopolymerization, the dipole moment, the intramolecular and the intermolecular effects that would alter the electron density on the radical and the double bond, the contribution of partially ionic intermediates will be evaluated.

Scheme 5. Photopolymerization of glycerol (meth)acrylate based monomers.

Six hydroxyl-bearing methacrylate monomers with various pendant chains bearing ether (GM-5), ester (GM-1, GM-2, GM-3, GM-4) or phosphine oxide group (GM-6) were successfully synthesized and used as reactive diluents in dental composites. The structure - reactivity of the monomer relationship was also investigated [53]. The photo-, homo-, and copolymerization behaviors of these monomers with (Bis-GMA) were studied to afford

network polymers with appropriate mechanical properties for dental material applications. Especially, the crosslinked polymer from the monomer GM-6 was reached as potential flame retardant thanks to its phosphine oxide groups. The influence of acetal groups on acrylate reactivity was also investigated by Kilambi *et al.* [54]. Indeed, the high reactivity of several acrylates bearing 5-membered ring cycloacetal (5-CAA) and 6-membered ring acetal (6-CAA) in radical photopolymerization compared to hexyl acrylate was demonstrated. Jansen *et al.* also studied the photopolymerization of SolA and demonstrated the relationship between its low dipole moment and its low reactivity [55].

Several teams are interested by the peculiar (meth)acrylate monomers bearing cyclocarbonate group including GCA, GCMA, CCCM and CGCA whose the structures are reported in Figure 1. The originality of these monomers is that they are not able of hydrogen bonding. Decker [56-58] and Podszun [59,60] demonstrated the high reactivity of the acrylates bearing cyclocarbonate group relative to acrylates bearing a linear secondary functionality. Additionally, Jansen *et al.* showed the direct relationship between the dipole moment and the rate polymerization [55]. For instance, GCA with a high dipole moment is correlated to a high photopolymerization rate unlike SolA with a low dipole moment correlated to a low photopolymerization rate. Additionally, Berchtold *et al.* investigated the influence of the temperature on the cyclocarbonate-based acrylates [61]. The latter proved to have little influence on the photopolymerization rate even if an increase is noted with this parameter. Otherwise Beckel *et al.* [62] determined the anionic contribution related to the photopolymerization mechanism of (meth)acrylates in the presence of a strong acid (methanesulfonic acid). It could stabilize the radical species of the propagating (meth)acrylic chain leading to reduce the hydrogen abstraction reactions that contribute to the anionic characteristic. Kilambi *et al.* investigated the same influence of acid concentration in the

photopolymerization rate of cyclocarbonate acrylates in the presence of highly polar solvent such as propylene carbonate [63].

Recently, Podgorski *et al.* proposed 1,3-glycerol dimethacrylate (GDM) as an alternative monomer for triethyleneglycol dimethylacrylate in dental mixtures.[64] This dimethylacrylate is a promising photocurable dental diluent due to its low viscosity, good mechanical and water uptake properties. Park [65] and Podgorski [66] also reported the study of GDM as well as the corresponding glycerol trimethacrylate (GTM) in dentin adhesives. The experimental adhesives exhibit significantly higher storage and rubbery modulus related to the widespread diethyleneglycol diacrylate photocrosslinker. During the study of hydroxyl-containing di(meth)acrylate monomers such as MCMA-D and ECMA-D, Avci *et al.* demonstrated the effect of the hydroxyl groups on monomer on the bulk reactivity [67]. The nature of the dimethacrylate group has little influence on the reactivity. Corresponding trimethacrylates (ECMA-T and MCMA-T) are less reactive than dimethacrylates. Moszner *et al.* successfully synthesized two urethane dimethacrylates based on glycerol (UR-1, UR-2) and a tetramethacrylate (UR-3) [68]. As expected, the dimethacrylates have higher degree of double bond conversion related to the tetramethacrylate as a result of the higher density of the resulting network.

In summary, numerous studies have been realized on the theoretical aspects of the photopolymerization of the (meth)acrylate monomers based on glycerol to understand the influence of secondary function on polymerization rate. The rapid radical photopolymerization of these monomers is especially interesting for the elaboration of thermoset dental restoration applications as well as in adhesives, due to the presence of free hydroxyl groups in the glycerol part.

5. Polymerization by Acceptor – Donor process

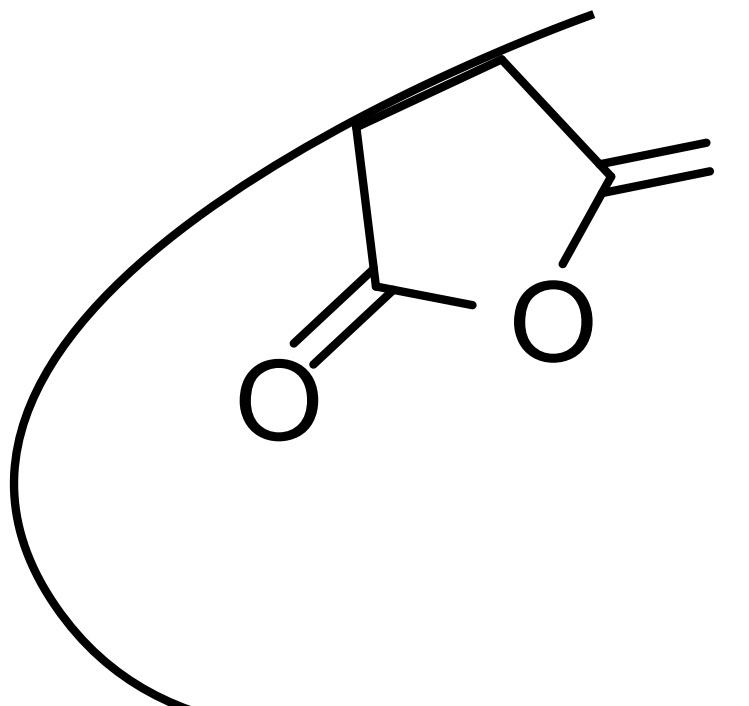
Alkyl and vinyl ethers do not radically homopolymerize, but copolymerize readily with electron-deficient olefins such as fumarates or maleates. These facile reactions proceed through an electron donor-acceptor complex, which generates zwitterion or diradical tetramethylenes as initiating species. Alternating copolymers is a peculiar class of polymers obtained by the reaction between two monomers which cannot homopolymerize. One synthetic method consists in the polymerization between a monomer rich in electrons named donor and a monomer poor in electron named acceptor [69-71]. Generally, this kind of copolymerization is initiated by a free radical or sometimes by a spontaneous reaction due to hydrogen transfer from donor to acceptor monomer (Scheme 6).

