



Aliphatic ketones and aldehydes as water-soluble photoinitiators for the photopolymerization of methacrylic acid



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ABSTRACT

Environmentally friendly water-soluble photoinitiators are strongly desirable for the practical applications of photopolymerization. This article reports that aliphatic ketones and formaldehyde can be used as effective water-soluble photoinitiators for the photopolymerization of methacrylic acid (MAA) when they are mixed with an appropriate amount of water (and ethanol as a co-solvent in some cases). Among the aliphatic ketones, including acetone, butanone and pentan-2-one, butanone is the most effective. The aliphatic ketones usually exhibit the highest photoinitiation efficiency at a concentration of 5–10 vol.% and a high volume ratio of water to ethanol. By using acetone as the photoinitiator, the factors affecting the photopolymerization of MAA, including atmosphere, UV intensity and monomer concentration, are studied. Oxygen strongly inhibits the photopolymerization. The percent conversion and polymerization rate increase with the increase of UV intensity. The percent conversion decreases whereas polymerization rate increases with the increase of initial monomer concentration.

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1. Introduction

Photopolymerization science and technology has drawn significant attention due to its important scientific and technical significance, and it holds numerous applications in coatings, adhesives, inks, printing plates, optical waveguides, microelectronics, biomaterials, etc [1–3]. Photoinitiator is usually required for a photopolymerization system, and it plays a vital role in initiating the polymerization by generating active radicals under UV light irradiation through cleavage and hydrogen abstraction reactions. Many efforts have been done to develop novel photoinitiators. The most studied photoinitiators are the derivatives of benzophenone (BP), thioxanthone (TX), and quinone, etc [2,4–12]. Some polymerizable and polymeric photoinitiators are developed to overcome the undesirable effects, such as yellowing and strong odor, induced by the low molecular weight photoinitiators [13–15].

The oil-soluble nature of the most widely used conventional photoinitiators leads to the usage of organic solvents in the photopolymerization processes. If the photopolymerization can be carried out in water, which is the cheapest and safe solvent and it can act as a cooling agent, then the serious environmental pollution induced by organic solvents can be solved. For this reason, the

synthesis of new water-soluble photoinitiators has drawn great attention in recent years. Generally, water-soluble photoinitiators are developed by introducing positive/negative ionic groups (e.g., quaternary ammonium salts, sulfonates, and carboxylic acids) or hydrophilic non-ionic groups into conventional oil-soluble photoinitiators [8,13,16–18]. However, the practical application of the water-soluble photoinitiators is strongly impeded by their complicated synthesis and the possible lower photoinitiation efficiency induced by direct substitution.

Aliphatic ketones are more often used as solvents rather than photoinitiators, due to their low photoinitiation efficiencies [19]. Acetone is the first aliphatic ketone found to be able to effectively initiate photografting polymerization when it is mixed with an appropriate amount of water [20,21]. Our recent work shows that some other aliphatic ketones (butanone, pentanone, hexanone, etc.) [22,23] and aliphatic aldehydes (formaldehyde and acetaldehyde) [24,25] can also be used as photoinitiators for photografting when they are mixed with a proper ratio of water or in some cases together with an alcohol (as a co-solvent). These aliphatic ketones and aldehydes can be used as water-soluble photoinitiators since they are either miscible with water or soluble in water in the presence of a co-solvent. By using aliphatic ketones as water-soluble photoinitiators for the photografting of acrylic acid (AA) and *N*-isopropylacrylamide (NIPAAm) onto polyethylene (PE) film surface, we obtained photografted poly(acrylic acid) and PNIPAAm thin films with ultra-high equilibrium swelling ratios and superfast

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swelling and response rates (<10 s) [26,27]. The use of aliphatic ketones and aldehydes as water-soluble photoinitiators has some exceptional advantages. For example, they are very cheap and commercially available, in addition, they function as both solvents and photoinitiators and hence they can be totally removed from the reacted systems.

Our theoretical calculations on the photoinitiation mechanism of acetone in water show that acetone exists in the form of hydrates in its aqueous solution, and the excited state of acetone dihydrate generates a radical which tends to abstract hydrogen atoms from a polymer substrate or a monomer [28]. Based on this mechanism, the aliphatic ketones and aldehydes can also be used as photoinitiators for photopolymerization. In this work, we report the photopolymerization of methacrylic acid (MAA) initiated by aliphatic ketones and formaldehyde in water or water/ethanol mixed solvents. The aliphatic ketones and formaldehyde can be used as effective water-soluble photoinitiators for photopolymerization.

2. Experimental

2.1. Materials

Methacrylic acid (MAA) and formaldehyde (40 wt.%) were purchased from Tianjin Bodi Chemicals Co. Ltd. (Tianjin, China), ethanol, acetone and butanone were from Beijing Chemical Factory (Beijing, China), and pentan-2-one was from Beijing Chemical Reagent Company (Beijing, China). These reagents were AR grade and used as received.

