

# 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

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**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.).<sup>1</sup> Currently, radical photo polymerization 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 (<sup>2</sup>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 peroxy radicals regenerating new silyls.<sup>3</sup> The germyl<sup>4</sup> and boryl<sup>5</sup> 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).<sup>6</sup>

## 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.<sup>7</sup> Polymerization induced phase separation can also be realized for systems monomer/dissolved polymer.<sup>8,9</sup> 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.<sup>7</sup>

## 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.<sup>10</sup> The key strategies for CRP are atom transfer radical polymerizations (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT) and nitroxide-mediated polymerizations (NMP) as well as various variations thereof.<sup>10,11</sup> 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.<sup>12</sup>

## Thiol-ene polymerization

Thiol-ene photo polymerizations 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.<sup>13,14</sup> The propagation mechanism of the thiol-ene photopolymerization is an alternation of addition and chain transfer reactions.<sup>15</sup> The most important factor governing the overall kinetics of thiol-ene polymerization is the ratio of the propagation rate constant ( $k_p$ ) to the chain-transfer rate constant, therefore, the reaction kinetics strongly depends on monomer structure.<sup>16,17</sup> The thiol-ene reaction has recently attracted researchers due to the recognition of its “click” characteristics.<sup>13–15</sup>

### Hybrid systems

“Hybrid systems” in this review are considered as hybrid materials/hybrid polymers,<sup>18</sup> 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.<sup>19,20</sup> Recent works indicate that the kinetics depends to a high degree on the stability of the monomer/filler dispersion<sup>21,22</sup> or particle size.<sup>23</sup> A decreased photopolymerization rate of an acrylate monomer was observed in the presence of nano-TiO<sub>2</sub>, which was associated with the light absorption by this filler in the range of photoinitiator absorption.<sup>24</sup> Recently a lot of attention has been devoted to carbon nanotubes, due to improved mechanical properties of the derived nanocomposites and their electrical conductivity. Both the photopolymerization rate as well as the final conversion substantially decreased with the increase in this filler content, which was ascribed to reduced penetration of the light into the cured films.<sup>25,26</sup>

Free-radical photopolymerization was applied also for preparation of nanocomposites, hybrid materials and hybrid polymers containing polyhedral oligomeric silsesquioxanes (POSS).<sup>27</sup> The resulting materials are often referred to as organic-inorganic hybrid nanocomposites and “nano” refers to the nanoscale dimensions of the POSS core. Most often POSS compounds multi-functionalized with polymerizable groups (vinyl, acrylate) form crosslinked POSS cores and act as anchor points within a polymer matrix; their presence affects the polymerization kinetics of monomer/POSS mixtures due to crosslinking.<sup>28–30</sup> 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.<sup>31</sup> When an IL remains entrapped in the polymer matrix, a gel material is formed, which has been termed ionogel.<sup>32</sup> Applications of ionogels include electrolytic membranes (with solid electrolytes), catalytic membranes, drug delivery systems and others.<sup>33,34</sup> Most often the radical polymerization of (meth) acrylates in ILs gives increased polymerization rates and higher molecular weights and yields that that in conventional organic solvents or in bulk. Acceleration of the

polymerization is associated with the increased propagation rate coefficients and reduced termination rate coefficients.<sup>34</sup> 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.<sup>35</sup> 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.<sup>34</sup>

### 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 photo polymerization technique.

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### Conflict of interest

The author declares no conflict of interest.

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