# **Preparation and properties of a Thermo-sensitive Film Based on** Latex Particles

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# Abstract

A reversible addition fragmentation chain transfer (RAFT) agent, 2-(dodecylthiocarbonothioylthio)propanoic acid (DTPA), was synthesized and characterized. Acrylic acid (AA) was polymerized in the presence of DTPA to give an amphiphilic macro RAFT agent (DTPA-AC-5), which had a calculated average degree of polymerization of five. Poly (butyl methacrylate -co- methyl methacrylate) (p-(BMA-MMA)) latex was prepared using sodium DTPA-AC-5 as a reactive surfactant. The emulsion had a solid concentration as high as 45 wt.% and was very stable. Latex films were prepared with the p-(BMA-MMA) emulsion and small amount of the binder polymer of PVA1788. The latex films could be easily washed away from the substrate with neutral water, but could no longer be removed after heat treatment at 160 °C for a short period of time. When an IR dye (with maximal absorption at 830nm) was incorporated into the latex films, they became sensitive to LD lasers emitting at 830 nm and negative images were obtained after exposed by LD laser and developed by neutral water. This indicated that the latex system could find uses in chemical-free thermal laser imaging applications.

Keyword: Latex particle, Latex film, Laser imaging

## Introduction

Water-developable information recording materials have attracted much attention because they should he environment-friendly, easy to operate and economic, etc [1-3]. Most water-developable materials involved chemical reactions, which were either induced by light or acid or other actions during the application processes. Recently, Agfa has developed a new plate system based on thermofusable plastic particles, and the image formation is a simply physical process [4]. However, the detail of the microparticles is not reported. In this paper, a kind of new polymer particle with an ionic surface was prepared and characterized. Preliminary works were also done to build a thermo-sensitive water-developable latex film and investigate its imaging performance.

# **Experimental**

## Materials and methods

Methyl methacrylate (MMA), butyl methacrylate (BMA), acrylic acid (AA), dodecane-1-thiol, 2-bromopropanoic acid, 4,4'-azobis(4-cyanovaleric acid)(ACVA) and poly (vinyl alcohol) (PVA1788) were commercial products from Beijing Chemicals Co. MMA and BMA were purified by vacuum distillation before use. CTP-1, an IR dye with a maximal absorption at 830 nm, was made in our laboratory. Deionized water was used in all the experiments. FTIR spectra were obtained with a Shimadzu FTIR-8400 infrared spectrophotometer. The average particle size and distribution were measured by dynamic light scattering (DLS) with a Dynapro Titan instrument (Wyatt, American). Differential scanning calorimetry (DSC) was recorded on a Netzsch DSC200PC analysis apparatus. The thickness of the latex films was measured with a FTS-S3c ultra surface analysis instrument (Taylor Hbson Ltd., England). Laser exposure was carried out on a home-made single beam laser diode emitting at 830 nm.

## Synthesis of DTPA and DTPA-AC-5

In a 250-mL, four-necked flask equipped with a mechanical stirrer and a reflux condenser was placed 8.00 g (0.20 mmol)of sodium hydroxide, 40 mL of deionized water . The mixture was stirred and cooled to room temperature. Tetraethylammonium bromide (3.20g, 0.01mol), THF (40 mL) and dodecane-1-thiol (40.48 g, 0.20 mol) were added to the mixture and stirred to yield a clear solution. Then, 15.23 g of CS<sub>2</sub> (0.20 mol) and subsequently 30.6 g of 2-bromopropanoic acid (0.20 mol) were added to the above solution in such a way that the temperature could be kept at 20-25 °C. The mixture was stirred at room temperature for 20 h and then at 50 °C for another 5 h. After cooling to room temperature, the yellowish organic layer was separated and poured into an excess amount of petroleum etherwith stirring to yield a yellow precipitate. The yellow product was recrystallized in methanol to give 57.5 g of DTPA. Yield: 82%. mp: 64-65 °C. FTIR (KBr, cm<sup>-1</sup>): 2918, 2852, 1701, 1421, 1209, 1084, 825. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): 4.82-4.90 (m, 1H), 3.32-3.38 (m, 2H), 1.66-1.74(m, 2H), 1.60-1.64 (d, 3H), 1.25-1.38 (m, 18H), 0.84-0.87 (m, 3H). ESI (m/e, percentage of relative intensity): 349. ELEM. ANAL. Calcd. For  $C_{16}H_{30}O_2S_3$ : C, 54.81; H, 8.62; S, 27.44. Found: C, 54.56%; H, 8.74%; S, 27.67%.

DTPA-AC-5 was prepared according to according to a reported procedure [5]. In a typical experiment, DTPA (3.5g, 0.01mol), AA (3.6g, 0.05mol), ACVA(0.29g, 1.03 mmol) and toluene (10 mL) were charged in a 100 mL flask, which was then flushed with nitrogen for 1 h. The temperature was raised to 60 °C and stirred for 8 h. The solution became viscous and additional 5 mL of toluene was added. The reaction solution was cooled to room temperature and then poured into 100 mL of petroleum ether. The yellowish precipitate was collected and fully washed with petroleum ether and dried in vacuo at 50 °C to afford 6.6 g (Yield: 93%) of DTPA. FTIR (film, cm<sup>-1</sup>): 3330-3400, 2920, 2850, 1706, 1420, 1210, 1088, 830.\_Number-average molecular weight (*M*m): 982; weight-average molecular weight (*M*w):1517; polydispersity index (PI): 1.54.

