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## Synthesis and characterization of photochromic copolymer grafting azoaromatic chromospheres on pullulan

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### ABSTRACT

Preparation of photochromic copolymer grafting 4-(4-nitro phenylazo)-1-naphthol units on pullulan molecular surface has been accomplished. Surface modification was carried out in aqueous by an inverse emulsion polymerization method. Polymerization products were characterized by IR, SEM, XRD and TG-DTA. UV-VIS spectroscopy has been used to monitor the photoisomerization of azobenzene moieties on pullulan molecular surface. The results indicated that functional copolymer has better photochromism property than its corresponding azobenzene moieties, reflecting the macromolecular backbone of pullulan should do actively effect on photoisomerization of azoaromatic moieties.

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### KEYWORDS

Pullulan;  
Azoaromatic compounds;  
Graft copolymer;  
Photochromic.

### INTRODUCTION

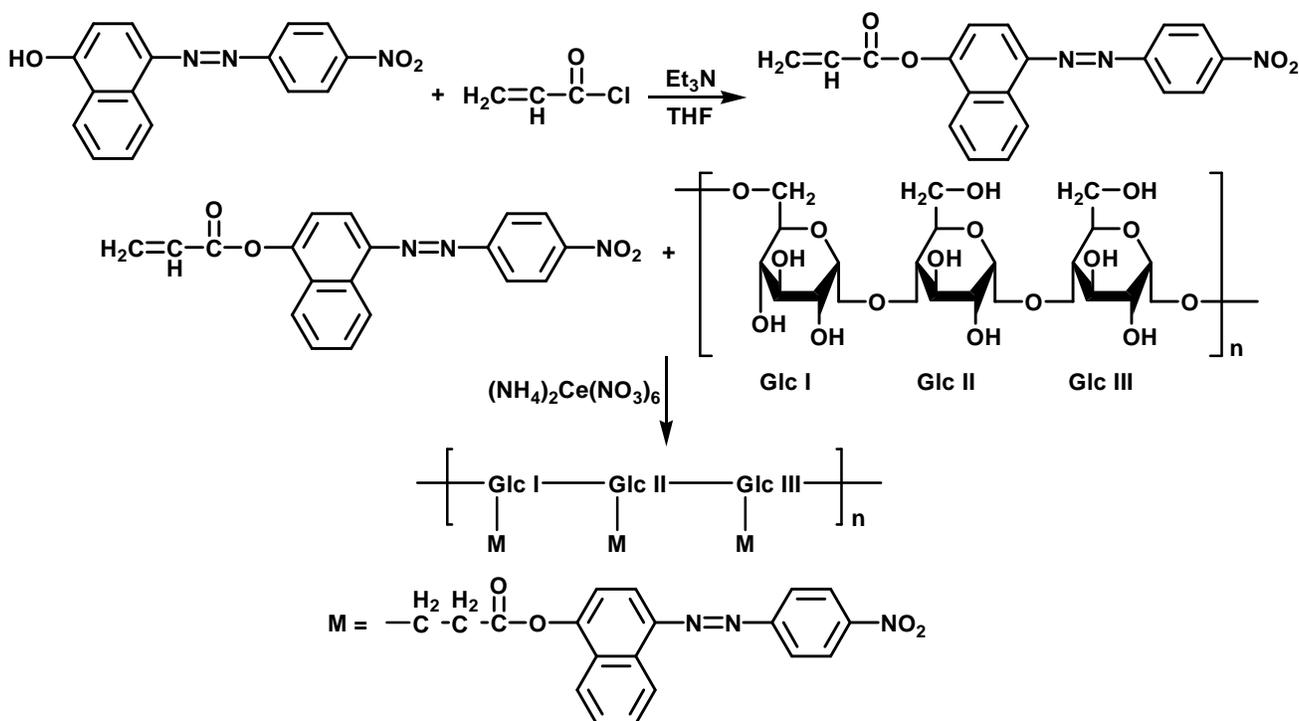
Azoaromatic compounds have attracted much attention due to their novel photochromic properties<sup>[1-6]</sup>. Synthesis of photochromic polymer containing azoaromatic chromophores have attracted interesting in recent years, because they can be used as materials for optical data storage, information processing, holographis and electrooptic applications<sup>[7-11]</sup>. At the same time, the application of these photochromic polymers was limited by their low solubility and stability in solvents as well as their low thermal stability<sup>[12-14]</sup>. Pullulan is a biodegradable water-soluble, extra-cellular neutral polysaccharide with a linear flexible chain of 1,6-linked maltotriose units, and produced from plant-based starch or sugars regenerated by natural photosynthesis of carbon dioxide and water<sup>[15,16]</sup>. Unlike starch and cellulose, pullulan is easily soluble in water

