Photoinitiated Polymerization: Advances, Challenges, and Opportunities

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ABSTRACT: The use of photoinitiated polymerization is continuously growing in industry as reflected by the large number of applications in not only conventional areas such as coatings, inks, and adhesives but also high-tech domains, optoelectronics, laser imaging, stereolithography, and nanotechnology. In this Perspective, the latest developments in photoinitiating systems for free radical and cationic polymerizations are presented. The potential use of photochemical methods for step-growth polymerization is also highlighted. The goal is, furthermore, to show approaches to overcome problems associated with the efficiency, wavelength flexibility, and environmental and safety issues in all photoinitiating systems for different modes of activation. Much progress has been made in the past 10 years in the preparation of complex and nanostructured macromolecules by using photoinitiated polymerizations. Thus, the new and emerging applications of photoinitiated polymerizations in the field of biomaterials, surface modification, preparation of block and graft copolymers, and nanocomposites have been addressed.

Introduction

In recent years, photoinitiated polymerization has received revitalized interest as it congregates a wide range of economic and ecological anticipations. For more than 30 years, photopolymerization has been the basis of numerous conventional applications in coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics.[1−5] Some other less traditional but interesting applications, including production of laser videodiscs, curing of acrylate dental fillings,[6] and fabrication of 3D objects[7] are also available. Many studies involving various photopolymerization processes have been continuously conducted in biomaterials[8] for bones and tissue engineering, microchips, optical resins and recoding media, surface relief gratings, anisotropic materials, polymeric photo-optical control materials, clay and metal nanocomposites, photoresponsive polymers, liquid crystalline materials, interpenetrated networks, microlens, multilayers, surface modification, block and graft copolymerization, two-photon polymerization, spatially controlled polymerizations, topochemical polymerization, solid-state polymerization, living/controlled polymerization, interfacial polymerization, mechanistically different concurrent polymerizations, pulsed laser polymerization, polymerizations in microheterogenous media, and so forth. Interest has also grown in identifying the reactive species involved in the polymerization process by laser flash photolysis, time-resolved fluorescence and phosphorescence, and electron spin resonance spectroscopy as well as monitoring the polymerization itself by different methods including real time IR spectroscopy, in-line NIR reflection spectroscopy, differential scanning calorimetry, *in situ* dielectric analysis, and recently developed optical pyrometry.

In contrast to thermally based applications, which usually requires elevated temperatures, photopolymerization can also be performed at room temperature and below. This is a striking advantage for both classical polymerization of monofunctional monomers and modern curing applications. In photopolymerization of monofunctional monomers fewer side reactions occur, such as chain transfer. In thermal polymerization, the probability of chain transfer commonly is high, which brings about a significant amount of branched macromolecules. Thus, low-energy stereospecific polymeric species, namely of syndiotactic configuration, which are difficult to synthesize by thermal polymerization, may be obtained by photopolymerization. Another important use is available for monomers with low ceiling temperature. They can only be polymerized at low temperatures; otherwise, depolymerization dominates over polymerization. By means of photopolymerization at low temperatures, these monomers are often easily polymerizable. Furthermore, biochemical applications, such as immobilization of enzymes by polymerization, also usually require low temperatures. As far as curing of coatings or surfaces is concerned, thermal initiation is often not practical, especially if large areas or fine structures are to be cured or if the curing formulation is placed in an application for which heating is unacceptable, such as dental fillings.

Photoinitiated polymerization is usually applied to a chain process that is initiated by light and both the initiating species and the growing chain ends are radicals[9] or cations[10] and, in some cases, anions or weak bases[11] (Scheme 1). However, the corresponding photoinitiated polycondensation process in which a macromolecule is obtained by a step-growth addition of low-molecular-weight materials is in its infancy. In most cases,[12−15] the photocondensation process is based on the dimerization of the nonconjugated olefins through singlet and triplet excited states, and the obtained macromolecules do not represent the classical polycondensate structure such as those of polyesters, polyamides, and polyurethanes. The only attempt[16] in this direction concerns *in situ* polyurethane formation upon photolysis of alkoxypyridinium end groups in the presence of toluene diisocyanate. Hydrogen abstraction of alkoxy radicals generated from the decomposition of the pyridinium ions results in the formation of hydroxyl groups capable of reacting with the isocyanates present in the solution. However, the process could not be controlled, and as the irradiation proceeded, an insoluble

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network was formed. This behavior was attributed to the formation of allophanate and biuret linkages from an isocyanate function and the previously formed urethane linkage because hydroxyl functions were available only when the pyridinium ions

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Steffen Jockusch received his Ph.D. degree in 1993 from the Martin Luther University Halle-Wittenberg in Merseburg (Germany) with Prof. H.-J. Timpe. In 1994, he joined Prof. Turro's research group at Columbia University as a postdoctoral fellow, and since 1997, he has been an associate research scientist. His research interests include spectroscopic investigations of reactive intermediates in photophysical and photochemical processes, supramolecular photochemistry, luminescent probes for biological applications, and photoinitiators for polymerization. He has published more than 140 scientific papers in peer-reviewed journals.
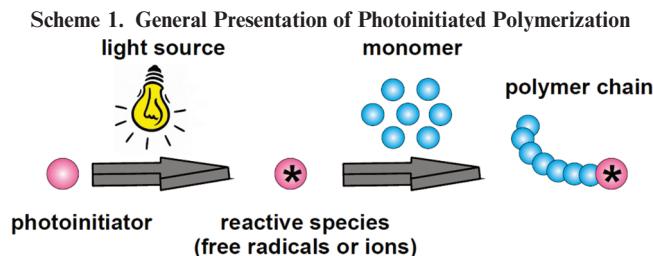
decomposed by light. It was recently reported that a true step-growth polymerization, i.e., polyesterification, can be achieved by a photochemical means by taking advantage of the high reactivity of the photochemically formed ketenes with hydroxyl compounds.[195] Photoinduced step-growth synthesis of conjugated polymers based on polythiophenes was also reported.[196]

Although free radical photopolymerization still dominates most of the interest and industrial applications, cationic polymerization has also gained importance in recent years. There are several advantages offered by the cationic mode over free radical photoinitiated polymerization. While free radical polymerization is limited to monomers with olefinic double bonds, compounds of quite different chemical nature, e.g., compounds containing epoxide or vinyl ether groups can be polymerized by photoinitiated cationic polymerization. Many monomers that are prone to cationic polymerization exhibit low volatility and negligible toxicity and possess good rheological properties. In contrast to free radical polymerization, molecular oxygen does not inhibit cationic polymerization and thick films can be cured in the presence of dry air. It is well-known that water vapor terminates cationic polymerization. In a dry environment, however, termination rates are low, permitting the polymerization to proceed in the dark even after irradiation. Furthermore, the problem of shrinkage during the free radical photopolymerization of acrylic formulations negatively affects applications that require accurate part shape and size. However, the problems associated with volume shrinkage are less pronounced in the photoinitiated cationic polymerization, particularly when epoxy-based formulations are used as they undergo polymerization via a ring-opening process. For these reasons, it is expected that in addition to free radical route also light-induced cationic polymerization will be the method of choice in various applications.[1]
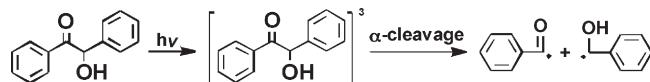
In the current Perspective we focused on the newly developed photoinitiating systems for free radical and cationic polymerization that bring some advantages or overcome existing problems

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Scheme 1. General Presentation of Photoinitiated Polymerization

Scheme 2. Photolytic α-Cleavage of Benzoin

Scheme 3. Type II Photoinitiation Mechanism with Benzophenone and Hydrogen Donors

and challenges in photopolymerization. We do not wish to review comprehensively all of the work to date on photopolymerization and applications as there are many books and review articles covering all aspects. The specific examples covered will be devoted to cationic photopolymerizations, though the free radical mode is more advanced and most of the recent studies concern the cationic mode. The discussion that follows will describe how some of the particular photopolymerization methods relate to synthetic macromolecular chemistry and then overview the most common methods with several examples of how each facilitates access to block and graft copolymers or allows the preparation of nano-composites. The environmental issues associated with photopo-lymerization will also be discussed.
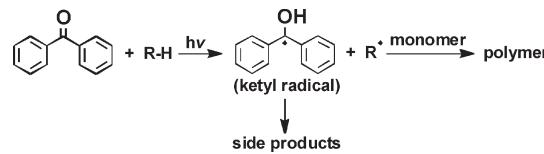
Photoinitiators: Structure, Efficiency, and Wavelength Tunability

Although it gives the name to the whole process, the role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating species. Thus, in spite of its lowest volume in a polymerizable formula-tion, a photoinitiator plays a major role in the polymerization. A photoinitiator or photoinitiator system is defined as a molecule or combinations of molecules that, upon absorption of light, initiate the polymerization.[17] In photocurable systems, photo-initiators affect mainly cure speed, yellowing, and cost.[18] How-ever, other factors such as commercial availability (or easy pre-paration), solubility particularly in a wide range of monomers, storage stability, and low migration, low odor, and nonyellowing properties in the cured films should also be taken into considera-tion. In addition, the light absorption properties of the selected photoinitiator need to match the emission wavelength of the light source.

Free Radical Systems

Photoinitiators for radical polymerization are classified as cleavage (type I) and H-abstraction type (type II) initiators.[19,20] The majority of type I photoinitiators are aromatic carbonyl compounds with appropriate substitution. For example, upon absorption of light, benzoin and derivatives, benzil ketals, aceto-phenones, aminoalkyl phenones, O-acyl-α-oximino ketones, α-hydroxyalkyl ketones, and acyphosphine oxides all sponta-neously undergo "α-cleavage", generating free radicals as depic-ted in Scheme 2 with benzoin as an example. Because of relatively lower absorbencies, the other cleavage initiator-based azo, per-oxy, and halogenated compounds are not widely used as photo-initiators. Each photoinitiator has advantages and disadvant-ages, and the selection of photoinitiator very much depends on the requirements of a particular application. For example, benzoin and derivatives are the most widely used photoinitiat-ors for free radical polymerization due to their high quantum

efficiency and reactivity of the radicals produced by photoin-duced cleavage. Moreover, these photoinitiators are particularly useful for industrial applications involving styrene monomers as the photoinduced cleavage reaction is very little affected by triplet quenchers including styrene.[21] However, these photoinitiators suffer from thermal instability arising from the presence of abstractable benzylic hydrogen and therefore can only be stored for limited time at ambient temperature. Benzil monoketals ex-hibit excellent initiator properties especially in micellar solu-tions,[22] and like acetophenones,[23] they show high storage stabi-lity and little tendency toward yellowing, which makes them very useful for clear coatings. Because of the long wavelength absorp-tion characteristics, aminoalkyl phenones[24−28] and acylphos-phine oxides are particularly useful for the polymerization of TiO₂ pigmented formulations and of glass fiber reinforced polyester laminates with reduced transparency where irradiation at longer wavelength is desired. Among them, acylphosphine oxides are more widely used because of their thermal stability and high reactivity of the photochemically formed phosphonyl radicals arising from the high electron density at the phosphorus atom and the pyramidal structure of the radicals providing more favorable steric conditions for the unpaired radical site to react with monomers.[29−31]

Because the initiation is based on a bimolecular reaction, the generation of free radicals from type II photoinitiators and curing rates is generally slower than the generation of free radicals from type I photoinitiators, which are based on unimolecular forma-tion of radicals. These systems are, therefore, more sensitive to quenching of excited triplet states of the photoinitiators, which are the reactive precursors of light-induced chemical changes for carbonyl compounds. Indeed, quenching by monomers with low triplet energy (e.g., styrene or N-vinylcarbazole) or by oxygen is often observed and may lead to relatively low curing rates when type I photoinitiators are employed.
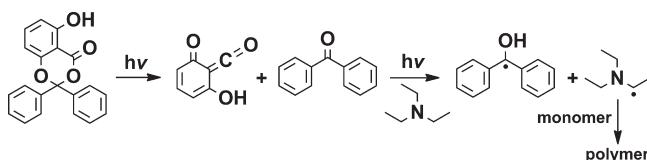
Photolysis of aromatic ketones, such as benzophenone, thio-xanthones, benzil, and quionones, in the presence of hydrogen donors leads to the formation of a ketyl radical produced from the carbonyl compound and another radical derived from the hydrogen donor.[32−34] The overall mechanism of the photoinitia-tion on the example of benzophenone is represented in Scheme 3. The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor.

The ketyl radicals are relatively stable radicals that are usually not reactive toward vinyl monomers due to steric hindrance and to the delocalization of unpaired electron. Furthermore, the ketyl radicals may act as chain terminators in the polymerization, leading to ketyl moieties incorporated into polymer chains and relatively short chains.[35] To avoid chain termination by ketyl radicals, additives such as onium salts[36−39] or certain bromo compounds[40] have turned out to be useful. These additives react with the ketyl radicals via oxidation and bromination, thus suppressing chain termination. In the case of onium salts, phenyl radicals, which initiate polymerizations instead of terminating growing chains,[41] are produced by the interaction of ketyl radi-cals with salt entities. Thus, the overall effect of these additives is an enhancement in polymerization rate.

