Recent Advances in Photo-Induced Free-Radical Polymerization

Abstract
The interest in the light-curable systems is continuously growing and the most widely applied photopolymerization reactions are those occurring according to the free-radical mechanism. This mini-review describes some representative trends in investigations of the photo-polymerizing systems.

Keywords: Photo-induced polymerization; Phase separation; Controlled/living polymerization; Thiol-ene; Hybrid systems; Ionogels; Polymer gels; Nanocomposites; Optoelectronics; Photoinitiators

Introduction
Free radical photopolymerization dominates most of the industrial applications of photocuring. The most popular are protective coatings, dental fillings, adhesives, inks, lithography (printing plates), stereolithography but also advanced high-technology purposes (micro and optoelectronics, holographic data storage, etc.) [1]. Currently, radical photopolymerization is also applied to prepare new advanced materials, e.g. nanocomposites, polymer gels, ionogels, polymers with controlled structure, etc. Compared to cationic photopolymerization the free radical initiation is more advanced mainly due to the availability of a wider range of monomers and photoinitiators. This mini-review describes some representative trends in investigations of the light-induced polymerization.

Discussion
The light-induced process offers special advantages: short polymerization time (seconds to minutes), low reaction temperature (room or ambient), full control of the process (the polymerization starts when the light is switched on and stops when the light is turned off) and spatial resolution. The general kinetics of the photo-induced radical polymerization have been described earlier ([2] and references cited herein). In this mini-review only some representative research trends in investigation of the photo-induced polymerization will be discussed.

New photoinitiating systems (PIS)
The development of new free radical initiators or initiating systems working upon low light intensity or soft irradiation conditions is the popular trend in this area of the research. One of the recent achievements is the introduction of the silyl chemistry into PISs. Generated silyl radicals consume oxygen reducing its inhibitory effect and scavenge peroxyls regenerating new silyls [3]. The germyl [4] and boryl [5] chemistries can play a similar role. Another interesting finding is the application of Perovskites as new radical photoinitiators (free radical generators in combination with iodonium salt) [6].

Polymerization-induced phase separation
Phase separation induced by a chemical reaction is widely applied to materials processing where the molecular architecture of interpenetrating polymer networks (IPNs) is a typical example. This can be realized by direct radical photo-initiated copolymerization of marginally compatible monomers with a progression into a thermodynamically unstable mixture of the monomers and their copolymer [7]. Polymerization induced phase separation can also be realized for systems monomer/dissolved polymer [8,9]. In this way photopolymerization kinetics may provide a convenient approach to control heterogeneity. The polymerization of such systems shows a multistage kinetics, which results from the appearance of two compositionally different phases, polymerizing more or less independently [7].

Controlled/living polymerization
Controlled/living radical polymerization (CRP) has been successfully exploited for preparing polymers with predetermined molecular weights and narrow molecular weight distribution, low polydispersities and precisely controlled architectures [10]. The key strategies for CRP are atom transfer radical polymerizations (ATRP), reversible addsion-fragmentation chain transfer polymerization (RAFT) and nitroxide-mediated polymerizations (NMP) as well as various variations thereof [10,11]. In all the CRP methods photochemical initiation can be applied. This type of initiation enables CRP to proceed under mild thermal conditions

Abbreviations: IPNs: Interpenetrating Polymer Networks; CRP: Controlled/Living Radical Polymerization; ATRP: Atom Transfer Radical Polymerizations; NMP: Nitroxide-Mediated Polymerizations; POSS: Polyhedral Oligomeric Silsesquioxanes;
ILs: Ionic Liquids

Ewa Andrzejewska* and Katarzyna Grajeck
Faculty of Chemical Technology, Poznan University of Technology, Poland

*Corresponding author: Ewa Andrzejewska, Institute of Chemical Technology and Engineering, Faculty of Chemical Technology, Poznan University of Technology, Berdychowo 4, 60-965 Poznan, Poland, Tel: +48 61 665 3637; Fax +48 61 665 3649; Email: ewa.andrzejewska@put.poznan.pl

Received: February 26, 2017 | Published: May 23, 2017

Abstract
The interest in the light-curable systems is continuously growing and the most widely applied photopolymerization reactions are those occurring according to the free-radical mechanism. This mini-review describes some representative trends in investigations of the photo-polymerizing systems.

Keywords: Photo-induced polymerization; Phase separation; Controlled/living polymerization; Thiol-ene; Hybrid systems; Ionogels; Polymer gels; Nanocomposites; Optoelectronics; Photoinitiators

Abbreviations: IPNs: Interpenetrating Polymer Networks; CRP: Controlled/Living Radical Polymerization; ATRP: Atom Transfer Radical Polymerizations; NMP: Nitroxide-Mediated Polymerizations; POSS: Polyhedral Oligomeric Silsesquioxanes; ILs: Ionic Liquids

Introduction
Free radical photopolymerization dominates most of the industrial applications of photocuring. The most popular are protective coatings, dental fillings, adhesives, inks, lithography (printing plates), stereolithography but also advanced high-technology purposes (micro and optoelectronics, holographic data storage, etc.) [1]. Currently, radical photopolymerization is also applied to prepare new advanced materials, e.g. nanocomposites, polymer gels, ionogels, polymers with controlled structure, etc. Compared to cationic photopolymerization the free radical initiation is more advanced mainly due to the availability of a wider range of monomers and photoinitiators. Typical chemistry utilized in free radical initiated UV-curable compositions include combinations of mono- and multi-functional (meth) acrylate monomers and (meth)acrylated oligomers, which react readily in the presence of radicals. This mini-review describes some representative trends in investigations of the light-induced polymerization.

