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Photoinduced Cross-Linking Polymerization of Monofunctional Vinyl Monomer without Conventional Photoinitiator and Cross-Linker

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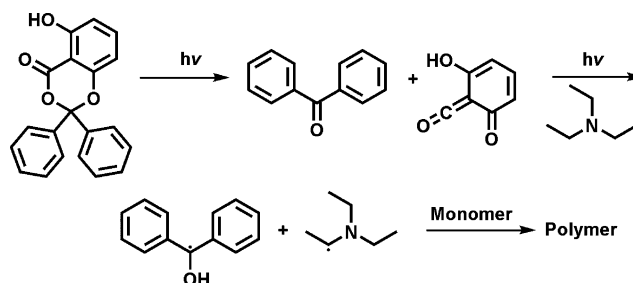
Received April 28, 2007

Revised Manuscript Received May 14, 2007

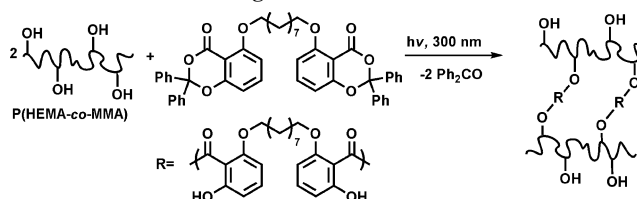
Introduction. The photoinitiated polymerization of acrylates and methacrylates is one of the most efficient and facile processes for the rapid production of polymeric cross-linked materials, especially materials with tailor-made properties and ambient temperature operations.^{1,2} Therefore, this technique is widely employed in coating industries in which a high demand is put on mechanical properties as well as on the optical properties of the materials. The strategies for photoinduced cross-linking can be broadly classified into two main approaches: (i) one-stage cross-linking of multifunctional monomers or copolymerization with difunctional monomers;^{3–5} (ii) two-stage cross-linking via prepolymers possessing photosensitive sites. The latter is less used due to the limited number of available photosensitive groups with high cross-linking efficiency. Considerable attention has been given to the polymers with cinnamate,^{6–9} chalcone,^{6,10} stilbene,^{11–13} maleimide, and anthracene¹⁴ pendant groups which undergo photoinduced cross-linking via cycloaddition reactions. Among the acrylic and methacrylic monomers, 2-hydroxyethyl methacrylate (HEMA) receives special interest due to its hydrophilic nature, which in the cross-linked form (hydrogel) provides the possibility to absorb a significant amount of water while maintaining a distinct three-dimensional structure (insoluble). Cross-linked polymeric materials prepared from HEMA are widely used for biomedical and pharmaceutical applications. Several techniques have been used to prepare HEMA-based cross-linked polymers. All the employed techniques involved either the use of bifunctional comonomers or chemical cross-linking reaction of the linear polymer through the hydroxyl groups present in the structure.

Benzodioxinones are relatively new photosensitive compounds which form salicylate esters when irradiated in the presence of alcohols and phenols. The acylation occurs under neutral conditions and is tolerant to a wide range of sterically hindered alcohols.¹⁵ We have recently proposed an elegant way to initiate free radical polymerization of vinyl monomers such as methyl methacrylate by two-step photolysis of benzodioxinones.¹⁶ In this system, benzophenone, actual photoinitiator, is formed only after photodecomposition of benzodioxinone. The subsequent step is the usual radical formation by the hydrogen abstraction of photoexcited benzophenone from a hydrogen donor such as amines and ethers. The overall process is depicted in Scheme 1. One obvious advantage of this method is the improved shelf life of curing formulations in which the photoinitiator benzophenone is photochemically masked and liberated only after photolysis.

Scheme 1. Photoinitiated Free Radical Polymerization by Using Benzodioxinone



Scheme 2. Photo-Cross-Linking of Poly(hydroxyethyl methacrylate-co-methyl methacrylate), P(HEMA-co-MMA), by Using Bisbenzodioxinone



The promising potential application of the benzodioxinone chemistry was demonstrated with polyester formation between photochemically formed ketene and alcohols. Photolysis of hetero-bifunctional monomers possessing both chromophoric benzodioxinone and aliphatic hydroxyl groups leads to a controlled polycondensation with the formation of oligoester.¹⁷

Previous work within this department has shown the suitability of this process for photoinduced cross-linking of polymers containing pendant hydroxyl groups (Scheme 2).¹⁸

Here we report the photoinduced cross-linking polymerization of a monovinyl monomer, namely 2-hydroxyethyl methacrylate (HEMA), without conventional initiator and cross-linker. An important issue of this concept is that structurally designed bisbenzodioxinones liberate both the photoinitiator and cross-linker only after stimulation by light.