For efficient polymerization, the bimolecular H-abstrac-tion reaction must compete with other side reactions, such as

nonreactive quenching (i.e., through energy transfer) of the photoexcited initiator by monomer or oxygen. The selection of a co-initiator (H-donor) that reacts rapidly with the electronically excited photoinitiator to produce a reactive, polymerization initiating radical is undoubtedly of great importance. Tertiary amines are more reactive co-initiators than alcohols or ethers.[42] Thiols are another class of co-initiators in thiol−ene photopolymerization systems. In this regard it is worth mentioning the pioneering work of Morgan and Ketley,[43] who used benzophenone to absorb light and initiate the polymerization of the radical chain process via a hydrogen abstraction reaction involving the excited benzophenone and a ground-state thiol. The thiol−ene photopolymerization system has recently been revitalized[44,45] and used as an effective way to cross-link thermoplastic elastomers.[46,47] These reactions were also utilized as environmentally friendly "click" coupling processes in various synthetic applications, since in contrast to the other methods, they usually proceed in the absence of solvent under benign reaction conditions without the use of any potentially toxic metal.[48−51]

Scheme 4. Stepwise Two-Photon Initiation Mechanism

Scheme 5. Poly(ethylene oxide) (a) and Dendritic Poly(ethylene imine) (b) as Hydrogen Donors in Type II Photoinitiators
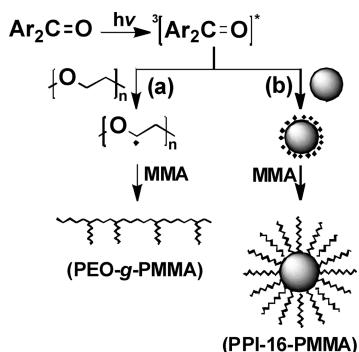

Table 1. Thioxanthone-Based One-Component Photoinitiators

Photoinitiator	Structure	Mode of action	Ref.
2-Mercaptothioxanthone		Hydrogen abstraction	58-60
2-(9-Thioxanthone-2-thio) acetic acid		Intramolecular radical generation	61, 62
2-(9-Thioxanthone) acetic acid		Intramolecular radical generation	61-63
Thioxanthone-anthracene (TX-A)		Endoperoxide formation	64

For many curing applications fully formulated mixtures, which contain all initiators monomers and additives, are supplied to customers. However, such formulations may not exhibit a good shelf life due to the initiation on storage. The use of benzodioxinones as photoinitiators may increase shelf life at the expense of initiation ability. It was shown[52] that structurally designed benzodioxinones liberate benzophenone only after stimulation by light which can further be excited to initiate free radical polymerization (Scheme 4). Liberation of both ketenes and benzophenone photoinitiator upon photolysis of benzodioxinones makes these compounds useful for cross-linking of hydroxyl-containing polymers[53] and also monofunctional vinyl monomers in the absence of a conventional photoinitiator and cross-linker.[54]
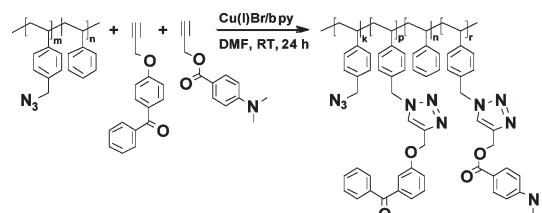
Among type II photoinitiators, thioxanthone derivatives in conjunction with tertiary amines are efficient photoinitiators with absorption characteristics that compare favorably with benzophenones.[55]

Although alkylamines are very efficient hydrogen donors, the high usage of such highly volatile and odorous compounds brings disadvantages to type II systems.[4,20] Poly(ethylene oxide)[56] and poly(ethylene imine)[57] based dendrimers of the following structures in Scheme 5 have been successfully used as polymeric hydrogen donors to replace low-molecular-weight amines in the formulations. Obviously, these molecules act as precursors for graft and star copolymers (Scheme 5).
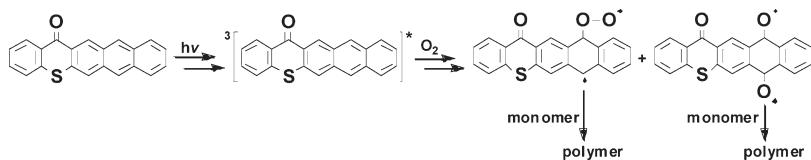
As part of our efforts to avoid problems associated with the amine hydrogen donors, we have recently reported several new thioxanthone derivatives as photoinitiators for free radical polymerization. Interestingly, these photoinitiators do not require an additional co-initiator, that is, a separate molecular hydrogen donor, since the hydrogen donor is incorporated into the photoinitiator structure. The structures and the mode of action of such one-component photoinitiators are shown in Table 1.
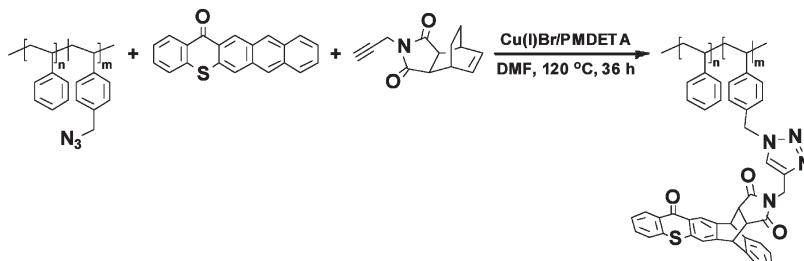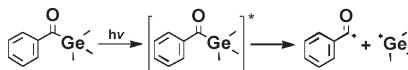
As one component photoinitiator, thioxanthone−anthracene (TX-A) deserves a special discussion. In contrast to all conventional photoinitiators, TX-A initiates the polymerization of acrylate and styrene monomers in the presence of air (Scheme 6).[64] Indeed, oxygen is required for the initiation process. We postulate that the initiation mechanism involves the formation of endoperoxides, which are formed by addition of photochemically generated singlet oxygen to the anthracene moiety. Thermal or photochemical cleavage of the endoperoxides generates initiating radicals. Since oxygen inhibition of photopolymerization is still a serious concern for the preparation of films, the involvement of oxygen in the initiation mechanism suggests that TX-A

Scheme 7. Click Reaction To Synthesize Polymeric Type II Photoinitiators Containing Benzophenone Chromophors and Hydrogen Donors Linked to the Polymer Chain

Scheme 6. Proposed Mechanism for Photoinitiation of Free Radical Polymerization with TX-A in the Presence of Oxygen

Scheme 8. Click Reaction To Synthesize Polymeric TX Photoinitiators

Scheme 9. Photolytic α-Cleavage of Benzoyltrimethylgermane with Visible Light

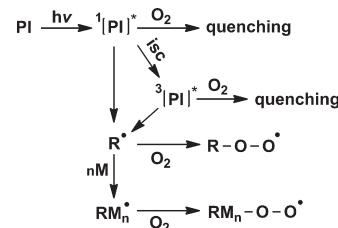may find use in a variety of practical applications of photocuring in air.

Photoinitiators and hydrogen donors can be incorporated into polymeric structures. In this way, the macromolecules having covalently bonded photoinitiator groups overcome the problems associated with high volatility and high migration often observed with low-molar-mass photoinitiators. Yin and co-workers[65−73] reported a number of examples of this kind of polymeric photoinitiators possessing both chromophoric TX groups and hydrogen donating sites in the structure.

Copper-catalyzed 1,3-dipolar azide−alkyne click chemistry[74] was proposed to be a versatile route to prepare such polymeric photoinitiators. For example, a novel one-component polymeric photoinitiator containing side-chain benzophenone and (dimethylamino)phenyl moieties was prepared in a one-pot synthesis via double click reactions (Scheme 7).[75]

In another report, 1,3-dipolar azide−alkyne [3 + 2] and thermoreversible Diels−Alder [4 + 2] click reactions were successfully combined for the synthesis of polymers bearing side-chain TX photoactive groups (Scheme 8). One of the consequences of the method is that such modification causes a dramatic change in the photochemistry of the precursor TX-A. The obtained polymeric photoinitiators were shown to efficiently initiate the free radical polymerization of mono- and multifunctional monomers via a type II mechanism in a conventional manner, i.e., in the presence of hydrogen donors.[76]

Most of the photoinitiators described up to now are sensitive to light at wavelengths below 400 nm. This enables an easy processsability because the sun and many artificial sources of light overwhelmingly emit light of longer wavelengths, and therefore, unintended photoinduced reactions during handling may be kept at low level. However, if the strong emission of mercury lamps or the sun in the visible region of the spectrum is to be used, photoinitiating systems that absorb visible light are required. Photoinitiators for visible light[77−79] have found particular interest because of their use in many targeted applications such as dental filling materials,[80−82] photoresists,[83] printing plates,[84] integrated circuits,[78] laser-induced 3D curing,[85,86] holographic recordings,[85,86] and nanoscale micromechanics.[77] Both cleavable and bimolecular hydrogen abstracting type photoinitiating systems, acting in the visible range, are well-known. Titanocene[77,87,88] and camphorquinone[89] in conjunction with an amine are typical examples for the respective systems. Recently, organic ketones containing germanium were introduced as a new class of cleavable photoinitiators[90,91] for free radical polymerization under visible light irradiation. In a mechanistic process analogous to acylphosphine oxides, these photoinitiators (upon irradiation) undergo α-cleavage to produce free radicals capable of initiating

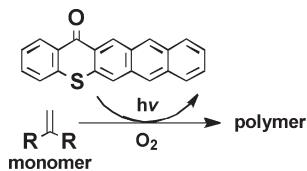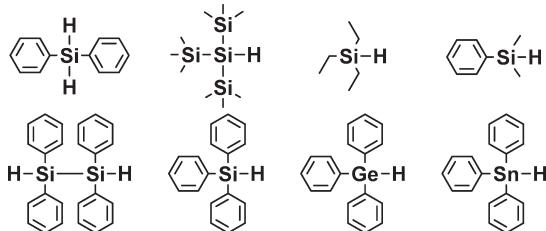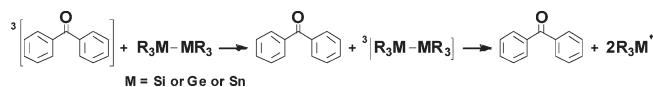**Scheme 10. Inhibition of Photoinitiation and Polymerization Reactions by Oxygen**

polymerization of methacrylates (Scheme 9). This is especially facile under aqueous acidic conditions.

Visible photoinitiation systems often involve dyes as light-absorbing chromophores. Numerous photoinitiated free radical polymerizations using dyes have been described and reviewed by several authors.[92−95] Initiating radicals are typically generated by photoinduced electron transfer and involve a co-initiator that participates in the electron transfer process. Energy transfer to monomers is not thermodynamically favorable in these systems due to low excitation energies of dyes. Depending on the nature of the dye involved, namely photoreducible or photo-oxidizable dyes, two distinct mechanisms need to be considered. These are electron transfer from the co-initiator to the excited, photoreducible dye and electron transfer from the excited, photo-oxidizable dye to the co-initiator.

One of the major drawbacks of photoinitiated free radical polymerization is related to the well-known oxygen inhibition. Various reactive species playing a role in the polymerization, such as excited states as well as initiating and propagating radicals are quenched by O_2 (Scheme 10). While quenching of the excited states results in inefficiency of the primary photochemical reaction, the diffusion-controlled reaction of oxygen with initiating and propagating radicals[96] yield highly stable peroxyl radicals which cannot participate in any further polymerization initiation reactions.[97−101] Therefore, the polymerization only proceeds efficiently after oxygen is consumed.[100,102]

The oxygen inhibition of photopolymerization can be used as advantage and is particularly important for dental applications. When dentists light cure resin composite restorations in increments or after manually contouring the surface layer to shape, the surface layer is exposed to air during polymerization which results in the formation of a resin-rich inhibited layer at the uppermost surface of the resin composite.[103]

Many strategies have been developed to combat O_2 inhibition including use of high-intensity lamps/high cure dosage,[102] inert atmospheres,[104] and additives such as amines[105,106] and thiols.[59,107−109] A number of cyclic and acylic N-vinylamides and N-alkylamides were also shown to have significant effect for the reduction of oxygen inhibition, resulting in rapid rates of polymerization in air even at low light intensities.[110] The use of TX-A (*vide supra*) as photoinitiator is one way to prevent oxygen inhibition since the presence of O_2 is essential for the polymerization to proceed (Scheme 11).[64]

Scheme 11. TX-A Uses Oxygen as Co-initiator

Chart 1. Silanes, Germanes, and Stannanes as Co-initiators To Overcome Oxygen Inhibition

Scheme 12. Photosensitized Metal—Metal Bond Cleavage

El-Roz et al.[111] have recently proposed an elegant way to overcome oxygen inhibition using silanes, germanes, and stannanes R_3XH as co-initiators and additives (Chart 1).

In highly viscous or thick samples, the reoxygenation process is quite slow, leading to an efficient polymerization after an inhibition period. However, in very low viscosity or thin samples, the reoxygenation remains efficient, leading to strongly reduced monomer conversions; moreover, the lower the light intensity, the lower the initial O_2 consumption. The compounds shown in Chart 1 allow for a dramatic increase in the photopolymerization rates and the final monomer conversions even with low light intensities and thin and low-viscous samples.
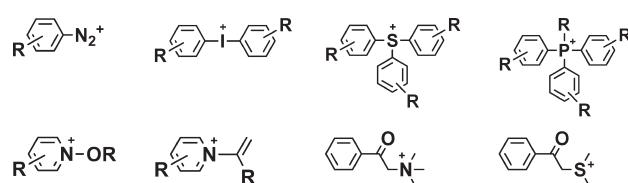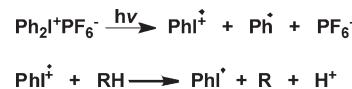
In these systems, less usual radicals such as silyl, germyl, and stannanyl radicals formed by hydrogen abstraction react with oxygen. Among them, Si-based systems appear promising as the intermediate silly radical can be generated through different routes. For example, photoinduced cleavage of polysilanes generates silyl radicals.[112−115] Various new initiating systems based on Si−Si, C−Si, S−Si, or Si−H bonds, leading to Si• radicals were proposed.[116−119]

The high reactivity of Si• toward the addition process to acrylate double bonds and their good behavior in photoinitiation of free radical polymerization under air were demonstrated.