Discussion
The light-induced process offers special advantages: short polymerization time (seconds to minutes), low reaction temperature (room or ambient), full control of the process (the polymerization starts when the light is switched on and stops when the light is turned off) and spatial resolution. The general kinetics of the photo-induced radical polymerization have been described earlier ([2] and references cited herein). In this mini-review only some representative research trends in investigation of the photo-induced polymerization will be discussed.

New photoinitiating systems (PIS)
The development of new free radical initiators or initiating systems working upon low light intensity or soft irradiation conditions is the popular trend in this area of the research. One of the recent achievements is the introduction of the silyl chemistry into PISs. Generated silyl radicals consume oxygen reducing its inhibitory effect and scavenge peroxyls regenerating new silyls [3]. The germyl [4] and boryl [5] chemistries can play a similar role. Another interesting finding is the application of Perovskites as new radical photoinitiators (free radical generators in combination with iodonium salt) [6].

Polymerization-induced phase separation
Phase separation induced by a chemical reaction is widely applied to materials processing where the molecular architecture of interpenetrating polymer networks (IPNs) is a typical example. This can be realized by direct radical photo-initiated copolymerization of marginally compatible monomers with a progression into a thermodynamically unstable mixture of the monomers and their copolymer [7]. Polymerization induced phase separation can also be realized for systems monomer/dissolved polymer [8,9]. In this way photopolymerization kinetics may provide a convenient approach to control heterogeneity. The polymerization of such systems shows a multistage kinetics, which results from the appearance of two compositionally different phases, polymerizing more or less independently [7].

Controlled/living polymerization
Controlled/living radical polymerization (CRP) has been successfully exploited for preparing polymers with predetermined molecular weights and narrow molecular weight distribution, low polydispersities and precisely controlled architectures [10]. The key strategies for CRP are atom transfer radical polymerizations (ATRP), reversible addsion-fragmentation chain transfer polymerization (RAFT) and nitroxide-mediated polymerizations (NMP) as well as various variations thereof [10,11]. In all the CRP methods photochemical initiation can be applied. This type of initiation enables CRP to proceed under mild thermal conditions...
by activating the dormant species at low temperature. Application of the UV light is not limited only to generation of initiating radical species but is used also for activation of catalysis, generation of controlling agents or increasing the polymer-end structure [12].

**Thiol-ene polymerization**

Thiol-ene photopolymerizations are reactions between multifunctional thiol and ene monomers; they occur rapidly with formation of low stress homogeneous polymer networks with narrow glass transitions and insensitivity to oxygen inhibition. In particular, thiol-ene photopolymers have gained increased attention in the design of functional materials for tissue engineering, nano-imprinting, shape memory or optical and microfluidic devices [13, 14]. The propagation mechanism of the thiol-ene photopolymerization is an alternation of addition and chain transfer reactions [15]. The most important factor governing the overall kinetics of thiol-ene polymerization is the ratio of the propagation rate constant (kp) to the chain-transfer rate constant, therefore, the reaction kinetics strongly depends on monomer structure [16, 17]. The thiol-ene reaction has recently attracted researchers due to the recognition of its “click” characteristics [13–15].

**Hybrid systems**

“Hybrid systems” in this review are considered as hybrid materials/hybrid polymers [18], including composites and nanocomposites. These materials can be readily obtained by photo-curing of monomers containing dispersed fillers and this technique is used for a long time in dental applications, protective coatings, etc. The most widely used fillers are aluminum oxide, layered silicates, calcium carbonate, silica and titanium dioxide, both modified and unmodified. Their influence on the photopolymerization kinetics can be very different; e.g. in the case of silica both increase, decrease, or no effect on the polymerization rate was observed [19, 20]. Recent works indicate that the kinetics depends to a high degree on the stability of polymerization rate was observed [19,20]. Recent works indicate that the kinetics depends to a high degree on the stability of polymerization kinetics of monomer/POSS mixtures due to crosslinking [28–30]. However, also such factors like possible aggregation of POSS molecules, possible phase separation and change in formulation viscosity after their addition should be taken into account.

**Ionogels**

In recent years ionic liquids (ILs) were widely studied as polymerization media in various types of polymerization processes [31]. When an IL remains entrapped in the polymer matrix, a gel material is formed, which has been termed ionogel [32]. Applications of ionogels include electrolytic membranes (with solid electrolytes), catalytic membranes, drug delivery systems and others [33, 34]. Most often the radical polymerization of (meth)acrylates in ILs gives increased polymerization rates and higher molecular weights and yields that are in conventional organic solvents or in bulk. Acceleration of the polymerization is associated with the increased propagation rate coefficients and reduced termination rate coefficients [34]. Somewhat different situation takes place in the thiol-ene photopolymerization, where in the case of a divinyl ether/dithiol system ILs accelerates the polymerization but the reaction is slower in ILs than in organic solvents [35].