Results and Discussion. Various photoinitiator systems continue to be developed and investigated for photocuring and cross-linking of monomers and polymer materials. The monomers most widely used for photopolymerization processes are acrylates. The reason is that they polymerize rapidly, and by introducing chemical modifications in the ester group, materials with very different properties may be obtained without sacrificing too much polymerization rate. Methacrylates generally polymerize more slowly but, due to the stiffer main chain, yield harder products. The cross-linked homo- and copolymers of HEMA have been widely studied and applied as biomaterials in the form of homogeneous transparent gels. They are usually prepared in bulk or in solution polymerization in the presence of free radical initiators and cross-linking agents. In our work, upon irradiation of bisbenzodioxinones, bisketene and the corresponding benzophenone are formed concomitantly. The excited triplet of benzophenone, which is populated by the successive absorption of the ground state benzophenone formed in the first stage, abstracts hydrogen from the hydrogen donors. The carbon-centered radicals stemming from the amine are able to initiate free radical polymerization of HEMA. At the same time, photo-cross-linking occurs via interchain ester formation through the reaction of bisketene formed simultaneously with

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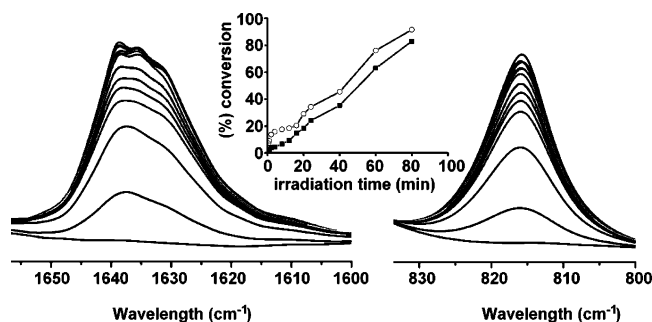


Figure 1. Representation of the decrease of the acrylate bands of HEMA at 1638 (a) and 815 (b) cm^{-1} followed by real-time FT-IR spectroscopy during photopolymerization: Rayonet 16 lamp nominally at $\lambda > 300 \text{ nm}$, $I = 3 \times 10^{-3} \text{ mW cm}^{-2}$, thickness = 1 mm. Inset: real-time FTIR kinetic profiles demonstrating the photoinduced polymerization of HEMA initiated by bisbenzodioxinone with triethylamine (■) or 2-(dimethylamino)ethyl methacrylate (○).

hydroxyl groups of HEMA or the corresponding growing polymer, as depicted in Scheme 3.

In addition to the visual observation of the viscosity increase and gelation of the dichloromethane solutions containing HEMA and bisbenzodioxinone in the presence of hydrogen donors such as triethylamine (TEA) or 2-(dimethylamino)ethyl methacrylate (DAEMA) under UV light at $\lambda > 300 \text{ nm}$, cross-linking reaction was followed by real-time FT-IR spectroscopy (Figure 1). The reaction profile of the system was monitored by the changes of the intensity of double-bond bands. It is found that the intensity of the absorbance peak at 815 cm^{-1} ($\text{C}=\text{C}-\text{H}$ twisting) and 1638 cm^{-1} ($\text{C}=\text{C}$ stretching) decreases with increasing time of exposure to UV irradiation. Another peak at 1163 cm^{-1} due to ($-\text{CO}-\text{O}-$ stretching) absorbance is designated as the reference peak for its invariability¹⁹ during photopolymerization. Thus, the percentage of conversion (c) of the $\text{C}=\text{C}$ bond can be calculated according to the following equation using integrated intensity at 1625 cm^{-1} (using 810 cm^{-1} , similar results can also be obtained):

$$c = 100 \times (1 - A_t S_0 / A_0 S_t) \quad (1)$$

where A_t and A_0 are the areas of the 1638 or 815 cm^{-1} peaks and S_t and S_0 the areas of the 1163 cm^{-1} peak at time t and $t = 0$, respectively. From the results in Figure 1, it is obvious that the methacrylate double bonds decrease rapidly.

Measuring changes in the characteristic monomer IR absorption bands allows the direct monitoring of polymerization

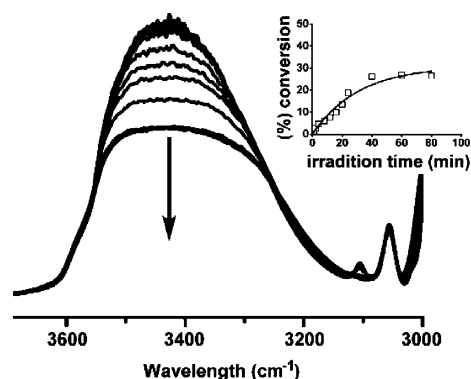
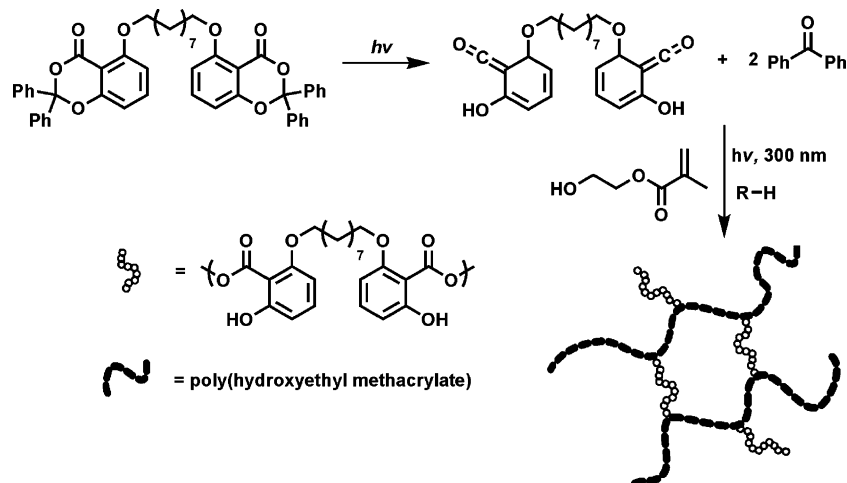