More recently, the same group has proposed new co-initiators based on group 14 elements (disilanes, polysilanes, digermanes, and distannanes). Upon photolysis in the presence of benzophenone, radicals formed from the metal−metal bond cleavage, which showed excellent initiating properties for free radical photopolymerization (Scheme 12).[120]

Cationic Polymerization

Photoinitiated cationic polymerization exhibits several advantages over the corresponding free radical mode.[121−123] Epoxy and vinyl ether based monomers that are prone to cationic polymerization are of low volatility and negligible toxicity and possess good rheological properties.[124] In contrast to free radical polymerization, molecular oxygen does not inhibit the polymerization, and hence films can be cured in the presence of dry air. Moisture generally terminates the polymerization. In a dry environment, however, the termination rate is rather low, permitting the

Chart 2. Onium Salt Photoinitiators for Cationic Polymerization

Scheme 13. General Scheme of Photoinitiated Cationic Polymerization

continuation of the polymerization even if the irradiation is ceased. For these reasons, it appears that in addition to free radical also cationic photoinitiation process is used in many technical applications. Photoinitiated cationic polymerizations are generally accomplished with the aid of onium salts. The past two decades have seen a rapid growth in the research of new photoinitiators for cationic polymerization. Since Crivello described in his seminal papers[125−127] the use of iodonium and sulfonium salts as photoinitiators for cationic polymerization, a variety of new onium salts have been developed (Chart 2).[128−134]

Among them, the onium-type photoinitiators such as iodonium,[125] sulfonium,[127,129] and alkoxypyridinium[128,135,136] salts are important due to their thermal stability, solubility in most of the cationically polymerizable monomers, and efficiency in generating reactive species upon photolysis.[137] Moreover, they possess high photolysis quantum yields and are efficient photoinitiators of cationic polymerization when irradiation is carried out using light in the short- to mid-wavelength UV regions (230−300 nm).[134]

The reaction mechanism for photoinduced cationic polymerization by onium salts is presented in the example of diaryliodonium salts in Scheme 13.

Photoinduced decomposition and subsequent reaction of the radical cation with solvent or monomer lead to the formation of Bronsted acid, H^+, which is responsible for further initiation. The photochemistry and applications of the direct initiation to cationic polymerization to a variety of epoxy and vinyl ethers have been well studied and subject to review articles[10,138−141] and chapters in books.[1−3,42] In recent years, however, interest has been directed toward the development of strategies to make onium salt photoinitiators responsive to light with wavelengths in the near-UV and visible region of the spectrum. Several strategies have been employed for improving the performance of these photoinitiators, particularly at long wavelengths. The activation wavelength can be tuned without any additive by introducing additional chromophoric groups to the structure of the onium salt.[141,142]

Photochemically induced structural transformations can also make them absorb at higher wavelengths. In this connection, we refer to our recent report on photoinitiated cationic polymerization by using phenacylbenzoylpyridinium salts.[143,144] These initiators were shown to exhibit keto−enol tautomerism with absorptions at λ < 300 nm and around 500 nm (Figure 1).

It was also reported[145] that azobenzene containing alkoxypyridinium salt exhibits UV-induced *cis−trans* isomerization with absorptions at around λ = 459 and 360 nm (Scheme 14). The ability of this salt to act as a photoinitiator for both cationic and free radical polymerization was demonstrated.

Regarding indirect activation of onium salts, three modes of action concerning the formation of cationic species capable of initiating polymerization of monomers are distinguished: (i) oxidation of free radicals,[146−148] (ii) electron transfer[136,149−157]
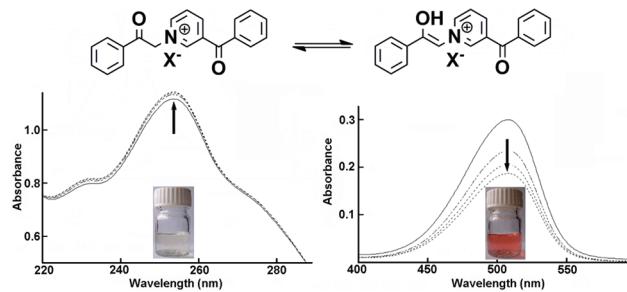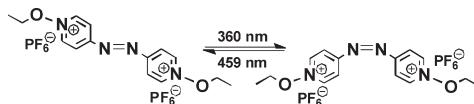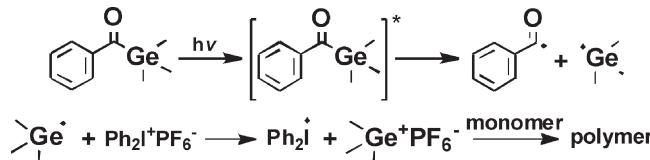
Figure 1. Photoinduced keto−enol tautomerism of a phenacylbenzoyl-pyridinium salt ($\lambda_{ex} > 507$ nm).[143]

Scheme 14. Photoinduced *Cis−Trans* Isomerization of an Azobenzene Containing an Alkoxypyridinium Salt

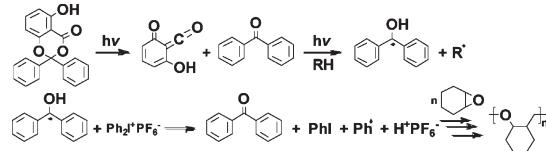**Scheme 15. Oxidation of Trimethylgermyl Radicals by Ph$_2$I$^+$PF$_6^-$**

between a photoexcited molecule and an onium salt, and (iii) excitation of charge transfer complexes[158,159] of onium salts. The so-called free radical promoted cationic polymerization is an elegant and fairly flexible type to extend the wavelength sensitivity to longer wavelengths.[148] In fact, free radicals may be produced by various modes: photochemically, thermally, or by irradiating the system with high-energy rays. Suitable radical sources for all modes of stimulation are available.[129,146,148,160−171]

Recently, acylgermanes originally developed as visible light photoinitiators for free radical polymerization[90,172] were also shown to activate cationic polymerization.[173,174] As in the case of all free radical promoted cationic polymerizations, the photochemically formed electron donating radicals (germyl radicals) are readily oxidized to germanium ions capable of initiating cationic polymerization (Scheme 15).
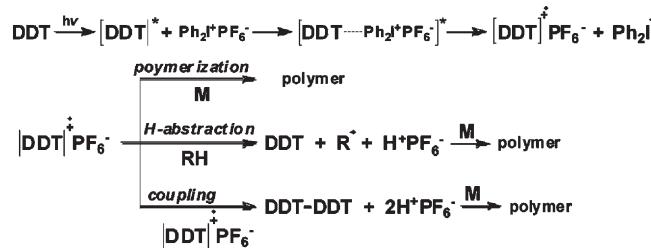
Bisacylgermanes such as dibenzoyldiethylgermane were also shown to be active in promoting cationic polymerization. Because these photoinitiators exhibit better absorption characteristics[91] and sequential decomposition behavior, they can be used as precursors for polygermanes[175] and block copolymers[173] of monomers polymerizable by cationic and radical mechanisms.

Recently, free radical promoted cationic polymerization through silyl radicals has been revitalized. For example, Lalevee et al.[176,177] have reported that silyl and germyl radicals generated respectively by UV laser irradiation of disilanes and silanes and germanes in the presence of aromatic ketones readily reduce diaryliodonium salts, resulting in efficient cationic polymerization of epoxides. Silanes can be used[118] also in conjunction with visible light photoinitiators such as eosin and camphorquinone for the decomposition of diaryliodonium salt. Benzyl alcohol was shown[178] to be an efficient hydrogen donor for camphorquinone to generate free radicals by the absorption of visible light. Subsequently, the electron donor radicals formed this way participate in the free radical chain induced decomposition of a diaryliodonium salt. In this connection, it is interesting to note that silanes can be used to initiate cationic polymerization via a

Scheme 16. Photoinitiated Cationic Polymerization of Cyclohexene Oxide by Photoacid Generation in a Stepwise Two-Photon Absorption Process

Scheme 17. 3,5-Diphenyldithieno[3,2-*b*:2,3-*d*]thiophene as Sensitizer for Iodonium Salt Decomposition via Electron Transfer To Generate Photoacids

nonphotochemical route. Certain onium salts such as phenacyl-sulfonium salts undergo facile reduction by silanes bearing Si−H groups in the presence of a noble metal catalyst. Such a redox reaction can be employed as a convenient initiator system for the cationic polymerizations of epoxides, oxetanes, and vinyl ethers.[179]

Another long wavelength photoinitiating system based on the free radical oxidation involves the use of substituted vinyl halides (*vide supra*). Radical promoted cationic polymerizations were performed in the presence of onium salts and zinc halides.[180−183]

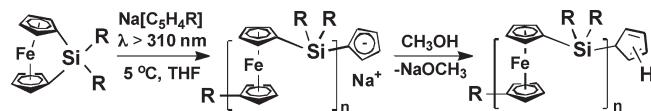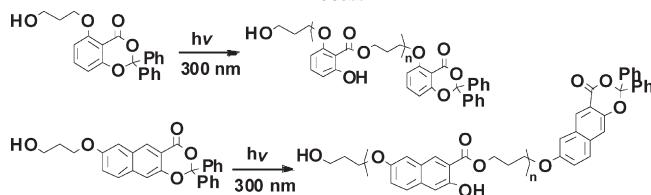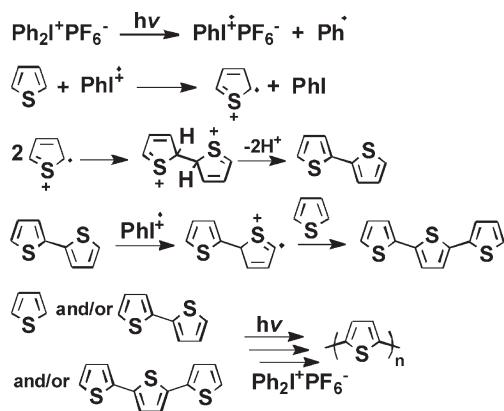An interesting but useful application of free radical promoted cationic polymerization is two-photon absorption photoacid generation.[184] It was shown that benzodioxinone can act as caged sensitizers for diphenyliodonium salt to generate acids for initiation of cationic polymerization. The first absorbed photon uncages the sensitizer.[184] The released sensitizer absorbs a second photon to reduce the iodonium salt yielding in protonic acids for initiation of cationic polymerization as presented in Scheme 16 for the polymerization of cyclohexene oxide.

The second mode of indirect activation of onium salts for long wavelength initiation is photosensitization by electron transfer. Polynuclear aromatic compounds are known[136,138,149−154,185] to sensitize and consequently decompose onium salts via electron transfer in the exciplex (Scheme 17). We have recently demonstrated that similar photosensitization action can be achieved by highly conjugated thiophene derivatives such as 3,5-diphenyl-dithieno[3,2-*b*:2,3-*d*]thiophene (DDT).[186]

Such polymerizations can be conducted at the visible range by using highly conjugated thiophene derivatives with electron donor substituents as photosensitizers.[187]

Anionic Polymerization

Although the photoinitiated cationic polymerization is in an advanced state, there have been only few attempts on the anionic counterpart. Fukuchi et al.[188] reported the anionic coordination polymerization of epoxides by a new catalyst system consisting of titanium tetraisopropoxide and photochemically generated phenol. Photoinitiated anionic polymerization of cyanoacrylates has been reported.[11] It was claimed that isocyanate ions, generated by ligand exchange reaction upon photolysis, were the initiating species. Alkyl cyanoacrylates undergo anionic polymerization in the presence of tertiary amines such as pyridine.[189] The polymerization proceeds via a zwitterionic mechanism. Kutal and co-workers[190] reported the use of the Pt(acac)$_2$ complex in

Scheme 18. Photoinitiated Anionic Polymerization of Ferrocenophanes

Scheme 19. Generating Oligoesters by a Photochemical Step-Growth Process

Scheme 20. Photoinduced Step-Growth Polymerization of Thiophene by Iodonium Salts
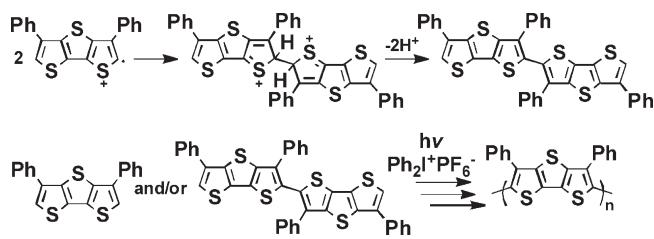

photoinitiated anionic polymerization of ethyl cyanoacrylate (ECA). Initiating species were claimed to be free acetylacetonate anions produced by photoexcitation of the complex. Yagci and co-workers[191−193] demonstrated that weak base generating photoinitiator systems can be used to initiate zwitterionic polymerization of cyano acrylates. *N*-Alkoxypyridinium and *N*-phenacylpyridinium type salts were shown to be effective initiators for such zwitterionic polymerization.

