



## Preparation and application of melamine-formaldehyde photochromic microcapsules



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### ABSTRACT

Melamine-formaldehyde microcapsules encapsulating photochromic compounds with particle size less than 5  $\mu\text{m}$  had been prepared by in situ polymerization, and their application in textile was also studied. The Fourier transform infrared spectroscopy (FTIR), biological microscope and laser particle analyzer were utilized to characterize the structure, morphology, size and size distribution of melamine-formaldehyde photochromic microcapsules. The UV-visible spectrophotometer was used for monitoring the UV-vis absorption of different mass fraction of photochromic compounds in dioctyl phthalate (DOP) solvent and the kinetics and fatigue resistance of photochromic microcapsules and photochromic print cloth. As a result, the mixed photochromic solution of photochromic compound and DOP solvent appeared maximum absorption peak in a certain wavelength range after exposed in a mercury lamp (375 W) for 10 min when the mass ratio was 2%. The lifetime of photochromic microcapsules could extend from 6–7 h to 69–75 h under continuous UV, when stirring rate, emulsification time and mass ratio of core materials/wall materials were 1000 rpm, 5 min and 1:1, respectively. Meanwhile the photochromic painting paste had excellent water resistance, acid/alkali resistance, soaping resistance, light resistance and fatigue resistance.

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### 1. Introduction

The organic photochromic materials have been applied to optical memory and switching device because of their sensitive color changing and bright color [1–5]. They have brought us a colorful life. However, the photochromic materials are susceptible to be affected by the environmental factors such as oxygen, pH value, light and temperature which leads to oxidation and deterioration. These environmental factors limited the applications of photochromic materials in textiles and other civilian fields [2].

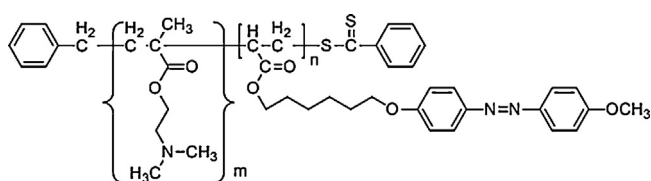
Polymers exhibit unique advantages as matrices of photochromic systems, since photochromic materials were required in the form of films, sheets, fibers and so on [3]. And in order to improve the fatigue resistance and extend lifetime of photochromic compounds, polymeric matrices are preferred to overcome the oxidation and deterioration. A deeper understanding of how photochromic compound is incorporated with polymeric matrix has been formed through continuous studies on photochromic polymers [4]. Usually, photochromic molecules are incorporated into

polymer matrices by binding them covalently to polymer backbones [5,6] or by dissolving or suspending them in polymer matrix (doping) [7]. Recently, various types of photochromic compounds have already been doped into polymer matrices [8–10]. Amphiphilic azobenzene diblock copolymer p(DMAEMA-*b*-AZOMn) was synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization (Scheme 1) in films and the color changed from yellow to orange after irradiation by ultraviolet and visible (UV) light, because its self-assembly morphology could change from rods to microspheres by controlling hydrophobic aggregation of azobenzene diblock in H<sub>2</sub>O/THF dispersion media and the length of the pAZOM block [11]. Docture Ercole F [12] synthesized a series of naphthopyran photochromic polymers by Atom Transfer Radical Polymerization (ATRP). Crosslinked and hyperbranched polymer structures were proved to cause a decrease in coloration and decoloration rates compared with linear structure. However, photochromic polymers prepared by binding photochromic compounds covalently to polymer backbones have some disadvantages, such as complex reaction, low conversion ratio and worse photochromic reactivity. Most frequently, photochromic compounds are doped into polymers [13], such as poly(methyl methacrylate) (PMMA) and epoxy resin thin film. The optimal exposure of photoinduced anisotropy pyrrolfulgide/PMMA film was found to be at about 5 J/cm<sup>2</sup>, and two sets

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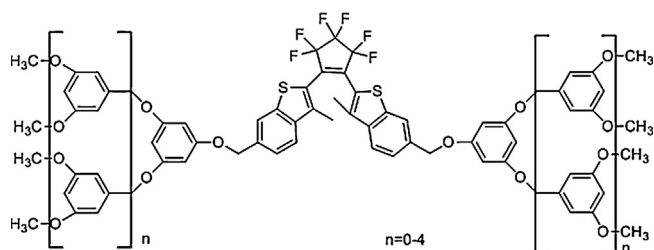
**Table 1**  
The detailed experimental formula for preparation of photochromic MF microcapsules.