and dimethyl sulfoxide (DMSO), even though its molecular weight is higher, and consequently deem to be a promising material for synthetic polymer. So much increasing attention has been paid to chemical modification of pullulan<sup>[17-21]</sup>.

The purpose of our present work is to investigate the feasibility of grafting vinyl monomer containing 4-(4-nitro phenylazo)-1-naphthol (NPANO) onto pullulan (Scheme 1). We aim to develop functional copolymer with photochromic properties, perfectly solubility and thermal stability.

We know that azobenzene compounds have -N=N- bonds which can photoisomerize from trans to cis isomer<sup>[22-24]</sup>. Micromolecular azobenzene compounds generally have more excellent photochromism than macromolecular ones<sup>[25,26]</sup>. In our present experiment, the photochromism property of pullulan which grafted azobenzene compounds has been monitored by UV-

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Scheme 1 : Synthesis procedure and chemical structure of the graft copolymer

Vis spectroscopy in DMSO solution under 365 nm ultraviolet light irradiated. Surprisingly, the results showed that pullulan copolymer had much better photochromism property than corresponding vinyl monomer containing NPANO. We consider the results demonstrated pullulan's macromolecular backbone should exert an influence on photochromism property of the copolymer in a dramatic way.

## EXPERIMENTAL

### Materials and methods

Pullulan (M/W = 150,000) supplied by NWN Bioengineering Lab (China), was dried at 40°C for 20 h before use. 4-(4-nitrophenylazo)-1-naphthol (Shanghai chemical Co. Ltd, China) was dried over anhydrous  $\text{CaCl}_2$  and stored in a refrigerator. The vinyl monomers were prepared according the method described in the literatures<sup>[27,28]</sup>. Ceric ammonium nitrate (CAN) (Beijing Chemical Co. Ltd, China) was dried in air oven at 100°C for about 5 h, used as a 0.1 M solution in molar nitric acid (Baiying Chemical Co. Ltd, China). Other chemicals were of analytical grade and used as received.

### Graft copolymerization

Polymerization reaction was carried out in a 250mL

Three-neck flask equipped with a stirrer and condenser. Pullulan was added to distilled water, stirred for about 30 min at 45°C, then cooled to room temperature under continuous stirring. When the mixtures were fully mixed, the required amount of vinyl monomers, paraffin oil, Span 80 and CAN (used as initiator) were added in. The  $\text{N}_2$  gas was purged into the flask to remove the presence of the oxygen. Under nitrogen atmosphere, the three-neck flask was placed in a microwave reactor with a power of 70W for 2 h at 60°C. After reaction, the crude products were extracted with benzene in a Soxhlets extractor for 24 h to remove homopolymer, and pure copolymer were then dried at 40°C to constant weight.

The Percentage of grafting (G%) and grafting efficiency (GE%) was calculated from the equation given below:

$$\text{Percentage of grafting} = \frac{\text{Weight of graft polymer}}{\text{weight of backbone}} \times 100$$

$$\text{Grafting efficiency} = \frac{\text{weight of graft polymer}}{\text{weight of graft polymer} + \text{weight of homopolymer}} \times 100$$

Various grafted copolymers with different G% and GE% were prepared by changing the reaction condi-

tions. A representative condition is 5 g pullulan, 40.0 ml water, 20 mmol vinyl monomers and 0.25 mmol CAN. The G% and GE% of the resulted sample were 65% and 70%.

### Infrared (IR) spectroscopy

The IR spectra of copolymer and pullulan powdered in KBr wafer were collected using a Perkin-Elmer FTIR 1725 spectrometer. Spectra were recorded in the range of 4000-5000 $\text{cm}^{-1}$ .

### Scanning electron microscopy

The surface morphology of copolymer and pullulan samples were studied using a JSM-120 microscope (Japan). The specimen in the form of films were mounted on the specimen stabs and coated with thin film of gold by the ion sputtering method, then tested on vacuum.