Manners[194] reported that sila[1]ferrocenophanes undergo ring-opening polymerization when treated with $Na[C_5H_5]$ and UV light (Scheme 18). This reaction proceeds through an Si−Cp bond cleavage mechanism as the incoming Cp anion displaces one of the Cp ligands in the ferrocenophane.

Step Growth

As stated in the Introduction, there is only limited number of reports on the photoinduced step-growth polymerization. The first true step-growth polymerization by a photochemical means was reported for the formation of polyester via photodecomposition of benzodioxinones.[195] Thus, hetero-bifunctional monomers, namely, benzodioxinone and naphtodioxinone compounds, possessing both chromophoric and aliphatic hydroxyl groups in the structure were used in the process. Photolysis of these compounds yielded oligoesters with narrow molecular weight distribution (Scheme 19).

Another example is photoinduced step-growth polymerization of thiophene by onium salts.[196] It was shown that besides electropolymerization, conducting polythiophenes can also be obtained by means of UV irradiation of thiophene in the presence a diphenyliodonium salt. Alkoxylpyridinium and triphenylsulfonium salts were also found to facilitate the polymerization of thiophene. The polymerization is accompanied by the formation

Scheme 21. Photoinduced Step-Growth Polymerization of Diphenyldithienothiophene by Iodonium Salts Generates Highly Conjugated Polythiophenes

of a polymer film on the surface of the reaction vessel surface. Detailed laser flash photolysis and EPR studies[197] revealed that polymerization mechanism involves electron transfer from photochemically generated phenyliodinium radical cations to thiophene (Scheme 20).

Highly conjugated thiophenes can also be obtained by photochemical means. Thus, step-growth polymerization of a conjugated thiophene derivative was achieved by coupling reactions of radical cations accompanied by proton release (Scheme 21).[198] Radical cations were generated by electron transfer from the photoexcited thiophene derivative to iodonium salt as described for the initiation of cationic polymerization (*vide supra*).
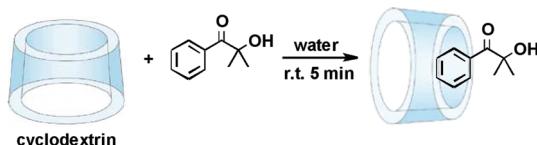
Environmental, Safety, and Health Considerations

The photopolymerization world today is requiring high demands on performance of the related products in a period where sustainability, cost, environment, safety, and health aspects are high on the priority list of both industry and society. However, many contradictory requirements like low volatile organic compound (VOC) with good hardness as well as solvent-free with good adhesion have to be combined while making progress against these demanding targets. In fact, the photopolymerization itself is an ecological alternative to thermal processes because no VOCs are released in this technology. Therefore, in industry thermally applied systems are being increasingly replaced by processes operated by photochemical means. Organic solvent pollution in conventional photopolymerization is still a serious environmental issue. Additionally, water can contribute energetically and economically by acting as a cooling agent (i.e., because of its heat absorption). Because of its tolerance to water, there has been increased interest[199,200] in photoinitiated free radical polymerizations performed in nonorganic solvent, such as aqueous dispersed coatings and water-developable resins. For this reason, great attention has been paid to synthesize new water-soluble photoinitiators in recent years.[201−205] In general, new water-soluble photoinitiators can be developed by introducing water solubilizing groups such as quaternary ammonium salts, sulfonic acid, and carboxylic acids[112,206−208] or hydrophilic groups[209,210] into oil-soluble initiators which are known to exhibit high activities in solvents. The possible disadvantage of this method is that it usually involves complicated synthesis, and the direct substitution on the photoinitiator often affects the photoactivity.
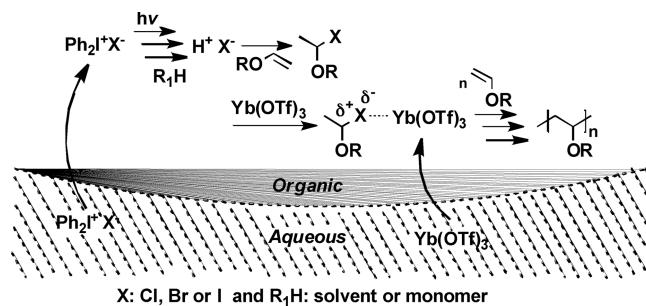
Cyclic oligosaccharides, formed from 1,4-glucopyranose units known as cyclodextrins, exhibit a torus-shaped structure with a hydrophobic cavity and a hydrophilic exterior.[211,212] These molecules are able to encapsulate hydrophobic molecules or hydrophobic side groups of polymer as guests into their cavities to form host/guest complexes in aqueous solution and in emulsion.[213,214]

Recently, Ritter and co-workers[203] developed a new method to make a nearly water-insoluble photoinitiator (2-hydroxy-2-methyl-1-phenylpropan-1-one) water-soluble by complexation with β-cyclodextrin (Scheme 22).

Scheme 22. A Nearly Water-Insoluble Photoinitiator Becomes Water-Soluble by Complexation with β-Cyclodextrin

Scheme 23. Photoinitiated Cationic Phase Transfer Polymerization of Vinyl Ethers

X: Cl, Br or I and R₁H: solvent or monomer

Scheme 24. Photoinitiated Cationic Cross-Linking of Divinyl Ethers with Diphenyliodonium Halides

X: Cl, Br or I and R₁H: solvent or monomer

Scheme 25. Cationic Polymerization of Vinyl Ethers Initiated by Photolysis of Vinyl Halides in the Presence of Zinc Iodide

A comparative kinetic study of polymerization reactions initiated with both complexed and uncomplexed photoinitiator revealed a higher polymerization rate and better polymerization yield in the presence of the cyclodextrin/photoinitiator complex. Obviously, this complexation opens a new way for using water-insoluble initiators more effectively in sufficiently high concentrations in aqueous polymerization systems. Indeed, many other examples of cylcodextrin-based aqueous photopolymerizations have been reported,[215−219] and the methodology was used for the preparation of hydrogels.[220,221]
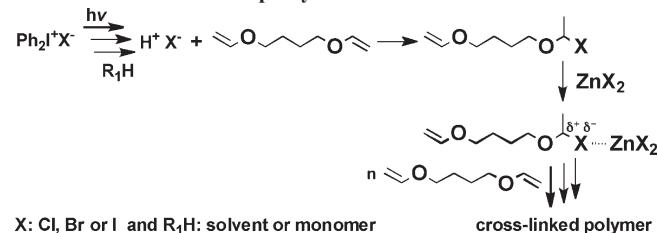
It is well-known that, regardless of the type of initiation, cationic polymerization in general is terminated by the presence of very small amounts of water. In contrast to free radical polymerization, such polymerizations must be carried out under stringently dry conditions, which require more effort and time. In fact, most reactions involving the use of ionic species such as carbocations, Lewis acids, and coordination compounds are very sensitive to even traces of moisture because it deactivates or decomposes the intermediates or catalysts. Accordingly, cationic polymerizations are also terminated or undergo chain transfer reactions as a result of deactivating effect of water. On the other hand, as stated above for free radical mode, the use of water as a solvent in photopolymerization is environmentally friendly. Following Sawamato's strategy[222] described for thermally activated cationic polymerization of certain monomers, Yagci and co-workers[223] developed heterogeneous photoinitiated cationic polymerization of mono- and divinyl ethers in the presence of the water-tolerant Lewis acid, ytterbium triflatemethanesulfonate (Yb(OTf)₃), in an aqueous medium. Although there have been several reports[224,225] on aqueous cationic polymerization, it is the first report on light-induced cationic polymerization in the presence of a large amount of water.

The polymerizations were performed in heterogeneous systems consisting of an aqueous phase containing Yb(OTf)₃ and photoinitiator diphenyliodonium salt and an organic phase of acetonitrile containing monomer. The polymerization consists of two steps: (i) photoinduced adduct formation and (ii) subsequent propagation with the aid of Yb(OTf)₃ (Scheme 23). The fast polymerization exhibited an explosive character so that the monomer conversion and molecular weights of the resulting polymers are very dependent on the experimental conditions, such as temperature, stirring manner, and rate.
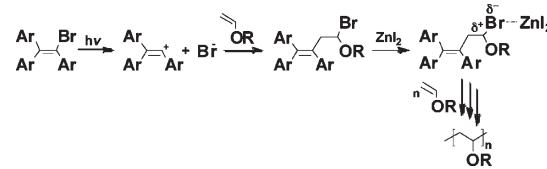
Because of the economical and environmental advantages offered by photoinitiated polymerizations in aqueous media, it is expected that in the near future these polymerizations will be employed more widely in many applications employing waterborne systems.
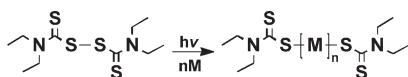
In addition to epoxides, vinyl ethers are important monomers for UV-curable coatings as they offer environmentally friendly formulations that are alternatives to commonly used acrylate monomers, which possess strong odor and skin irritating properties.[226] Although photoinitiated cationic polymerizations are efficiently applied for the curing of epoxy and vinyl ether based formulations, the nature of the non-nucleophilic counteranions limits the use of onium salts in wider applications. The limitations associated with the non-nucleophilic counterion of onium compounds, especially SbF_6^- and AsF_6^-, include high toxicity and high cost because of their central heavy metals. It was reported[227,228] that long-term exposure of these metal salts to human skin led to increased incidences of various cancers. Furthermore, the preparation of such initiators from their corresponding onium salts with halides requires additional steps, i.e., counteranion exchange; thus, this makes them expensive.[10,125] The use of diphenyliodonium salts with highly nucleophilic counteranions in photoinitiated cationic cross-linking of divinyl ethers (Scheme 24) was recently reported.[180] The system is comprised only of a diphenyliodonium salt with a highly nucleophilic counteranion (Cl⁻, Br⁻, or I⁻) and a zinc halide.

The long wavelength acting indirect systems involving aromatic photosensitizer such as anthracene and perylene or an aromatic carbonyl compound such as 2,2-dimethoxy-2-phenylacetophenone, benzophenone, and thioxanthone were also shown to be effective in the photoinitiation.

This concept was further extended to totally eliminate the use of iodonium salts as the component of the photoinitiating system.[182] The cationic polymerization of vinyl ethers was initiated upon irradiation at $\lambda = 350$ nm with vinyl halides in the presence of zinc iodide (Scheme 25). A mechanism involving formation of an adduct between the monomer and the products resulting from the photoinduced homolysis of the vinyl halide followed by electron transfer is proposed. In the subsequent step, the terminal carbon−halide bond in this adduct is activated by the coordinating effect of zinc iodide. This polymerization exhibited some characteristics of pseudo-living cationic polymerization.

An alternative approach to eliminate the contamination of the polymeric products by the inorganic residues arising from the counteranion of the onium salt is the use of phosphonates as

Scheme 26. Photoinitiated Living Polymerization of Vinyl Monomers with Dithiocarbamates
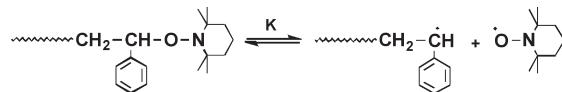

nonionic type initiators.[229] Although these compounds were shown to be effective in initiating polymerization of vinyl ethers, the high temperatures required for the activation limit their practical application.

Possibilities of Controlled/Living Polymerizations by Photochemical Processes
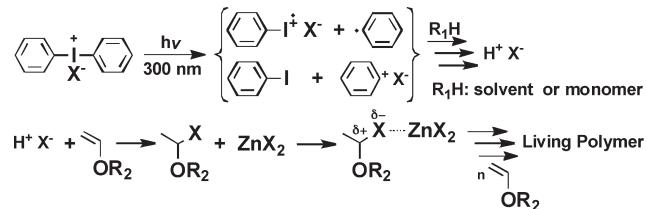
The control of the polymerization is extremely important from the synthetic point of view. The discovery of living anionic polymerization more than 50 years ago stimulated attempts at living cationic and radical polymerizations, which were realized at much later dates.[230] Living polymerization involves synthesis of polymers without significant irreversible chain transfer and chain termination. During the past 15 years, the use of controlled/living polymerization processes has revolutionized the synthesis of polymers with well-defined structures.[231] Controlled/living polymerization techniques in anionic, cationic, metathesis, and group transfer polymerizations have been developed. Recent approaches to achieve controlled/living polymerization in cationic and also radical systems are based on the stabilization of unstable growing species by the reversible formation of the corresponding covalent and dormant species that rapidly exchange. However, photoinitiated polymerization processes lack the control of the final polymer properties, and structurally well-defined polymers and block copolymers cannot be prepared by photochemical means. By photolysis of existing radical and cationic initiators, a controllable amount of initiating species is formed. The concentration of initiating species and finally growing polymer chains may be conveniently adjusted by choosing appropriate light intensities. Conversely, the polymers formed by controlled/living polymerization or by photoinitiation with photoinitiators do often differ in molecular weight distribution. Since initiating species in photopolymerizations are generated continuously, growing polymer chains with large differences in chain length are present at the same time. Therefore, polymers usually have a broad molecular weight distribution. In the case of controlled/living polymerizations, formation of polymer molecules with the same length gives rise to to polydispersities close to unity, provided chain-braking side reactions are negligible. Although with limited success, there have been a number of attempts to extend such control to polymerizations conducted photochemically.[232] The earlier approach based on reversible combination of growing radicals with a scavenging radical was applied in thermal and photoinitiated radical polymerization. According to Otsu,[233] photochemical polymerization of vinyl monomers with dithiocarbamates, referred to as iniferter (initiator−transfer−terminator),[234] is characterized by the initial rapid growth and an increase in molecular weight with conversion (Scheme 26).

