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## Macromolecular Nanotechnology

## A thermo-sensitive imaging coating derived from polymer nanoparticles containing infrared absorbing dye



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## ABSTRACT

The present study relates to a method for incorporating a near infrared dye (the absorption maximum at approximately 830 nm, IR-830) into polymer particles via miniemulsion polymerization and the preparation of an infrared laser-imageable coating based on the polymer particles as well as the potentiality in developing environment-friendly computer-to-plate (CTP) precursor. Polymer particles containing the IR-830 were prepared through miniemulsion polymerization technology in the presence of sodium dodecyl sulfate and hexadecanol as the emulsifier blend. Polyvinyl alcohol was used as a water soluble polymer binder resin for the production of latex coatings. Using the above prepared materials as the main components, an IR laser-imageable coating was prepared. Upon computer-controlled laser exposure, the IR dye-containing polymer particles absorb IR laser energy and produce high temperature, causing great changes of the imaged areas of the latex coating. As a result, the imaged areas could not be removed with water cleaning, whereas the polymer particles of the non-imaged areas remain unchanged, and still could be easily removed by water cleaning. When developing with water, negative graphics were obtained. The results of the research can be used in developing chemical-free CTP plates required by green printing industry.

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## 1. Introduction

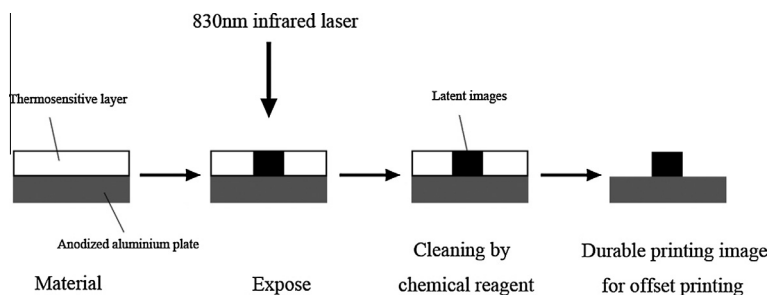
Lithographic printing presses use a so-called printing master such as a printing plate which is mounted on a cylinder of the printing press. The printing masters are generally obtained by the image-wise exposure and processing of an imaging material called plate precursor. Computer to plate (CTP) is an imaging technology used in modern printing processes. In this technology, an image created in a desktop publishing (DTP) application is output directly to a printing plate, which can form a latent image by using the heat or the light of a laser [1]. There are several kinds of CTP plates such as photopolymer plates, silver halogen plates and thermal plates [2]. As thermal materials offer the advantage of daylight stability, thermal sensitive

printing plate precursors which form latent images by 830 nm infrared laser have become very popular at present. The latent images which are produced by 830 nm infrared laser exposure are not yet ready for printing and must be transformed into a durable printing image such as chemical development (Scheme 1). However, traditional development processes will generate a large number of pollution by using chemical reagents, therefore, chemical-free plates are extremely desirable for environment reasons.

Emulsion polymerization is a unique technique which could produce polymers under the environmentally-friendly process [3]. This technology using water as a reaction medium and easy handling of the final latex, thus, it is used to form continuous films in adhesives, paper coating, paints, etc. [4,5]. Miniemulsion polymerization offers the efficient method for the encapsulation of different materials. Thus it is popularly used to form complex structured

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**Scheme 1.** The imaging process of conventional CTP technology.

polymeric nanoparticles [6–9]. Many different materials, ranging from organic and inorganic pigments, magnetite, or other solid nanoparticles, to hydrophobic and hydrophilic liquids, such as fragrances, drugs, or photoinitiators, can be encapsulated to prepare functionalized nanoparticles [10–13]. Oil-soluble dyes dispersed in water to form colored polymer latex particles with encapsulation strategies have been gathering great attention in recent years. Many researches encapsulated oil-soluble dyes into polymer latex particles by miniemulsion polymerization method. For example, Takasu et al. [14–16] prepared polymer particles containing copper phthalocyanine dyes and styryl dyes as oil-soluble dye via miniemulsion polymerization using azo-bisobutyronitrile as initiator. Zhao et al. [17] prepared polystyrene/Sudan black B latex particles also by a miniemulsion polymerization technique. All the above cases can obtain stable and durable colored latex.

Thermal sensitive printing plate precursors usually employ infrared radiation (IR) dye and polymer resin. When these materials are exposed to infrared laser, the IR dye absorbs the laser energy to generate heat triggering physico-chemical process, such as ablation, polymerization, insolubilization by cross-linking of a polymer, heat-induced solubilization or particle coagulation of a thermoplastic polymer latex. With the above mentioned process, the printing plate precursors can finally form a latent image. Thermal sensitive printing plate precursors with particle coagulation of a thermoplastic polymer imaging mechanism can easily realize chemical-free plate making, because unexposed polymer particles are aqueous coating layer made by thermoplastic polymer latex. Thus, the latent images can be transformed into a durable printing image by water. In this case, encapsulation of oil-soluble IR dyes into thermoplastic polymer particles via miniemulsion polymerization can make the water development printing plate come true. The mechanism of this case is

shown in **Scheme 2**. Although many researchers concerned encapsulation oil-soluble dyes into polymer particles by miniemulsion polymerization, to the best of our knowledge, few articles concerning IR dye encapsulation in polymer particles via miniemulsion polymerization method and its application in thermal sensitive imaging system have been published as so far.

In this paper, we present the preparation of the IR dye-containing polymer nanoparticles and study the use in lithographic printing plate, which can be imaged using digitally controlled laser output and developed with neutral water.

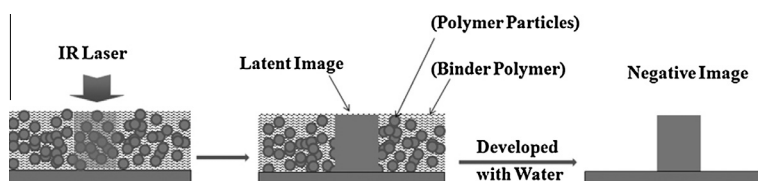
## 2. Experimental

### 2.1. Materials

Styrene, acrylonitrile, methyl methacrylate (MMA) and butyl methacrylate (BMA) which were purchased from Beijing Chemicals Co. were distilled under reduced pressure and stored at  $-15\text{ }^{\circ}\text{C}$ . Sodium dodecyl sulfate (SDS) and hexadecanol as the emulsifier blend, L-ascorbic acid (LAA) and tert-butyl hydroperoxide (TBH) as redox initiator, polyvinyl alcohol (PVA) as binder polymer and the IR dye (**Fig. 1**) with the maximum absorption near 830 nm (IR-830) were used as received. They were all commercial products from Acros Organics. Distilled deionized water (DDW) was used as the polymerization medium.

### 2.2. Preparation of the polymer nanoparticles containing IR-830 by miniemulsion polymerization

The aqueous phase was formed by a mixture of SDS (0.4 g), LAA (0.15 g) and DDW (50 ml) with magnetic stirrer for several minutes. Styrene (9 g) and acrylonitrile (6 g) solution of hexadecanol (0.1 g) and various amount



**Scheme 2.** Schematic diagram of the laser imaging process by water development.

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