### Thermogravimetric analysis

The samples of pure pullulan and copolymer were tested on a Shimadzu Thermal Analyzer DT-40 TGA system in the temperature range of 25-500 $^{\circ}\text{C}$  with a heating rate of 10K/min.

### X-ray diffraction studies

The X-ray powder diffraction (XRD) of the representative copolymer sample and pure pullulan was performed on a D/max-RB diffractometer, using  $\text{Cu K}\alpha$  radiation with a scanning angle ( $2\theta$ ) of 5–80 $^{\circ}$  and a voltage and current of 40 kV and 100mA.

### UV-Vis absorption spectroscopy

The absorption spectra were determined by means of U-3400 UV-Vis spectrophotometer (Japan) with matched quartz absorption cells and the solvent as the reference standard. The sample solutions (approximately

2.5mg grafted copolymer and vinyl monomers were dissolved in 100mL freshly distilled DMSO respectively) were irradiated under 365 nm light from ultraviolet lamp.

## RESULTS AND DISCUSSION

### Infrared spectra analysis

The IR spectra of pure pullulan and copolymer are shown in figure 1. Both of the spectra had similar absorption peaks at 3450-3520 $\text{cm}^{-1}$  due to O-H stretching and bending modes, respectively. Additional characteristic bands of pullulan appeared at 1108 $\text{cm}^{-1}$  due to C-O stretching and bending vibration. The IR spectra of copolymer showed new absorption at 2925 $\text{cm}^{-1}$  of  $-\text{CH}_2$  stretching, 1655 $\text{cm}^{-1}$  of C = O stretching, and 1545  $\text{cm}^{-1}$  were related to stretching vibration of the phenyl groups. From the FT-IR spectra, it can be concluded that azo vinyl monomers were grafted on pullulan successfully.

### SEM analysis

The SEM micrographs of Pullulan and copolymer are shown in figure 2 and figure 3. Surface morphology of Pullulan before grafting shows a floccus structure, which has been changed to thorn form after grafting. In other respects, Pullulan surface have a smoother and more homogeneous appearance than grafted copolymers. The heterogeneous appearance of surfaces is another proof of grafting.

### Thermogravimetric analysis

Thermogravimetric analysis (TGA) of Pullulan showed that decomposition of Pullulan started at 210 $^{\circ}\text{C}$ , and it was a single step degradation process (Figure 4). The rate of weight loss increased initially but after 80% weight loss, the rate was found to decrease. It was con-

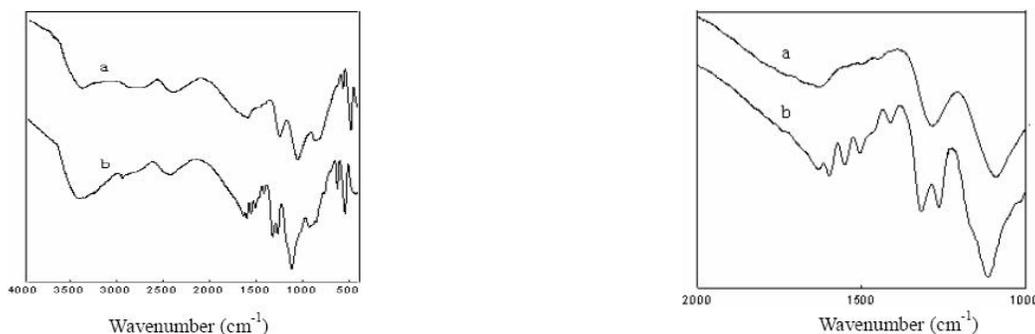
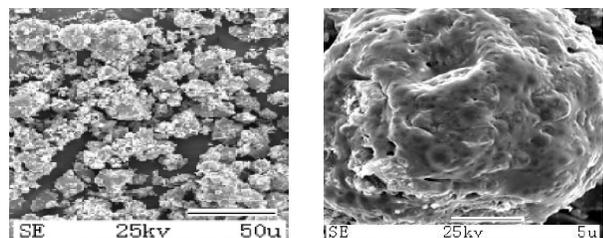
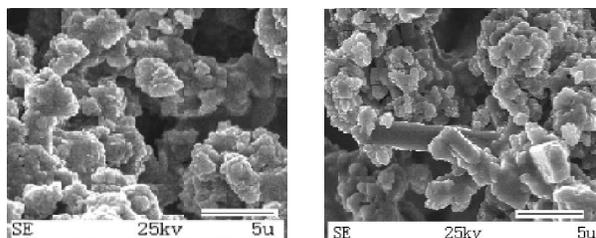