Although polymers with complex architecture (block, star, or amphiphilic polymers, etc.) can successfully be synthesized, this system deviates from truly controlled/living conditions[235] and suffers from poor photochemical initiation. The main reason for the deviation from living conditions is related to the dimerization and initiation of additional chains by dithiocarbamyl radicals. Despite the industrial and academic growing needs in this field and possibility of opening a large range of applications for photopolymers, no efficient controlled/living photopolymerization has been described up to now. The most widely studied methodology for this purpose is nitroxide-mediated photopolymerization (NMP). Analogous thermally activated nitroxide-mediated radi-

Scheme 27. Nitroxide-Mediated Radical Polymerization

Scheme 28. Photoinitiated Living Cationic Polymerization of Isobutyl Vinyl Ether by Iodonium Salts and Zinc Halides
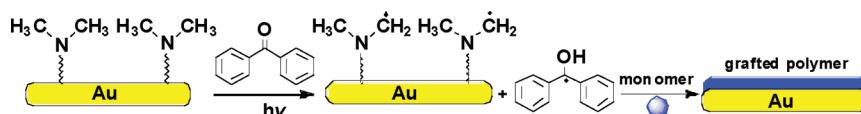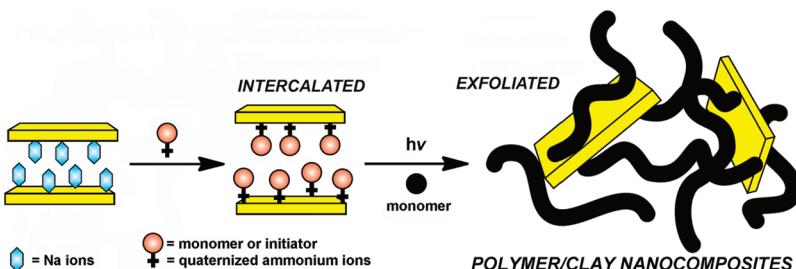

cal polymerization (NMRP), also referred as stable free radical polymerization (SFRP), is one of the versatile methods for the controlled/living polymerizations. NMRP is generally based on the use of nitroxyl radicals (nitroxides) or alkoxyamines (Scheme 27).[236,237]

Scaiano et al.[238] proposed that the homolysis of TEMPO-based alkoxyamines (where TEMPO is 2,2,6,6-tetramethylpiperidinyloxy-4-yl radical) can be photosensitized by appropriate sensitizers such as xanthone or a pyrene derivative at their triplet and singlet excited states, respectively. Although the photosensitization step was successful, only a limited number of radicals were generated. Alternatively, Yoshida[239−243] attempted to activate the radical generation process by using photoacid generator iodonium salt. However, this system is still unclear as the function of the iodonium salt is not known.

Several attempts were also made to covalently attach different chromphoric groups to the TEMPO moiety.[244,245] Although some success was achieved, the conditions for true controlled/living radical polymerization were not attained. More recently, Guillaneuf et al.[246] reported a new alkoxyamine possessing directly attached chromophoric groups without a separation unit to facilitate the homolysis of alkoxyamine. It was demonstrated that this compound acts as a photoiniferter for the polymerization of *n*-butyl acrylate, and a linear growth of the polymer chain combined with a partial living character has been achieved.

Also in the case of photoinitiated cationic polymerization, it is difficult to achieve controlled/living conditions. A few heterocyclic monomers such as oxolane and *tert*-butylazirdine have been polymerized under living conditions by using pre-existing carbenium ions with a stable counterion.[247] It was demonstrated that in the photoinitiated cationic polymerization of cyclic ethers, using iodonium and sulfonium salts with such non-nucleophilic counteranions, the polymerization accelerates during photolysis because more and more active centers are generated photochemically.[146,248] This process continues until either all the salt is used up or if the light source is removed. The polymerization then proceeds thermally at a steady rate according to the number of propagating centers present. Thus, photoinitiated controlled/living cationic polymerization of certain cyclic monomers can be achieved by short photolysis followed by thermal processes.

Recently, photoinduced living cationic polymerization of isobutyl vinyl ether (IBVE) in the presence of various diphenyliodonium salts and zinc halides was reported.[249,250] Photochemically generated protonic acid reacts with IBVE to form the monomer HX adduct. The terminal carbon−halide bond in this adduct is activated by the coordinating effect of zinc halide. This activation leads to generation of a suitable nucleophilic counteranion by stabilizing the growing carbocation. Thus, chain-breaking processes are prevented, and living cationic polymerization of IBVE proceeds (Scheme 28).

Scheme 29. Grafting a Polymer onto Self-Assembled Monolayers by Free Radical Polymerization

Scheme 30. Formation of Polymer–Clay Nanocomposites by Photopolymerization

This methodology was further extended to indirect photoinitiating systems using free radical sources and photosensitizers.[181] In this connection it should be pointed out that in these systems the photochemical step is involved only in the generation of reactive species, and the propagation proceeds by a thermal reaction.

Recently, a conceptually different approach for living photopolymerization involving photoexcitation of monomers has been reported.[251] Irradiation of metal-containing ferrocenophane monomers at $\lambda > 310$ nm or with sunlight in the presence of an anionic initiator leads to living polymerizations, in which the conversion and molecular weight of the resulting polymer can be controlled by the irradiation time. Block copolymers and functional polymers can be synthesized by this process.

New and Emerging Applications

Photopolymerizations, especially those leading to cross-linked networks, results in significant changes in material physical properties such as phase, solubility, adhesion, color, optical index, and electrical conductivity. Therefore, photoinduced cross-linking polymerization has been widely used in microfabrication, coating,[252] and surface modification of devices and materials, including adhesives and sealants, printing materials, optical and electrooptical materials, and electronic materials.[253] Photopolymerizations involving linear chain formation has also been applied to various fields including preparation of block[254] and graft copolymers[255] and surface grafting.[256] In the case of block and graft copolymers, the reactive sites are generated at definite positions in the macromolecule by taking advantage of the selective absorptivities of certain chromophores. Despite the uncontrolled nature, the photoinduced polymerizations in the presence of suitable monomer lead to the formation of block and graft copolymers by using main-chain and side-chain polymeric photoinitiators, respectively. In this manner, copolymers with almost quantitative block or graft yields can be obtained, for the fact that side reactions and, thus, homopolymer formation are minimized as a result of the low polymerization temperature. Radical and cationic modes, and also their combination with other polymerization methods, were shown to be effective in such processes. The latter methodology is particularly useful for extending possible block and graft copolymers of monomers with different chemical nature and thus polymerize by different mechanisms.[257] Typically, block copolymers of polystyrene-*b*-poly(cyclohexene oxide)[168] and poly(methyl methacrylate)-*b*-poly(ε-caprolactone)[258] can be prepared by the combination of conventional free radical and ring-opening polymerization with photopolymerizations, respectively. The synthetic strategies to prepare block and graft copolymers via photoinduced polymerizations were recently outlined.[259]

It was recently demonstrated that hydrogen abstraction type photoinitiation can be used to graft onto self-assembled monolayers (SAM). Indeed, alkylamines attached to SAM could participate in photopolymerization when activated by triplet sensitizers such as benzophenone. The overall process is presented in Scheme 29.[260]
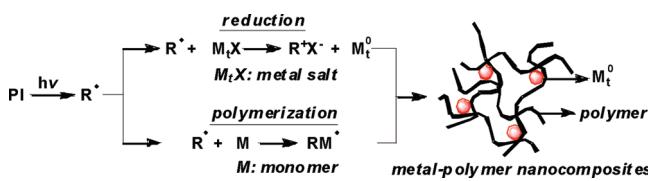
Another interesting application of photopolymerization concerns the preparation of polymer–clay nanocomposites. Such materials offer the opportunity to combine the desirable properties of polymers with those of clay arising from the small particle size and large surface area such as hardness, chemical resistance, thermal stability, and flame retardancy.[261–264] However, the major concern for the preparation of homogeneous clay-based nanocomposites is related to the control of the microstructure and phase separation between organic and inorganic components. The hydrogen or covalent bonding between the polymer matrix and inorganic clay phases favors interfacial interactions which eventually leads to superior properties compared to classical composites. Photochemical routes[265,266] can allow polymer molecules to grow inside the clay galleries upon irradiation and consequently form covalent bonds between organic and inorganic phases. Attachment of either photoinitiator[267] or monomeric[268] sites into clay layers and subsequent photopolymerization of immersed monomers facilitate propagation and exfoliation processes concomitantly, leading to the formation of homogeneous clay–polymer nanocomposites (Scheme 30).

The other possibility for *in situ* photoinduced preparation of polymer/clay nanocomposites is by polymerization with diphenyliodonium salt as photoinitiator via an activated monomer mechanism.[269]
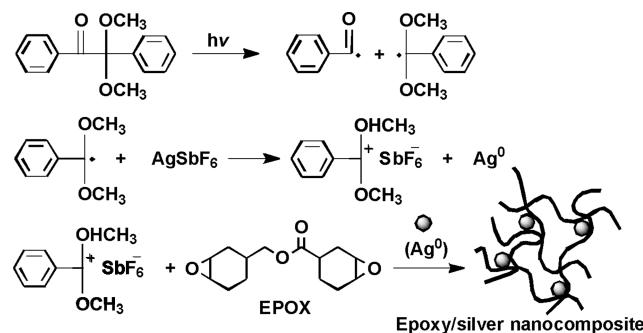
Polymeric structures including linear polymers, block and graft copolymers, and networks decorating metal nanoparticles combine the physical properties of small size metal nanoparticles with those of polymeric materials in a beneficial manner. Many advanced optoelectronic and sensor devices are based on the fabrication of these materials.[270–273] Because of their high surface free energy, nanoparticles tend to agglomerate. Again, a key challenge for a potential technological use is the achievement of homogeneous dispersion of the thermodynamically unstable nanoparticles. Various methods have been applied. The generally applied methodology is detaining nanoparticles during the preparation by adding protecting agents or setting them in an inert environment. Among them, photochemical methods involving light-induced reduction of metal ions such as Ag and Au complexes are of particular interest as they find a wide range of applications including synthesis of metallic colloids and metallization and patterning of films.

Recently, a novel approach has been introduced for the preparation of metal–polymer nanocomposites.[274–278] In this

Scheme 31. Synthesis of Metal−Polymer Nanocomposites by Free Radical Polymerization

Scheme 32. Synthesis of Metal−Polymer Nanocomposites by Cationic Polymerization

approach nanoparticle formation and UV cross-linking process were accomplished in one pot by simply irradiating appropriate formulations, obtaining the homogeneous distribution of the nanoparticles within the polymer network without any macroscopic agglomeration. Silver or gold nanoparticles and initiating species were formed in a single redox process. The overall strategy is represented in Scheme 31.

The nature of the photochemically generated radicals and the redox properties of the salt are quite crucial for the success of the process. Appropriate combinations of electron donor radicals with certain metal salts induce metal formation and chain propagation concomitantly. For example, photoinduced cleavage of 2,2-dimethoxy-2-phenylacetophenone (DMPA) is a good source of electron donor radicals, namely alkoxybenzyl radicals.[278] Thus, irradiation of DMPA in the system in the presence of $AgPF_6$ leads to its reduction with rapid generation of both metallic silver and initiating cations without any undesirable side reactions (Scheme 32).

The process is not limited to the cationically polymerizing epoxy resins. Acrylates and methacrylates that polymerize by a free radical mechanism can also form nanocomposites by the described *in situ* method. Providing that electron donor radicals are generated, visible light sensitive photoinitiators can also be used for both free radical and free radical promoted cationic polymerizations. Silver nanoparticle containing systems exhibited excellent antimicrobial properties.

Another one-step photochemical strategy for the preparation of polymer composites containing silver nanoparticles was recently proposed.[279] In this approach, a diaminofluorene compound was employed both as a photoreductant agent of silver precursors and as a free radical photoinitiator to produce silver nanoparticles in a poly(ethylene glycol) matrix at the same time. Neckers and co-workers[280] reported that gold nanoparticles can be incorporated into a polymer matrix without the use of conventional photoinitiator. The charge-separated states of the gold nanoparticles attached to the bithiophene group generated upon exposure to UV light are active intermediates that can cause polymerization of an acrylic monomer. Gold nanoparticles were uniformly distributed in the polymer matrix, and polymer nanocomposite with a unique texture was obtained by a one-step photochemical process.

Sol−gel hybrid nanomaterials for practical application as micro-optical elements in optical communication, optical data storage, information displays, sensing, and imaging systems can be obtained by applying photopolymerization techniques.[281] The typical approach is to conduct concomitant alkoxysiloxane sol−gel polycondensation and free radical[282] or cationic[283] photopolymerizations. In this way a single-component solvent-free hybrid coating formulation can be cured photochemically by a straightforward one-step process.

Photopolymerization is widely used in lithographic techniques, particularly for the fabrication of powerful integrated circuits.[284,285] However, conventional photolithography cannot achieve the high resolution especially when the feature size decrease is required. Two-photon photopolymerization appears to overcome such limitations, and three-dimensional nanostructures (3D) can be fabricated.[286−290]

Two recent examples illustrate application of conceptually different approaches in optical lithography based on two-photon absorption. It was demonstrated that initiating species can be generated by single-photon absorption at one wavelength while inhibiting species are generated by single-photon absorption at a second, independent wavelength. The second photon reduces the polymerization rate, resulting in the delay of the gelation of bifunctional monomer.[291] In this way, spatial control over the polymerization was achieved, and structures with desired feature size and monomer conversions were formed which are not attainable with use of single- and two-photon absorption photopolymerization. A similar approach was reported, where multiphoton absorption of pulsed 800 nm light was used to initiate cross-linking in a polymer photoresist and one-photon absorption of continuous-wave 800 nm light was used to deactivate the photopolymerization simultaneously.[292] This method allowed to fabricate features with scalable resolution along the beam axis, down to a 40 nm minimum feature size.