A special case are IL monomers, in which the IL moiety and the polymerizable function are linked together; especially strong development in research is observed for new materials based on such monomers [34].

**Conclusion**

Photopolymerization is an important area of investigation due to its wide industrial applications and huge potential in simple and fast production of materials with particular properties. Many modern applications need materials with special morphology and composition (e.g. IPN, block or graft copolymers of various architecture, hybrid polymers, ionogels, etc.); such materials can be readily prepared using photopolymerization technique.

**References**

1. Yagi Y, Jockusch S, Turro NJ (2010) Photoinitiated Polymerization: Advances, Challenges, and Opportunities. Macromolecules 43(15): 6245–6260.
2. Andrzejewska E (2001) Photopolymerization kinetics of multifunctional monomers. Prog Polym Sci 26(4): 605–665.
3. Tehfe MA, Loundour F, Lalèvé J, Fouassier JP (2013) Photopolymerization Reactions: On the Way to a Green and Sustainable Chemistry. Appl Sci 3(2): 490–514.
4. Tehfe MA, Blanchard N, Fries C, Lalèvé J, Alkousa X et al. (2010) Bis (germyl) ketones: Toward a New Class of Type I Photoinitiating Systems Sensitive Above 500 nm? Macromol Rapid Comm 31(5): 473–478.
5. Teltéd S, Schweitzer S, Morlet-Savary F, Graff B, Tscharmb T, et al. (2013) Soft Photopolymerization Initiated by Dye-Sensitized Formation of NHC-Boryl Radicals under Visible Light. Macromolecules 46(1): 43–48.
6. Mokbel H, Dumur F, Raveau B, Morlet-Savary F, Simonnet-Jegat C, et
al. (2016) Perovskites as new radical photoinitiators for radical and
cationic polymerizations. Tetrahedron 72(48): 7686-7690

7. CS Pfeifer, ZR Sherton, CR Szczepanski, MD Barros, ND Wilson, et al. (2014) Tailoring heterogeneous polymer networks through
copolymerization-induced phase separation: influence of composition
and processing conditions on reaction kinetics and optical
properties. J Polym Sci Part A: Polym Chem 52(13): 1796-1806.

8. Szczepanski CR, Pfeifer CS, Stansbury IW (2012) A new approach to
network heterogeneity: Polimerization induced phase separation
in photo-initiated, free-radical methacrylic systems. Polymer
53(21): 4694-4701.

9. Marcinkowska A, Andrzejewska E (2014) Methacrylate-based
polymer blends containing oligomeric 1,2-polybutadienes. J Therm
Anal Calorim 115(2): 1719-1726.

10. Brauneker WA, Matyjaszewski K (2007) Controlled/living radical
polymerization: Features, developments, and perspectives. Prog
Polym Sci 32(1): 93-146.

11. Dadashi-Silab S, Tadelen MA, Yaghi Y (2014) Photoinitiated
atom transfer radical polymerization: Current status and future
perspectives. J Polym Sci Part A: Polym Chem 52(20): 2878-2888.

12. Yamago S, Nakamura Y (2013) Recent progress in the use of photo
irradiation in living radical polymerization. Polymer 54(3-5): 981-
994.

13. Lowe AB (2010) Thiol-ene "click" reactions and recent applications
in polymer and materials synthesis. Polym Chem 1(1): 17-36.

14. Lowe AB (2014) Thiol-ene "click" reactions and recent applications
in polymer and materials synthesis: a first update. Polym Chem
5(17): 4620-4670.

15. Hoyle CE, Bowman CN (2010) Thiol-Ene Click Chemistry. Angew
Angew Chem Int Ed Eng19(9): 1540-1573.

16. Reddy SK, Cramer NB, Bowman CN (2006) Thiol-Vinyl Mechanisms.
2. Kinetic Modeling of Ternary Thiol–Vinyl Photo polymerizations.
Macromolecules 39(10): 3681-3687.

17. Northrop BH, Coffey RN (2012) Thiol-Ene Click Chemistry: Computer
aided calculations and kinetic analysis of the influence of alkene
functionalities. J Am Chem Soc 134(33): 13804-13817.

18. Alemán J, Chadwick AV, He J, Hess M, Horie K, et al. (2007)
Definitions of terms relating to the structure and processing of
gels, networks, and inorganic-organic hybrid materials (IUPAC
Recommendations 2007). Pure Applied Chem 79(10): 1801-1829.

19. Sadej-Bajerlein M, Gojewski H, Andrzejewska E (2011) Monomer/
modified nanosilica systems: photo polymerization kinetics and
composite characterization. Polymer 52(7): 1495-1503.

20. Ziółkowska P, Andrzejewska E, Szybowicz M, Nowicka A, Sadej-
Bajerlein M, et al. (2014) Particle clustering in photocurable
nanocomposites: Dependence of curing kinetics and viscoelastic
properties. J Appl Polym Sci 131(4): 39895.