Figure 1 : IR spectra of pullulan (a) and graft copolymer (b)

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(a) (b)  
Figure 2 : SEM photos of pullulan



(c) (d)  
Figure 3 : SEM photos of graft copolymer

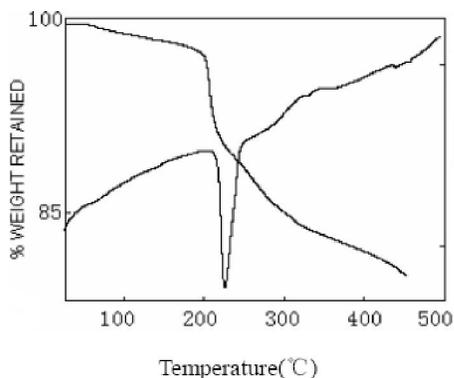


Figure 4 : TGA curves of the Pullulan

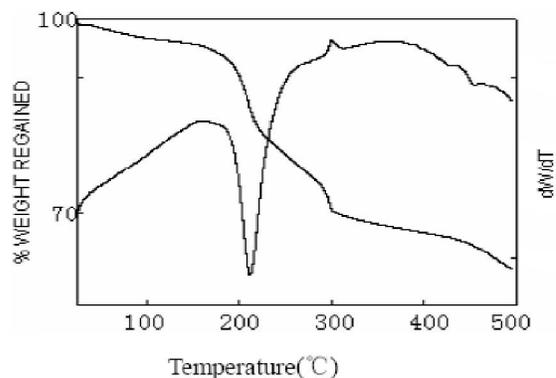


Figure 5 : TGA curves of the graft copolymer

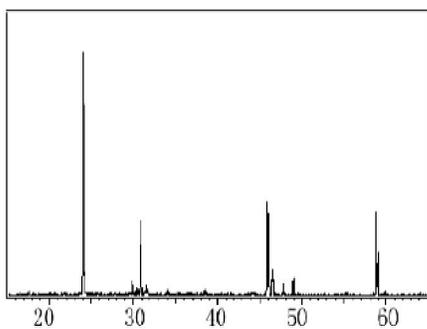


Figure 6 : XRD spectra of pullulan

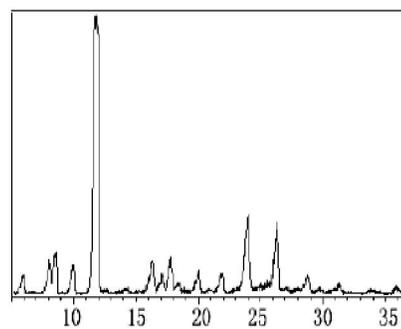


Figure 7 : XRD spectra of graft copolymer

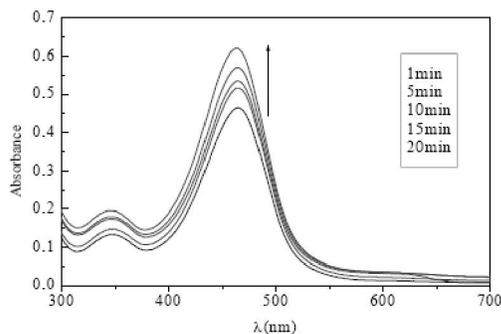


Figure 8 : UV spectra of azo monomers sample for different irradiation times in ethanol solution at 25°C

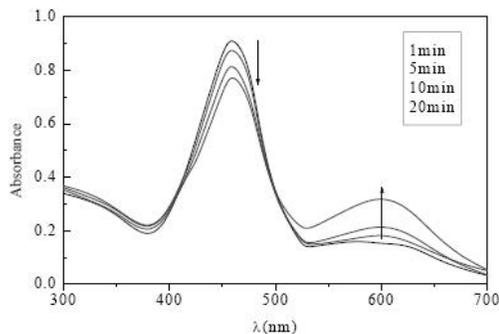


Figure 9 : UV spectra of graft copolymer sample for different irradiation times in ethanol solution at 25°C

sidered that the endothermal behaviour for pullulan should be related to its decomposition. The degradation of grafted copolymer started above 187°C. The degradation appeared to be a two stage process (Figure 5). The first stage of weight, from 187°C to 240°C,

was due to decomposition of lateral group. The second stage, from 240°C to 295°C, may be a result of pullulan decomposition. It indicated that the monomers have been grafted on pullulan, and significantly altered the thermal stability of Pullulan.