Figure 2. Representation of the decrease of the hydroxy bands of HEMA at $3200\text{--}3600 \text{ cm}^{-1}$ followed by real-time FT-IR spectroscopy during photopolymerization (experimental details are the same as given in Figure 1).

process continuously. Based on the data calculated by eq 1, the conversion curves under polychromatic light are plotted in Figure 1 for the mixture of HEMA and bisbenzodioxinone with two hydrogen donors (TEA and DAEMA). The conversion profiles for both hydrogen donors clearly show that more than 80% of double bonds undergo polymerization within 80 min. It is interesting to note the slightly higher reactivity observed with DAEMA. This is probably due to the fact that DAEMA contains hydrogen-donating sites as well as polymerizable methacrylate group. Thus, DAEMA both initiates and participates in the polymerization as a coreactant. This system has the advantage of being the part of the cross-linked network and avoids potential consequences in bio- and food-packing applications where it is necessary to prevent low molecular weight contaminants from migration.

The polymerization of the monomethacrylate HEMA by the radicals, produced from the photochemical decomposition of benzodioxinone and subsequent hydrogen abstraction, leads to only linear polymers being formed, whereas the bisketenic intermediates, formed in parallel, give rise to the cross-linked structures through ester formation with the hydroxyl groups. This step of the process was also investigated with FT-IR spectroscopy. The reaction of hydroxyl groups was followed by the change of the $\text{O}-\text{H}$ band at $3600\text{--}3200 \text{ cm}^{-1}$. As can be seen from Figure 2, where the partial IR spectral changes of the formulation containing benzodioxinone, HEMA, and TEA are recorded, the intensity of the band decreased with the irradiation time until 30% of hydroxyl groups are consumed

Scheme 3. Photoinduced Cross-Linking Polymerization of 2-Hydroxyethyl Methacrylate without Conventional Photoinitiator and Cross-Linker



and thereafter leveled off. These observations confirm that the cross-linking reaction has taken place with some hydroxyl groups along the poly(hydroxyethyl methacrylate) (PHEMA) backbone formed. It is also noted that there are some hydroxyl groups unreacted which have not been reacted with ketene groups. This may be due to the steric reasons as HEMA polymerizes fast and OH groups in the backbone are too close to hinder the access to some of the OH groups, thus preventing ester formation from occurring at all possible sites. However, about 30% conversion of hydroxyl groups would still yield the desired network formation.

The model compound, namely 7-(2-bromoethoxy)benzodioxinone, has strong structural characteristics and photolysis under similar experimental conditions and yields soluble side-chain-modified polymers which can be analyzed with spectral methods. The appearance of the peaks belonging to the aromatic protons at 7–8.2 ppm in the NMR spectrum of the irradiated polymer is a typical indication for the analogous cross-linking through ester formation (see Supporting Information). Moreover, an aromatic ester could clearly be observed in the IR spectra of the cross-linked polymer (see Supporting Information). The new three bands at 1608 and 1580, and 1655 cm^{-1} observed in the IR spectrum of the cured film represent the aromatic and ester groups that exist in the network structure.

In summary, we have demonstrated a novel photoinduced simultaneous polymerization and cross-linking of monovinyl monomers containing pendant hydroxyl groups by using specially designed benzodioxinones. These molecules have the ability to generate initiating species as well as cross-linking agents that brings out photoinduced polymer network formation. The present method may provide a basis for coating a surface with layers from monovinyl monomers and is potentially useful for the preparation of hydrogels for use in bio applications.

Supporting Information Available: Experimental procedures for synthesis of 7-(2-bromoethoxy)-2,2-diphenyl-4*H*-benzo[d] 1,3 dioxin-4-one and model study, real-time infrared spectroscopy photopo-

lymerization studies, ^1H NMR spectra of 7-(2-bromoethoxy)-benzodioxinone, P(HEMA-*co*-MMA), and their photolysis product, and FT-IR spectra of homo-PHEMA and cross-linked product of photolysis of HEMA and bisbenzodioxinone. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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MA0709811