2.2. UV equipment

The UV equipment with a shutter assembly was supplied by RunWing Mechanical & Electronic Co. Ltd. (Shenzhen, China). The input power of the UV high pressure mercury lamp was 2 kW. The output UV intensity was measured with a UV Radiometer manufactured by the Optical Instrument Factory, Beijing Normal University, China.

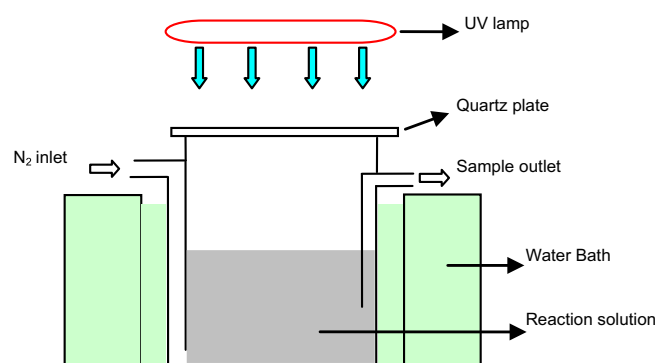
2.3. UV–visible spectroscopy of aliphatic ketones in water/ethanol mixed solvents

The UV–visible spectra of acetone, butanone and pentan-2-one in pure water, ethanol and mixed solvents containing water and ethanol with different volume ratios were obtained with a UV–visible spectrophotometer (TU-1901, Beijing Puxi Universal Apparatus Co., Ltd. Beijing, China). Ketone concentration in the solvents was fixed to be 0.059 mol L⁻¹.

2.4. Photopolymerization

Monomer solutions were prepared by thorough mixing proper volumes of monomer with aliphatic ketone (aldehyde) and water or together with ethanol. Polymerization was carried out in a 4.5 cm diameter vessel containing 20.0 mL solution, a quartz plate was put on the vessel to separate the UV light and prevent the heating of solution, as shown in Scheme 1. The solution was exposed to UV irradiation and stirred with a magnetic stirrer. The solutions were bubbled with high-purity nitrogen during the reaction. The reaction temperature was controlled to be 40 °C by using a water bath and the temperature variation was about ± 1 °C. The measured UVC (254 ± 10 nm) intensity at the position of liquid surface was 11.6 mW cm⁻², if not otherwise stated.

A small amount of the solution (normally 0.5 mL) was extracted from the vessel after a required reaction time, and it was kept on a



Scheme 1. The photopolymerization apparatus.

weighed PE film in a fume hood at ambient temperature to allow the evaporation of the unreacted monomer and solvent, and then vacuum dried for 24 h at 45 °C.

The percent conversion of monomer to polymer (C_p) is given by Eq. (1):

$$C_p = \frac{m_p}{m_0} \times 100\% \quad (1)$$

where m_p is the mass of polymer formed and m_0 is the mass of monomer.

2.5. Molecular weight measurement

The molecular weights and polydispersity indices (PDIs) of the polymers were measured with a Waters 1515 gel permeation chromatograph (GPC) using 0.10 mol L⁻¹ NaNO₃ as the eluent at a flow rate of 0.5 mL min⁻¹. Molecular weights were calibrated with poly(acrylic acid) standards (molecular weight ranges from 1×10^3 Da to 1×10^6 Da).

3. Results and discussion

Acetone and formaldehyde are miscible with water, therefore homogeneous acetone or formaldehyde aqueous solutions can be formed by mixing acetone or formaldehyde with water. But for the other aliphatic ketones, their solubility in water decreases with increasing chain length, so an appropriate ratio of a co-solvent (ethanol in this work) is necessary for the formation of homogeneous aliphatic ketone aqueous solutions. In the experimental descriptions, the mixed solvents of an aliphatic ketone, water and sometimes ethanol were expressed as: x ketone/ y water/ z ethanol or x ketone/ y water, where x , y and z are the volume ratios of ketone, water and ethanol before mixing, respectively. For the formaldehyde aqueous solution, x and y are the mass ratios. For a given ketone (formaldehyde)/water (/ethanol) system, the mixed solvents are expressed simply as $x/y/z$ or x/y , and $x + y + z$ or $x + y$ is equal to 100.

3.1. Photopolymerization initiated by aliphatic ketones and formaldehyde

For comparison the photoinitiation efficiencies of aliphatic ketones (acetone, butanone and pentan-2-one) and formaldehyde, the volume ratio of ketone or formaldehyde was fixed to 10 vol.%. Since at such a volume ratio butanone and pentan-2-one could not be totally dissolved in water, certain ratios of ethanol were added. The photopolymerization reactions in this work usually required a long reaction time. For saving time, in the following work the

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