Because of the fact that photopolymerization offers several advantages such as short reaction time, mild reaction conditions, *in situ* gelation, and biocompatibility, it is also used in the fabrication of biomaterials. For example, hydrogels are one class of biomaterials obtained by photopolymerization.[293] Biomaterials formed by photopolymerization have been used in tissue-engineering applications with numerous roles including noncell involved fillers or dressings, cell growth guiders or promoters, and matrixes for two- and three-dimensional cell cultures.

Conclusions and Perspectives

As presented in this Perspective, photopolymerization is an important area of polymer science from both industrial and academic perspectives. Developments in this field are rapidly reflected in the UV curing technology which encompass a wide range of uses in both high volume applications such as coatings, adhesives, and printing inks as well as advanced high-technology purposes such as microelectronics, photo- and stereolithography, and halographic data storage media. Free radical polymerization is still the most widely used process in those applications, which utilizes photoinitiators generating radicals through cleavage and hydrogen abstraction reactions. Recent developments of new photoinitiating systems for cationic polymerization acting in the near-UV and visible spectral region indicate that the cationic mode would also find wider application in the near future.

References and Notes

(1) Fouassier, J.-P. In *Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications*; Hanser/Gardner Publications: Munich, 1995.

(2) Davidson, R. S. *Exploring the Science, Technology and Applications of U.V and E.B. Curing*; SITA Technology Ltd.: London, 1998.

(3) Roffey, C. G. *Photogeneration of Reactive Species for UV Curing*; Wiley: Chichester, 1997.

(4) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1–61.

(5) Bunning, T. J.; Natarajan, L. V.; Tondiglia, V. P.; Sutherland, R. L. *Annu. Rev. Mater. Sci.* **2000**, *30*, 83–115.

(6) Anseth, K. S.; Newman, S. M.; Bowman, C. N. *Adv. Polym. Sci.* **1995**, *122*, 177–217.

(7) Sun, H. B.; Kawata, S. *Adv. Polym. Sci.* **2004**, *170*, 169–273.

(8) Fisher, J. P.; Dean, D.; Engel, P. S.; Mikos, A. G. *Annu. Rev. Mater. Res.* **2001**, *31*, 171–181.

(9) Arsu, N.; Reetz, I.; Yagci, Y.; Mishra, M. K. *Photoinitiated Radical Vinyl Polymerization in Handbook of Vinyl Polymers: Radical Polymerization, Process, and Technology*; Mishra, M. K., Yagci, Y., Eds.; CRC Press: Boca Raton, FL, 2009; Vol. *20*, pp 141−204.

(10) Yagci, Y.; Reetz, I. *Prog. Polym. Sci.* **1998**, *23*, 1485–1538.

(11) Kutal, C.; Grutsch, P. A.; Yang, D. B. *Macromolecules* **1991**, *24* (26), 6872–6873.

(12) Alimoglu, A. K.; Bamford, C. H.; Ledwith, A.; Yagci, Y. *Makromol. Chem.* **1992**, *193*, 1551–1556.

(13) Bamford, C. H.; Ledwith, A.; Yagci, Y. *Polymer* **1978**, *19*, 354–356.

(14) DeSchryver, F. C.; Anand, L.; Smets, G.; Switten, J. *J. Polym. Sci., Part B: Polym. Phys.* **1971**, *9*, 777–780.

(15) Kardush, N.; Stevens, M. P. *J. Polym. Sci., Part A: Polym. Chem.* **1972**, *10*, 1093–1096.

(16) Hizal, G.; Sarman, A.; Yagci, Y. *Polym. Bull.* **1995**, *35*, 567–573.

(17) Monroe, B. M.; Weed, G. C. *Chem. Rev.* **1993**, *93*, 435–448.

(18) Decker, C. *Macromol. Rapid Commun.* **2002**, *23*, 1067–1093.

(19) Gruber, H. F. *Prog. Polym. Sci.* **1992**, *17*, 953–1044.

(20) Hageman, H. J. *Prog. Org. Coat.* **1985**, *13*, 123–150.

(21) Kuhlmann, R.; Schnabel, W. *Angew. Makromol. Chem.* **1978**, *70*, 145–157.

(22) Fouassier, J. P.; Lougnot, D. J. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 2935–2952.

(23) Borer, A.; Kirchmayr, R.; Rist, G. *Helv. Chim. Acta* **1978**, *61*, 305–324.

(24) Leopold, D.; Fischer, H. *J. Chem. Soc., Perkin Trans. 2* **1992**, 513–517.

(25) Arsu, N.; Davidson, R. S. *J. Photochem. Photobiol., A* **1994**, *84*, 291–297.

(26) Fouassier, J. P.; Lougnot, D. J.; Paverne, A.; Wieder, F. *Chem. Phys. Lett.* **1987**, *135*, 30–34.

(27) Delzenne, G. A.; Laridon, U.; Peeters, H. *Eur. Polym. J.* **1970**, *6*, 933–943.

(28) Laridon, U. L.; Dewinter, W. F.; Kokelenber, H. E. EP14012-A; JP55100543-A; US4282309-A; CA1125084-A; EP14012-B; DE3063210-G; JP88059130-B, **1980**.

(29) Sumiyoshi, T.; Schnabel, W. *Makromol. Chem.* **1985**, *186*, 1811–1823.

(30) Sumiyoshi, T.; Schnabel, W.; Henne, A. *J. Photochem.* **1986**, *32*, 191–201.

(31) Sumiyoshi, T.; Schnabel, W.; Henne, A. *J. Photochem.* **1986**, *32*, 119–130.

(32) Ledwith, A.; Purbrick, M. D. *Polymer* **1973**, *14*, 521–522.

(33) Ledwith, A.; Bosley, J. A.; Purbrick, M. D. *J. Oil Colour Chem. Assoc.* **1978**, *61*, 95–104.

(34) Davidson, R. S. *Adv. Phys. Org. Chem.* **1983**, *19*, 1–130.

(35) Hutchiso, J.; Lambert, M. C.; Ledwith, A. *Polymer* **1973**, *14*, 250–254.

(36) Baumann, H.; Timpe, H. J. *Acta Polym.* **1986**, *37*, 309–313.

(37) Baumann, H.; Oertel, U.; Timpe, H. J. *Eur. Polym. J.* **1986**, *22*, 313–318.

(38) Fouassier, J. P.; Ruhlmann, D.; Takimoto, Y.; Harada, M.; Kawabata, M. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2245–2248.

(39) Kayaman, N.; Onen, A.; Yagci, Y.; Schnabel, W. *Polym. Bull.* **1994**, *32*, 589–596.

(40) Fouassier, J. P.; Erddalane, A.; Morletsavary, F.; Sumiyoshi, I.; Harada, M.; Kawabata, M. *Macromolecules* **1994**, *27*, 3349–3356.

(41) Yagci, Y.; Aydogan, A. C.; Sizgek, A. E. *J. Polym. Sci., Part C: Polym. Lett.* **1984**, *22*, 103–106.

(42) Dietliker, K. *Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints*; SITA Technology: London, 1991; Vol. *3*.

(43) Morgan, C. R.; Magnotta, F.; Ketley, A. D. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, *15*, 627–645.

(44) Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5301–5338.

(45) Cramer, N. B.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3311–3319.

(46) Decker, C.; Viet, T. N. T. *Macromol. Chem. Phys.* **1999**, *200*, 1965–1974.

(47) Decker, C.; Viet, T. N. T. *J. Appl. Polym. Sci.* **2000**, *77*, 1902–1912.

(48) Campos, L. M.; Killops, K. L.; Sakai, R.; Paulusse, J. M. J.; Damiron, D.; Drockenmuller, E.; Messmore, B. W.; Hawker, C. J. *Macromolecules* **2008**, *41*, 7063–7070.

(49) Killops, K. L.; Campos, L. M.; Hawker, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 5062–5064.

(50) Uygun, M.; Tasdelen, M. A.; Yagci, Y. *Macromol. Chem. Phys.* **2010**, *211*, 103–110.

(51) Sumerlin, B. S.; Vogt, A. P. *Macromolecules* **2010**, *43*, 1–13.

(52) Tasdelen, M. A.; Kumbaraci, V.; Talinli, N.; Yagci, Y. *Polymer* **2006**, *47*, 7611–7614.

(53) Kumbaraci, V.; Talinli, N.; Yagci, Y. *Macromol. Rapid Commun.* **2007**, *28*, 72–77.

(54) Tasdelen, M. A.; Kumbaraci, V.; Talinli, N.; Yagci, Y. *Macromolecules* **2007**, *40*, 4406–4408.

(55) Davis, M. J.; Doherty, J.; Godfrey, A. A.; Green, P. N.; Young, J. R. A.; Parrish, M. A. *J. Oil Colour Chem. Assoc.* **1978**, *61*, 256–263.

(56) Tasdelen, M. A.; Moszner, N.; Yagci, Y. *Polym. Bull.* **2009**, *63*, 173–183.

(57) Tasdelen, M. A.; Demirel, A. L.; Yagci, Y. *Eur. Polym. J.* **2007**, *43*, 4423–4430.

(58) Karasu, F.; Arsu, N.; Yagci, Y. *J. Appl. Polym. Sci.* **2007**, *103*, 3766–3770.

(59) Cokbaglan, L.; Arsu, N.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2003**, *36*, 2649–2653.

(60) Keskin, S.; Jockusch, S.; Turro, N. J.; Arsu, N. *Macromolecules* **2008**, *41*, 4631–4634.

(61) Aydin, M.; Arsu, N.; Yagci, Y. *Macromol. Rapid Commun.* **2003**, *24*, 718–723.

(62) Aydin, M.; Arsu, N.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2005**, *38*, 4133–4138.

(63) Karasu, F.; Arsu, N.; Jockusch, S.; Turro, N. J. *Macromolecules* **2009**, *42*, 7318–7323.

(64) Balta, D. K.; Arsu, N.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2007**, *40*, 4138–4141.

(65) Jiang, X. S.; Yin, J. *Macromolecules* **2004**, *37*, 7850–7853.

(66) Jiang, X. S.; Yin, H. *Polymer* **2004**, *45*, 5057–5063.

(67) Jiang, X. S.; Yin, J. *Macromol. Rapid Commun.* **2004**, *25*, 748–752.

(68) Jiang, X. S.; Xu, H. J.; Yin, H. *Polymer* **2004**, *45*, 133–140.

(69) Jiang, X. S.; Yin, J. *J. Appl. Polym. Sci.* **2004**, *94*, 2395–2400.

(70) Jiang, X. S.; Luo, X. W.; Yin, J. *J. Photochem. Photobiol., A* **2005**, *174*, 165–170.

(71) Jiang, X. S.; Wang, W. F.; Xu, H. J.; Yin, J. *J. Photochem. Photobiol., A* **2006**, *181*, 233–237.

(72) Jiang, X. S.; Yin, J. *Macromol. Chem. Phys.* **2008**, *209*, 1593–1600.

(73) Jiang, X. S.; Luo, J.; Yin, J. *Polymer* **2009**, *50*, 37–41.

(74) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.

(75) Temel, G.; Aydogan, B.; Arsu, N.; Yagci, Y. *Macromolecules* **2009**, *42*, 6098–6106.

(76) Gacal, B.; Akat, H.; Balta, D. K.; Arsu, N.; Yagci, Y. *Macromolecules* **2008**, *41*, 2401–2405.

(77) Jakubiak, J.; Rabek, J. F. *Polimery* **1999**, *44*, 447–461.

(78) Allen, N. S. *J. Photochem. Photobiol., A* **1996**, *100*, 101–107.

(79) Valdesaguilera, O.; Pathak, C. P.; Shi, J.; Watson, D.; Neckers, D. C. *Macromolecules* **1992**, *25*, 541–547.

(80) Moszner, N.; Salz, U. *Prog. Polym. Sci.* **2001**, *26*, 535–576.

(81) Moszner, N.; Salz, U.; Zimmermann, J. *Dent. Mater.* **2005**, *21*, 895–910.

(82) Moszner, N.; Salz, U. *Macromol. Mater. Eng.* **2007**, *292*, 245–271.

(83) Moon, J. H.; Ford, J.; Yang, S. *Polym. Adv. Technol.* **2006**, *17*, 83–93.

(84) Hiller, J.; Mendelsohn, J. D.; Rubner, M. F. *Nat. Mater.* **2002**, *1*, 59–63.

(85) Fouassier, J. P.; Morlet-Savary, F. *Opt. Eng.* **1996**, *35*, 304–312.

(86) Fouassier, J. P. *Surf. Coat. Int.* **1994**, *77*, 252–258.

(87) Degirmenci, M.; Onen, A.; Yagci, Y.; Pappas, S. P. *Polym. Bull.* **2001**, *46*, 443–449.

(88) Davidenko, N.; Garcia, O.; Sastre, R. *J. Biomater. Sci., Polym. Ed.* **2003**, *14*, 733–746.

(89) Jakubiak, J.; Allonas, X.; Fouassier, J. P.; Sionkowska, A.; Andrzejewska, E.; Linden, L. A.; Rabek, J. F. *Polymer* **2003**, *44*, 5219–5226.