## X-ray diffraction studies

XRD analysis showed that both Pullulan and copolymer exhibit crystallinity (Figure 6 and Figure 7). In the case of Pullulan, the crystalline peaks appear in the  $2\theta$  range of  $24-60^\circ$ . However, in the grafted products, some crystalline peaks of Pullulan disappeared but other new crystalline peaks ( $2\theta = 8^\circ, 10^\circ, 12^\circ, 25^\circ$ ) appeared. It may be concluded that grafting leads to disruption in the crystalline structure of Pullulan, and new crystalline came into being.

## UV-Vis absorption spectroscopy

Figure 8 and figure 9 illustrated the behavior of photoisomerization at 365nm UV irradiation on the vinyl monomer and pullulan copolymer in DMSO solution at room temperature. As it can be seen from figure 8, the absorption maximum for the trans isomer is found at 467.0nm. With the increase of irradiation time, the  $\lambda_{\max}$  position didn't shift, and the cis isomers could not be observed, which showed that photoisomerization did not take place. Figure 9 is the UV spectroscopy of copolymer before and after irradiation, the trans isomer absorption peak around 467.0nm, and the cis isomer absorption peak around at 600nm. As the solution was irradiated, the intensity of absorption at 467.0nm ( $\lambda_{\max}$ ) decreased, which due to the  $\pi-\pi^*$  transition, while the cis isomer absorption at 600nm increased, which due to the  $n-\pi^*$  transition. We can also observe two isobestic points at 419.9nm and 485.0 nm, indicating that the photoisomerization is only chemical transformation without other side reactions, such as photodegradation<sup>[29,30]</sup>.

As described above, the pullulan copolymer have much better photochromism property than the corresponding vinyl monomer. We speculated when azobenzene compounds were parts of pullulan, or bound to them, it seemed possible that pullulan conformation might be made to influence the photochromism property of the azobenzene compounds. Hence the backbone of pullulan in the main chain should be take into account, the structure of pullulan is a saturated system, which couldn't affect the  $\lambda_{\max}$  position, so the conformation of macromolecular backbone must be a key factor in photoisomerization process. We consider the effect of macromolecular conformation have two facets usually, one is positive, the other is negative. Negatively

effect always might hinder the photoisomerization process of the azobenzene compounds, even impairs or balance out completely the appearance of absorption spectra and displacement completely<sup>[31,32]</sup>. However positive effect strengthen, promote the photoisomerization process. Based on the available evidence revealed in our present work, we deduced that pullulan macromolecule backbone is normally coiled, it may be made to overcrowd by binding azobenzene compounds in the trans form, and therefore the pullulan macromolecule backbone have a trend to relax into its neutral coil conformation. Upon irradiation by 365 nm UV light, if the trans form turn to the cis form, azobenzene compounds could not to binds so tightly as they do in the trans form. When they leave the pullulan macromolecule domain, so do their charges, allowing the pullulan macromolecule backbone to relax into its neutral coil conformation. As a result of this mutual influence, the pullulan copolymer did a positive effect to retroactive its structure and promote the photoisomerization process of azobenzene compounds. We also consider if the pullulan copolymer macromolecule is forced into a changed conformation in solution, there might occur a conversion of energy. We will continue our studies on the interesting phenomenon and get down to brass tacks.

## CONCLUSIONS

In this study, the feasibility of grafting azobenzene compound NPANO onto pullulan using CAN initiator was performed. The existence of graft polymerization was proved by the FTIR spectra, SEM analysis, thermogravimetric analysis and X-ray diffraction studies. All of the results indicated that graft reaction has occurred. We also found the copolymer has better photochromism property than corresponding vinyl monomer containing NPANO. We considered that macromolecular backbone of pullulan should have actively effect on photochromism property of the copolymer.

## ACKNOWLEDGEMENT

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