| Samples | Mass fraction of photochromic compounds in DOP (%) | Emulsification time (min) | Stirring speed (rpm) | Quality proportion of core material and wall material |
|---------|--|---------------------------|----------------------|---|
| A1      | 0.5  | –                         | –                    | –   |
| A2      | 1  | –                         | –                    | –   |
| A3      | 1.5  | –                         | –                    | –   |
| A4      | 2  | –                         | –                    | –   |
| A5      | 2.5  | –                         | –                    | –   |
| A6      | 0  | 5                         | 1000                 | 1:1   |
| B1      | 2  | 1                         | 1000                 | 1:1   |
| B2      | 2  | 3                         | 1000                 | 1:1   |
| B3      | 2  | 5                         | 1000                 | 1:1   |
| B4      | 2  | 7                         | 1000                 | 1:1   |
| B5      | 2  | 9                         | 1000                 | 1:1   |
| C1      | 2  | 5                         | 500                  | 1:1   |
| C2      | 2  | 5                         | 1000                 | 1:1   |
| C3      | 2  | 5                         | 1500                 | 1:1   |
| D1      | 2  | 5                         | 1000                 | 2:1   |
| D2      | 2  | 5                         | 1000                 | 1:1   |
| D3      | 2  | 5                         | 1000                 | 1:2   |
| D4      | 2  | 5                         | 1000                 | 1:3   |



**Scheme 1.** The p(DMAEMAm-*b*-AZOMn) diblock copolymer.

of polarization spot-patterns recorded in the pyrrofulgide/PMMA film by respectively using two beams of different linear polarization (cross angle 45°) could only be revealed by using two orthogonal polarizers at certain polarization angles [14]. 7',8'-dichloro-1,3,3-trimethylspiro[indoline-2,3'-[3H] benzo [b][1,4] oxazine] (SO) was doped in PMMA and epoxy resin for better fatigue resistance, respectively [15]. It turned out that constant of photocoloration rate of SO in both matrices was almost the same, which was unexpected. On the contrary, the rate of photobleaching reaction of photomerocyanine in PMMA was twice slower than that in the epoxy resin due to the presence of the two chlorine atoms at positions 7' and 8' of the benzooxazine moiety destabilize, and the photomerocyanine in epoxy resin film. SO doped in epoxy resin shows much better fatigue resistance than that doped in PMMA. Furthermore, photochromic dendrimer diarylethenes with a C-2-connected bisbenzothienylethene core (Scheme 2) showed strong memory effect of cyclizable conformation of the open form when generated from the closed form by visible light irradiation in polycarbonate films, and the high conversion ratio reached to ca. 60–70% [16]. A value of 3400 cycle was reached using a film of poly-1,2-bis-(2-methyl-3-thienyl) perfluorocyclopentene in PMMA without using any inhibitor [17]. Photochromic polymers by doping play an importance role in slowing the photoresponsivity,



**Scheme 2.** Bisbenzothienylethene-cored dendrimer.

such as molecular liquidity and heterogeneity of polymeric matrix which would do some influence on the photochromism of blends.

Based on these, photochromic polymer microparticles and nanoparticles have great potential in various photonic applications due to their good photostability and brightness [18–20]. Harbron et al. [21] physically doped photochromic dyes into poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) to get composite nanoparticles. It showed that photochromic dye-doped MEH-PPV nanoparticles exhibited reversible quenching and recovery, but the very low quantum yield of MEH-PPV nanoparticles drops (<0.01) made further applications less feasible. However, the photoswitching of nanoparticles synthesized by conjugating photochromic spiropyran molecules onto poly[9,9-dioctyl fluorenyl-2,7-diyl]-co-1,4-benzo-{2,1'-3}-thiadiazole]] (PFBT) [22] could be repeated for multiple cycles, 86% of PFBT emission intensity was quenched after UV light irradiation while PFBT emission was recovered by irradiation with visible light. Also, PMMA/spirooxazine microspheres prepared by in situ suspension polymerization of MMA in the presence of photochromic spirooxazine dye (concentration of 1 wt%) had smooth surface with microspheres size about 30 μm. Upon UV irradiation the color turned blue, and then bleached within a few minutes [23]. The authors also studied the effect of different temperature on the first-order constant of decoloration rate of PMMA/spirooxazine microspheres, and it indicated that open-to-close occurred more readily at high temperature.

Microencapsulation as an effective technique could protect active small molecules against environment effects, such as acid, alkali, air and oxidization. Micro-encapsulated pigment dispersions were formulated into pigmented ink jet inks and showed great fastness, permanence and usability [24]. However, the microencapsulation of photochromic compounds of organic polymers was hardly achieved. Feczko et al. [25] tried to prepare poly(methyl methacrylate) and ethyl cellulose nanocapsules containing a photochromic dye, 5-chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3-(3H) naphth [2,1-b](1,4) oxazine], by emulsion-solvent evaporation method. But it turned out that poly(methyl methacrylate) and ethyl cellulose were not suitable materials for textile in practical applications.

Melamine-formaldehyde resin is an important thermosetting resin material with outstanding transparency and the resistance to heat, abrasion, weathering acid and alkali. Due to these advantages, in this study, melamine-formaldehyde microcapsules were used to encapsulate photochromic compounds and the performance of photochromic microcapsules was also studied.

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