# Synthesis of p-(BMA-MMA) latex particles

The macro RAFT agent, DTPA-AC-5, was used to prepare p-(BMA-MMA) nanoparticles. 0.60 g of DTPA-AC-5, 0.08 g of ACVA initiator and 0.18 g of NaOH was dissolved in 15 mL of water. Then 11.40 g of a mixture of BMA and MMA (1:1 in weight ratio) was added. The stirred mixture was purged with nitrogen for 1 h. The mixture was heated in an oil bath at 60 °C and kept for 6 h. the solid content of the emulsion was 44.7 wt.%.

# **Results and Discussion**

# Preparation of the RAFT agent DTPA-AC-5 and the latex particle

The synthetic route of DTPA, DTPA-AC-5 and the latex particle were depicted in Scheme 1. The RAFT agent, DTPA, was obtained in high yield. The structures of the compound were confirmed by elemental analysis, IR, <sup>1</sup>H NMR and MS. The polymerization of AA was carried out in the presence of one-fifth the molar concentration of RAFT agent in toluene (Scheme 1) to give a macro RAFT agent. The resulting product, (AA)x-RAFT, was characterized by Gel permeation chromatography (GPC) (relative to styrene standards). The value of M<sub>n</sub> measured by GPC is 982, which is less than the calculated value of DTPA-AC-5 (M<sub>n</sub>=836). But no conclusions can be drawn because the (AA)x-RAFT molecular weight value is relative to styrene standards. Generally speaking, the found Mn is close to the calculated one for DTPA-AC-5. The PI value is 1.54, which is less than those observed for polymers prepared through traditional radical polymerization (typically greater than 2). All these indicate that DTPA-mediated polymerization of AA is characterized by "live" radical polymerization. The obtained macro RAFT agent should have a polymerization degree of about five.

Emulsion copolymerization of BMA with MMA was conducted using the sodium salt of DTPA-AC-5 as the surfactant. DTPA-AC-5 was a reactive surfactant for it also took part in the emulsion polymerization and became part of the formed particle. Furthermore, the hydrophilic moieties of DTPA-AC-5, namely the sodium carboxylate groups, were located at the surface of the latex particles, which formed a stable hydrophilic layer around the surface. The particles were found narrowly distributed in size (polydispersity 5%) and the mean diameter was 63 nm according to the DLS result (Fig. 1).

## DSC analysis of the latex particle

Glass transition temperature of the latex particle was monitored using DSC. As shown in Fig. 2, the solid latex particle showed a glass transition at 57  $^{\circ}$ C, which was attributed to the copolymer, p-(MMA-BMA). In addition to the peak at 57  $^{\circ}$ C, no more apparent peaks were found even when the temperature reached 220  $^{\circ}$ C.

# Preparation of thermo-sensitive latex film and Laser-induced imaging performance

A sample film was first prepared by spin-casting the mixture of the prepared emulsion, PVA1788 and an IR dye (with maximum absorption at 830nm) onto an aluminum substrate, and dried at room temperature to evaporate the solvent. The mass fractions of the dry latex film were about 90% for the solid latex particles, 9% for PVA1788 and 1% for the IR dye. The polymer film was dried in vacuo at 30-40 °C.

The contact angle of the latex film with water was measured to be  $33^{\circ}$ . However, after the film was treated at 160 °C for 10 seconds, the contact angle with water became larger than 90° (92.5 °). The affinity change should be related with the thermo-induced modification of the particle structures. Before heating, the ionic species (carboxyl groups) were at the outer of the latex particles, therefore the film was hydrophilic. The particles in the film should be fused and united together upon heating, and the polar groups existed in the surface of the particles was embedded by the inner polymer, poly(BMA-MMA).

Then the sample was exposed with the laser scanning device. Finally, the exposed film was developed with neutral water and detected by SEM. Figure 2 is a typical micrograph after exposed by laser and developed with water. Once the sample was exposed to IR laser beam, the temperature of the exposed area increased sharply and the latex particles would melt and united together. Because the hydrophobic core constituted the majority (about 90 %) of the latex particles, the exposed area couldn't be removed from the substrate. On the other hand, the film in unexposed area could be washed away by water because the latex particles remained intact and separated from each other. The exposure dose was fixed at about 350 mJ/cm<sup>2</sup>. The dark strips were exposed areas of the latex film.



Scheme 1. Synthesis of DTPA, DTPA-AC-5 and the latex particles.



Figure 2 DLS result of the emulsion.

#### Conclusion

In this study, a new reactive emulsifier was synthesized and used to prepare latex particles with the charged surface through soapless emulsion polymerization. A thermo-sensitive latex film based on the latex particles was built. This kind of material was water-developable and gave satisfactory images, suggesting that it might be used in thermal-imaging applications.

Sciences in 2003. Since 2003 he has been involved in the development of new functional polymers and their properties as information recording materials, including core-shell particles, thermo-sensitive polymers and photosensitive polymers.



Figure 2. DSC curve of the latex particle (in nitrogen, heating rate: 10 °C min<sup>-1</sup>).



**Figure 2** SEM photograph of the pattern from thermo-sensitive latex film (thickness: 2.4 μm) exposed by IR laser and developed in neutral water.

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