(90) Moszner, N.; Fischer, U. K.; Ganster, B.; Liska, R.; Rheinberger, V. *Dent. Mater.* **2008**, *24*, 901–907.

(91) Ganster, B.; Fischer, U. K.; Moszner, N.; Liska, R. *Macromolecules* **2008**, *41*, 2394–2400.

(92) Timpe, H. J.; Neuenfeld, S. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2329–2336.

(93) Jockusch, S.; Timpe, H. J.; Schnabel, W.; Turro, N. J. *J. Phys. Chem. A* **1997**, *101*, 440–445.

(94) Oster, G. *Nature* **1954**, *173*, 300–301.

(95) Koizumi, M.; Watanabe, A.; Kuroda, Z. *Nature* **1955**, *175*, 770–771.

(96) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095–5099.

(97) Decker, C. *Makromol. Chem.* **1979**, *180*, 2027–2030.

(98) Wight, F. R. *J. Polym. Sci., Part C: Polym. Lett.* **1978**, *16*, 121–127.

(99) Biernat, M.; Rokicki, G. *Polimery* **2005**, *50*, 633–645.

(100) O'Brien, A. K.; Bowman, C. N. *Macromolecules* **2006**, *39*, 2501–2506.

(101) Lee, T. Y.; Guymon, C. A.; Jonsson, E. S.; Hoyle, C. E. *Polymer* **2004**, *45*, 6155–6162.

(102) Decker, C.; Jenkins, A. D. *Macromolecules* **1985**, *18*, 1241–1244.

(103) Shawkat, E. S.; Shortall, A. C.; Addison, O.; Palin, W. M. *Dent. Mater.* **2009**, *25*, 1338–1346.

(104) Studer, K.; Decker, C.; Beck, E.; Schwalm, R. *Prog. Org. Coat.* **2003**, *48*, 92–100.

(105) Bartholomew, R. F.; Davidson, R. S. *J. Chem. Soc. C* **1971**, 2342–2346.

(106) Bartholomew, R. F.; Davidson, R. S. *J. Chem. Soc. C* **1971**, 2347–2351.

(107) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1679–1682.

(108) Andrzejewska, E. *Prog. Polym. Sci.* **2001**, *26*, 605–665.

(109) Guttenplan, J. B.; Cohen, S. G. *J. Org. Chem.* **1973**, *38*, 2001–2007.

(110) Miller, C. W.; Hoyle, C. E.; Jonsson, S.; Nason, C.; Lee, T. Y.; Kuang, W. F.; Viswanathan, K. N-vinylamides and reduction of oxygen inhibition in photopolymerization of simple acrylate formulations. *ACS Symp. Ser.* **2003**, *847*, 2–14.

(111) El-Roz, M.; Lalevee, J.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2009**, *42*, 8725–8732.

(112) Kminek, I.; Yagci, Y.; Schnabel, W. *Polym. Bull.* **1992**, *29*, 277–282.

(113) Peinado, C.; Alonso, A.; Catalina, F.; Schnabel, W. *J. Photochem. Photobiol., A* **2001**, *141*, 85–91.

(114) Chen, H. B.; Chang, T. C.; Chiu, Y. S.; Ho, S. Y. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 679–685.

(115) Peinado, C.; Alonso, A.; Catalina, F.; Schnabel, W. *Macromol. Chem. Phys.* **2000**, *201*, 1156–1160.

(116) Lalevee, J.; Allonas, X.; Fouassier, J. P. *J. Org. Chem.* **2007**, *72*, 6434–6439.

(117) Lalevee, J.; Dirani, A.; El-Roz, M.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2008**, *41*, 2003–2010.

(118) Lalevee, J.; El-Roz, M.; Allonas, X.; Fouassier, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2008–2014.

(119) Lalevee, J.; El-Roz, M.; Morlet-Savary, F.; Graff, B.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2007**, *40*, 8527–8530.

(120) El-Roz, M.; Lalevee, J.; Morlet-Savary, F.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2009**, *42*, 4464–4469.

(121) Yagci, Y. *Macromol. Symp.* **2006**, *240*, 93–101.

(122) Cho, J. D.; Hong, J. W. *J. Appl. Polym. Sci.* **2005**, *97*, 1345–1351.

(123) Sangermano, M.; Malucelli, G.; Bongiovanni, R.; Priola, A.; Annby, U.; Rehnberg, N. *Eur. Polym. J.* **2002**, *38*, 655–659.

(124) Yagci, Y.; Schnabel, W. *Macromol. Symp.* **1988**, *13–4*, 161–174.

(125) Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307–1315.

(126) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Part A: Polym. Chem.* **1978**, *16*, 2441–2451.

(127) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Part A: Polym. Chem.* **1979**, *17*, 977–999.

(128) Yagci, Y.; Kornowski, A.; Schnabel, W. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1987–1991.

(129) Denizligil, S.; Yagci, Y.; McArdle, C. *Polymer* **1995**, *36*, 3093–3098.

(130) Denizligil, S.; Resul, R.; Yagci, Y.; McArdle, C.; Fouassier, J. P. *Macromol. Chem. Phys.* **1996**, *197*, 1233–1240.

(131) Kasapoglu, F.; Onen, A.; Bicak, N.; Yagci, Y. *Polymer* **2002**, *43*, 2575–2579.

(132) Crivello, J. V.; Kong, S. Q. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1433–1442.

(133) Crivello, J. V.; Kong, S. Q. *Macromolecules* **2000**, *33*, 825–832.

(134) Gomurashvili, Z.; Crivello, J. V. *J. Polym. Sci., Polym. Chem.* **2001**, *39*, 1187–1197.

(135) Yagci, Y.; Endo, T. *Adv. Polym. Sci.* **1997**, *127*, 59–86.

(136) Yagci, Y.; Lukac, I.; Schnabel, W. *Polymer* **1993**, *34*, 1130–1133.

(137) Kasapoglu, F.; Yagci, Y. *Macromol. Rapid Commun.* **2002**, *23*, 567–570.

(138) Crivello, J. V.; Sangermano, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 343–356.

(139) Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4241–4254.

(140) Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 1–48.

(141) Fouassier, J. P.; Burr, D.; Crivello, J. V. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 677–701.

(142) Takata, T.; Takuma, K.; Endo, T. *Macromol. Rapid Commun.* **1993**, *14*, 203–206.

(143) Yonet, N.; Bicak, N.; Yagci, Y. *Macromolecules* **2006**, *39*, 2736–2738.

(144) Yonet, N.; Bicak, N.; Yurtsever, M.; Yagci, Y. *Polym. Int.* **2007**, *56*, 525–531.

(145) Durmaz, Y. Y.; Zaim, O.; Yagci, Y. *Macromol. Rapid Commun.* **2008**, *29*, 892–896.

(146) Yagci, Y.; Ledwith, A. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 1911–1918.

(147) Abdulrasoul, F. A. M.; Ledwith, A.; Yagci, Y. *Polymer* **1978**, *19*, 1219–1222.

(148) Yagci, Y.; Schnabel, W. *Macromol. Symp.* **1992**, *60*, 133–143.

(149) Crivello, J. V.; Bulut, U. *J. Polym. Sci., Polym. Chem.* **2005**, *43*, 5217–5231.

(150) Dossow, D.; Zhu, Q. Q.; Hizal, G.; Yagci, Y.; Schnabel, W. *Polymer* **1996**, *37*, 2821–2826.

(151) Crivello, J. V.; Lee, J. L. *Macromolecules* **1981**, *14*, 1141–1147.

(152) Chen, Y. H.; Yamamura, T.; Igarashi, K. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 90–100.

(153) Nelson, E. W.; Carter, T. P.; Scranton, A. B. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 247–256.

(154) Nelson, E. W.; Carter, T. P.; Scranton, A. B. *Macromolecules* **1994**, *27*, 1013–1019.

(155) Rodrigues, M. R.; Neumann, M. G. *Macromol. Chem. Phys.* **2001**, *202*, 2776–2782.

(156) Yagci, Y.; Schnabel, W.; Wilpert, A.; Bendig, J. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 287–291.

(157) Crivello, J. V.; Bulut, U. *Macromol. Symp.* **2006**, *240*, 1–11.

(158) Hizal, G.; Yagci, Y.; Schnabel, W. *Polymer* **1994**, *35*, 2428–2431.

(159) Hizal, G.; Emiroglu, S. E.; Yagci, Y. *Polym. Int.* **1998**, *47*, 391–392.

(160) Yagci, Y.; Borbely, J.; Schnabel, W. *Eur. Polym. J.* **1989**, *25*, 129–131.

(161) Hepuzer, Y.; Yagci, Y.; Biedron, T.; Kubisa, P. *Angew. Makromol. Chem.* **1996**, *237*, 163–171.

(162) Reetz, I.; Bacak, V.; Yagci, Y. *Macromol. Chem. Phys.* **1997**, *198*, 19–28.

(163) Atmaca, L.; Kayihan, I.; Yagci, Y. *Polymer* **2000**, *41*, 6035–6041.

(164) Dursun, C.; Degirmenci, M.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Polymer* **2003**, *44*, 7389–7396.

(165) Yagci, Y.; Degirmenci, M. Photoinduced free radical promoted cationic block copolymerization by using macrophotoinitiators prepared by ATRP and ring-opening polymerization methods. *ACS Symp. Ser.* **2003**, *854*, 383–393.

(166) Yagci, Y.; Kminek, I.; Schnabel, W. *Eur. Polym. J.* **1992**, *28*, 387–390.

(167) Yucesan, D.; Hostoygar, H.; Denizligil, S.; Yagci, Y. *Angew. Makromol. Chem.* **1994**, *221*, 207–216.

(168) Yagci, Y.; Onen, A.; Schnabel, W. *Macromolecules* **1991**, *24*, 4620–4623.

(169) Bottcher, A.; Hasebe, K.; Hizal, G.; Yagci, Y.; Stellberg, P.; Schnabel, W. *Polymer* **1991**, *32*, 2289–2293.

(170) Tasdelen, M. A.; Degirmenci, M.; Yagci, Y.; Nuyken, O. *Polym. Bull.* **2003**, *50*, 131–138.

(171) Yagci, Y. *Macromol. Symp.* **2000**, *161*, 19–35.

(172) Moszner, N.; Zeuner, F.; Lamparth, I.; Fischer, U. K. *Macromol. Mater. Eng.* **2009**, *294*, 877–886.

(173) Durmaz, Y. Y.; Kukut, M.; Moszner, N.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4793–4799.
(174) Durmaz, Y. Y.; Moszner, N.; Yagci, Y. *Macromolecules* **2008**, *41*, 6714–6718.
(175) Durmaz, Y. Y.; Kukut, M.; Moszner, N.; Yagci, Y. *Macromolecules* **2009**, *42*, 2899–2902.
(176) Lalevee, J.; Dirani, A.; El-Roz, M.; Allonas, X.; Fouassier, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3042–3047.
(177) Lalevee, J.; Blanchard, N.; El-Roz, M.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2008**, *41*, 4180–4186.
(178) Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 866–875.
(179) Molleo, M.; Crivello, J. V. *Macromolecules* **2009**, *42*, 3982–3991.
(180) Kahveci, M. U.; Tasdelen, M. A.; Yagci, Y. *Macromol. Rapid Commun.* **2008**, *29*, 202–206.
(181) Kahveci, M. U.; Tasdelen, M. A.; Yagci, Y. *Polymer* **2007**, *48*, 2199–2202.
(182) Kahveci, M. U.; Uygun, M.; Tasdelen, M. A.; Schnabel, W.; Cook, W. D.; Yagci, Y. *Macromolecules* **2009**, *42*, 4443–4448.
(183) Johnen, N.; Kobayashi, S.; Yagci, Y.; Schnabel, W. *Polym. Bull.* **1993**, *30*, 279–284.
(184) Tasdelen, M. A.; Kumbaraci, V.; Jockusch, S.; Turro, N. J.; Talinli, N.; Yagci, Y. *Macromolecules* **2008**, *41*, 295–297.
(185) Crivello, J. V. B. U. *Macromol. Symp.* **2006**, *240*, 1–11.
(186) Aydogan, B.; Gundogan, A. S.; Ozturk, T.; Yagci, Y. *Macromolecules* **2008**, *41*, 3468–3471.
(187) Aydogan, B.; Gunbas, G. E.; Durmus, A.; Toppare, L.; Yagci, Y. *Macromolecules* **2010**, *43*, 101–106.
(188) Fukuchi, Y.; Takahashi, T.; Noguchi, H.; Saburi, M.; Uchida, Y. *Macromolecules* **1987**, *20*, 2316–2317.
(189) Johnston, D. S.; Pepper, D. C. *Macromol. Chem. Phys.* **1981**, *182*, 421–435.
(190) Palmer, B. J.; Kutal, C.; Billing, R.; Hennig, H. *Macromolecules* **1995**, *28*, 1328–1329.
(191) Arsu, N.; Onen, A.; Yagci, Y. *Macromolecules* **1996**, *29*, 8973–8974.
(192) Onen, A.; Arsu, N.; Yagci, Y. *Angew. Makromol. Chem.* **1999**, *264*, 56–59.
(193) Kasapoglu, F.; Aydin, M.; Arsu, N.; Yagci, Y. *J. Photochem. Photobiol., A* **2003**, *159*, 151–159.
(194) Tanabe, M.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 11434–11435.
(195) Kumbaraci, V.; Talinli, N.; Yagci, Y. *Macromolecules* **2006**, *39*, 6031–6035.
(196) Yagci, Y.; Yilmaz, F.; Kiralp, S.; Toppare, L. *Macromol. Chem. Phys.* **2005**, *206*, 1178–1182.
(197) Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2007**, *40*, 4481–4485.
(198) Aydogan, B.; Gundogan, A. S.; Ozturk, T.; Yagci, Y. *Chem. Commun.* **2009**, 6300–6302.
(199) Kim, J. B.; Jang, J. H.; Ko, J. S.; Choi, J. H.; Lee, K. K. *Macromol. Rapid Commun.* **2003**, *24*, 879–882.
(200) Pfeiffer, F.; Felix, N. M.; Neuber, C.; Ober, C. K.; Schmidt, H. W. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1257–1262.
(201) Yang, J. W.; Zeng, Z. H.; Chen, Y. L. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2563–2570.
(202) Li, S. J.; Wu, F. P.; Li, M. Z.; Wang, E. J. *Polymer* **2005**, *46*, 11934–11939.
(203) Alupei, I. C.; Alupei, V.; Ritter, H. *Macromol. Rapid Commun.* **2002**, *23*, 55–58.
(204) Lougnot, D. J.; Turck, C.; Fouassier, J. P. *Macromolecules* **1989**, *22*, 108–116.
(205) Liska, R.; Knaus, S.; Gruber, H.; Wendrinsky, J. *Surf. Coat. Int., Part B-C* **2000**, *83*, 297–303.
(206) Kojima, K.; Ito, M.; Morishita, H.; Hayashi, N. *Chem. Mater.* **1998**, *10*, 3429–3433.
(207) Visconti, M.; Cattaneo, M. *Prog. Org. Coat.* **2000**, *40*, 243–251.
(208) Tasdelen, M. A.; Karagoz, B.; Bicak, N.; Yagci, Y. *Polym. Bull.* **2008**, *59*, 759–766.
(209) Ivanchev, S. S.; Pavljuchenko, V. N.; Byrdina, N. A. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 47–62.
(210) Akat, H.; Gacal, B.; Balta, D. K.; Arsu, N.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2109–2114.
(211) Harada, A. *Acta Polym.* **1998**, *49*, 3–17.
(212) Wenz, G. *Angew. Chem., Int. Ed.* **1994**, *33*, 803–822.
(213) Jeromin, J.; Ritter, H. *Macromolecules* **1999**, *32*, 5236–5239.
(214) Storsberg, J.; Ritter, H. *Macromol. Rapid Commun.* **2000**, *21*, 236–241.