Scheme 6. Synthesis of alternating copolymers by acceptor-donor polymerization.

Donor vinylic and allylic monomers deriving from glycerol such as allylSol copolymerize with fumarate and maleate acceptors by radical acceptor-donor polymerization as illustrated in Figure 10. Pichavant *et al.* described alternating copolymers coming from renewable feedstocks like allyl ribosides [72]. The reactivity of these acceptor monomers are compared by employing UV-initiated free radical copolymerization. The model monomer blends are photo-polymerized in solution as well as in liquid films of bulk reactants. The results showed the lower reactivity of allyloxy derivatives compared to the one of vinyl ethers in the same polymerization conditions. In addition, allyl riboside and allyl isopropylidene riboside exhibit an attractive behavior, associating higher reactivity in the series of allyloxy monomers together with high final conversion levels. Pichavant *et al.* extended their study on the reactivity of various vinyl ethers (VinylSol) and vinyloxy derivatives of ribose in the presence of diethyl fumarate or diethyl maleate in the donor-acceptor copolymerization [73]. The high reactivity of vinyl ethers in free radical copolymerization with butadienoates was checked during a kinetic study. The reactivity of the maleate mixtures is lower than fumarates. So, vinyloxy monomers based on sugar reveal a higher reactivity than alkyl vinyl ether, providing new potentialities as alternative biosourced monomers.

Figure 10. Alternating copolymers synthesized from vinylSol, vinylGC, and allylSol.

The alternating copolymers between vinylSol and maleic anhydride was carried out by Crivello *et al.* [74] Interestingly, a further crosslinking was performed leading to the formation of ester cross linkers. The hydrolysis of some anhydride groups permitted the formation of carboxylic acid groups which induced the hydrolysis of the ketal moieties. The resulting diols reacted with the residual anhydrides to provoke the ester crosslinking (Scheme 7.) The presence of both anhydride and acid sensitive protected diol groups in the same polymer thus makes this polymer a potential candidate for moisture curable coatings.



Scheme 7. Crosslinking of alternating copolymers based on vinylSol.

Ha *et al.* [75] reported the miscibility of blends based on PVC and an alternating poly(vinylGC-*co*-AN) copolymer obtained by reaction between acrylonitrile and vinylGC. As a result, a blend of vinylGC and acrylonitrile (AN) is entirely miscible as the optical clarity,

the thermal analysis, and the light scattering studies demonstrate it. Moreover, Ha *et al.*[75] also described a blend of poly(vinylGC-*co*-AN)/SAN in order to develop an integrated process for the catalytic conversion of CO₂ to useful polymer materials. Their miscibility over the entire range of blend compositions was confirmed. Otherwise Moon *et al.* [76] investigated the synthesis of a copolymer bearing cyclic carbonate (vinylGC) and its miscibility with SAN or PVC. Interestingly, the vinylGC was synthesized from oxirane derivative using a catalytic conversion of carbon dioxide. The blended copolymer exhibited a higher thermal stability than poly(vinylGC).

To conclude, various polymers based on glycerol were synthesized *via* donor-acceptor polymerization process. This reaction is thermally or photochemically induced and conducted in solution as well as in liquid film of bulk reactants. Furthermore, the blended copolymer like poly(vinylGC-*co*-AN)/SAN was achieved in order to improve poly(vinylGC) thermal stability. Moreover, the potential moisture curable coatings based vinylSol was also described.

6. Conclusions and outlook

A variety of polymers containing glycerol derivatives can be synthesized *via* radical polymerization processes such as for instance free radical polymerization (FRP), controlled/living radical polymerization (CRP), photopolymerization as well as acceptor-donor alternating polymerization. The FRP proved to be the simplest method in comparison with CRP in term of reaction conditions. Nevertheless only CRP technique allowed predictable molecular weight, well-defined compositions, and controlled architectures. Thanks to this possibility, the obtained polymers can be employed in many different applications. Typically, the polymers containing acetal protecting functionality lead to amphiphilic structures, or thermoresponsive polymers. Hence, these kinds of polymer can find applications in the biomedical field such as drug delivery, for instance. Only ATRP and one example of NMP have been described in the literature for glycerol-based monomers, it would be a tremendous opportunity to use the RAFT process for this kind of monomers.

Furthermore, the photopolymerization is also a stimulant method which permitted a wide application in industry due to its main advantages: solvent free, energy efficient... However, most of the publications in this field are limited in fundamental studies. Only potential reported application using monomers multifunctionality bearing cyclocarbonate dealt with restorative dental materials to improve mechanical properties.

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