(215) Balta, D. K.; Bagdatli, E.; Arsu, N.; Ocal, N.; Yagci, Y. *J. Photochem. Photobiol., A* **2008**, *196*, 33–37.
(216) Li, S. J.; Li, L. D.; Wu, F. P.; Wang, E. J. *J. Photochem. Photobiol., A* **2009**, *203*, 211–215.
(217) Weiner, A. A.; Bock, E. A.; Gipson, M. E.; Shastri, V. P. *Biomaterials* **2008**, *29*, 2400–2407.
(218) Li, S. J.; Wu, F. P.; Wang, E. J. *Polymer* **2009**, *50*, 3932–3937.
(219) Wei, H. L.; He, J. Y.; Sun, L. G.; Zhu, K. Q.; Feng, Z. G. *Eur. Polym. J.* **2005**, *41*, 948–957.
(220) Lee, N. Y.; Jung, Y. K.; Park, H. G. *Biochem. Eng. J.* **2006**, *29*, 103–108.
(221) Hiemstra, C.; Zhou, W.; Zhong, Z. Y.; Wouters, M.; Feijen, J. *J. Am. Chem. Soc.* **2007**, *129*, 9918–9926.
(222) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3827–3832.
(223) Kahveci, M. U.; Tasdelen, M. A.; Cook, W. D.; Yagci, Y. *Macromol. Chem. Phys.* **2008**, *209*, 1881–1886.
(224) Kostjuk, S. V.; Radchenko, A. V.; Ganachaud, F. *Macromolecules* **2007**, *40*, 482–490.
(225) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 4660–4666.
(226) Nuyken, O.; Braun, H.; Crivello, J. Poly(vinyl ether)s, Poly(vinyl ester)s, and Poly(vinyl halogenide)s Swift. In *Handbook of Polymer Synthesis*; Kricheldorf, H. R., Nuyken, O., Eds.; Plastic Engineering: New York, 2005; Vol. *70*, pp 151–240.
(227) Duan, G. L.; Zhu, Y. G.; Tong, Y. P.; Cai, C.; Kneer, R. *Plant Physiol.* **2005**, *138*, 461–469.
(228) Gebel, T. *Chem. Biol. Interact.* **1997**, *107*, 131–144.
(229) Kim, M. S.; Sanda, F.; Endo, T. *Polymer* **2001**, *42*, 9367–9370.
(230) Szwarc, M. *Nature* **1956**, *178*, 1168–1169.
(231) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J. *Prog. Polym. Sci.* **2006**, *31*, 1068–1132.
(232) Tasdelen, M. A.; Durmaz, Y. Y.; Karagoz, B.; Bicak, N.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3387–3395.
(233) Otsu, T.; Yoshida, M. *Macromol. Rapid Commun.* **1982**, *3*, 127–132.
(234) Otsu, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2121–2136.
(235) Lambrinos, P.; Tardi, M.; Polton, A.; Sigwalt, P. *Eur. Polym. J.* **1990**, *26*, 1125–1135.
(236) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987–2988.
(237) Moad, G.; Rizzardo, E. *Macromolecules* **1995**, *28*, 8722–8728.
(238) Scaiano, J. C.; Connolly, T. J.; Mohtat, N.; Pliva, C. N. *Can. J. Chem.* **1997**, *75*, 92–97.
(239) Yoshida, E. *Colloid Polym. Sci.* **2008**, *286*, 1663–1666.
(240) Yoshida, E. *Colloid Polym. Sci.* **2009**, *287*, 767–772.
(241) Yoshida, E. *Colloid Polym. Sci.* **2009**, *287*, 1417–1424.
(242) Yoshida, E. *Colloid Polym. Sci.* **2010**, *288*, 73–78.
(243) Yoshida, E. *Colloid Polym. Sci.* **2010**, *288*, 7–13.
(244) Goto, A.; Scaiano, J. C.; Maretti, L. *Photochem. Photobiol. Sci.* **2007**, *6*, 833–835.
(245) Hu, S.; Malpert, J. H.; Yang, X.; Neckers, D. C. *Polymer* **2000**, *41*, 445–452.
(246) Guillaneuf, Y.; Bertin, D.; Gigmes, D.; Versace, D. L.; Lalevee, J.; Fouassier, J. P. *Macromolecules* **2010**, *43*, 2204–2212.
(247) Rempp, P.; Merrill, E. W. *Polymer Synthesis*; Hüthig und Wepf: Basel, 1991; p 157.
(248) Ledwith, A. *Makromol. Chem.* **1979**, *3*, 348–358.
(249) Kwon, S.; Chun, H.; Mah, S. *Fibers Polym.* **2004**, *5*, 253–258.
(250) Kwon, S.; Lee, Y.; Jeon, H.; Han, K.; Mah, S. *J. Appl. Polym. Sci.* **2006**, *101*, 3581–3586.
(251) Tanabe, M.; Vandermeulen, G. W. M.; Chan, W. Y.; Cyr, P. W.; Vanderark, L.; Rider, D. A.; Manners, I. *Nature Mater.* **2006**, *5*, 467–470.
(252) Khudyakov, I. V.; Purvis, M. B.; Turro, N. J. *ACS Symp. Ser.* **2003**, *847*, 113–126.
(253) Peiffer, R. W. *ACS Symp. Ser.* **1997**, *673*, 1–14.
(254) Hizal, G.; Yagci, Y.; Schnabel, W. *Polymer* **1994**, *35*, 4443–4448.
(255) Yagci, Y.; Schnabel, W. *Prog. Polym. Sci.* **1990**, *15*, 551–601.
(256) Dyer, D. J. *Adv. Polym. Sci.* **2006**, *197*, 47–65.
(257) Yagci, Y.; Tasdelen, M. A. *Prog. Polym. Sci.* **2006**, *31*, 1133–1170.
(258) Degirmenci, M.; Hizal, G.; Yagci, Y. *Macromolecules* **2002**, *35*, 8265–8270.
(259) Muftuoglu, A. E.; Tasdelen, M. A.; Yagci, Y. *Photoinduced Synthesis of Block Copolymers in Photochemistry and UV Curing: New Trends*; Fouassier, J. P., Ed.; Research Signpost: Trivandrum, 2006; Vol. *29*.

(260) Dyer, D. J.; Feng, J. X.; Schmidt, R.; Wong, V. N.; Zhao, T. F.; Yagci, Y. *Macromolecules* **2004**, *37*, 7072–7074.

(261) Tasdelen, M. A.; Kreutzer, J.; Yagci, Y. *Macromol. Chem. Phys.* **2010**, *211*, 279–285.

(262) Alexandre, M.; Dubois, P. *Mater. Sci. Eng., R* **2000**, *28*, 1–63.

(263) Okamoto, M. *Mater. Sci. Technol.* **2006**, *22*, 756–779.

(264) Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539–1641.

(265) Akat, H.; Tasdelen, M. A.; Du Prez, F.; Yagci, Y. *Eur. Polym. J.* **2008**, *44*, 1949–1954.

(266) Yagci, Y., *J. Coat. Technol. Res.* **2010**, DOI: 10.1007/s11998-009-9219-8.

(267) Nese, A.; Sen, S.; Tasdelen, M. A.; Nugay, N.; Yagci, Y. *Macromol. Chem. Phys.* **2006**, *207*, 820–826.

(268) Oral, A.; Tasdelen, M. A.; Demirel, A. L.; Yagci, Y. *Polymer* **2009**, *50*, 3905–3910.

(269) Oral, A.; Tasdelen, M. A.; Demirel, A. L.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5328–5335.

(270) Watson, K. J.; Zhu, J.; Nguyen, S. T.; Mirkin, C. A. *Pure Appl. Chem.* **2000**, *72*, 67–72.

(271) Park, J. H.; Lim, Y. T.; Park, O. O.; Kim, J. K.; Yu, J. W.; Kim, Y. C. *Chem. Mater.* **2004**, *16*, 688–692.

(272) Shenhar, R.; Norsten, T. B.; Rotello, V. M. *Adv. Mater.* **2005**, *17*, 657–669.

(273) de Loos, F.; Reynhout, I. C.; Cornelissen, J.; Rowan, A. E.; Nolte, R. J. M. *Chem. Commun.* **2005**, 60–62.

(274) Uygun, M.; Kahveci, M. U.; Odaci, D.; Timur, S.; Yagci, Y. *Macromol. Chem. Phys.* **2009**, *210*, 1867–1875.

(275) Yagci, Y.; Sangermano, M.; Rizza, G. *Polymer* **2008**, *49*, 5195–5198.

(276) Yagci, Y.; Sangermano, M.; Rizza, G. *Macromolecules* **2008**, *41*, 7268–7270.

(277) Yagci, Y.; Sangermano, M.; Rizza, G. *Chem. Commun.* **2008**, 2771–2773.

(278) Sangermano, M.; Yagci, Y.; Rizza, G. *Macromolecules* **2007**, *40*, 8827–8829.

(279) Balan, L.; Jin, M.; Malval, J. P. *Macromolecules* **2008**, *41*, 9359–9365.

(280) Anyaogu, K. C.; Cai, X. C.; Neckers, D. C. *Macromolecules* **2008**, *41*, 9000–9003.

(281) Merhari, L. *Hybrid Nanocomposites for Nanotechnology: Electronic, Optical, Magnetic and Biomedical Applications*; Springer: New York, 2009.

(282) Soppera, O.; Croutxe-Barghorn, C.; Lougnot, D. J. *New J. Chem.* **2001**, *25*, 1006–1014.

(283) Chemtob, A.; Versace, D. L.; Belon, C.; Croutxe-Barghorn, C.; Rigolet, S. *Macromolecules* **2008**, *41*, 7390–7398.

(284) Ito, H. *Adv. Polym. Sci.* **2005**, *172*, 37–245.

(285) Thompson, S. E.; Parthasarathy, S. *Mater. Today* **2006**, *9*, 20–25.

(286) Kawata, S.; Sun, H. B.; Tanaka, T.; Takada, K. *Nature* **2001**, *412*, 697–698.

(287) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I. Y. S.; McCord-Maughon, D.; Qin, J. Q.; Rockel, H.; Rumi, M.; Wu, X. L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51–54.

(288) Sun, H. B.; Kawakami, T.; Xu, Y.; Ye, J. Y.; Matuso, S.; Misawa, H.; Miwa, M.; Kaneko, R. *Opt. Lett.* **2000**, *25*, 1110–1112.

(289) Tanaka, T.; Sun, H. B.; Kawata, S. *Appl. Phys. Lett.* **2002**, *80*, 312–314.

(290) Haske, W.; Chen, V. W.; Hales, J. M.; Dong, W. T.; Barlow, S.; Marder, S. R.; Perry, J. W. *Opt. Express* **2007**, *15*, 3426–3436.

(291) Scott, T. F.; Kowalski, B. A.; Sullivan, A. C.; Bowman, C. N.; McLeod, R. R. *Science* **2009**, *324*, 913–917.

(292) Li, L. J.; Gattass, R. R.; Gershgoren, E.; Hwang, H.; Fourkas, J. T. *Science* **2009**, *324*, 910–913.

(293) Wnek, G. E.; Bowlin, G. L. *Encyclopedia of Biomaterials and Biomedical Engineering*; Informa Healthcare: New York, 2008.