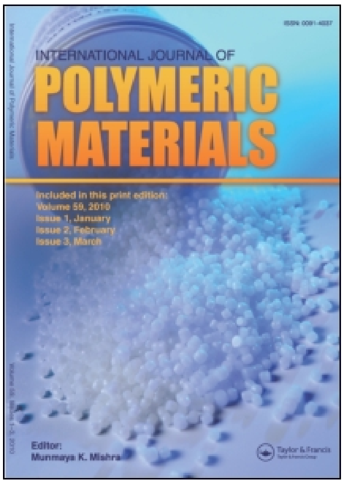


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Synthesis and Characterization of Photochromic Copolymer Grafting Azoaromatic Chromospheres on Pullulan

Xinghai Yu[a]; Zhengsheng Fu[b]; Honggang An[a]; Dongqing Wu[a]; Yuqi Han[a]; Hai Song[a]
[a] Department of Chemistry, Hexi University, Zhang Ye, China [b] College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou, China

To cite this Article Yu, Xinghai , Fu, Zhengsheng , An, Honggang , Wu, Dongqing , Han, Yuqi and Song, Hai(2011) 'Synthesis and Characterization of Photochromic Copolymer Grafting Azoaromatic Chromospheres on Pullulan', International Journal of Polymeric Materials, 60: 1, 40 — 50

To link to this Article: DOI: 10.1080/00914037.2010.504155

URL: http://dx.doi.org/10.1080/00914037.2010.504155

International Journal of Polymeric Materials, 60:40–50, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914037.2010.504155

Synthesis and Characterization of Photochromic Copolymer Grafting Azoaromatic Chromospheres on Pullulan

Xinghai Yu,[1] Zhengsheng Fu,[2] Honggang An,[1] Dongqing Wu,[1] Yuqi Han,[1] and Hai Song[1]

[1]Department of Chemistry, Hexi University, Zhang Ye, China
[2]College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou, China

Preparation of photochromic copolymer grafting 4-(4-nitro phenylazo)-1-naphthol units on a pullulan molecular surface has been accomplished. Surface modification was carried out in aqueous solution 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 a pullulan molecular surface. The results indicated that functional copolymer has a better photochromism property than its corresponding azobenzene moieties, reflecting the macromolecular backbone of pullulan should actively affect the photoisomerization of azoaromatic moieties.

Keywords azoaromatic compounds, graft copolymer, photochromic, pullulan

---

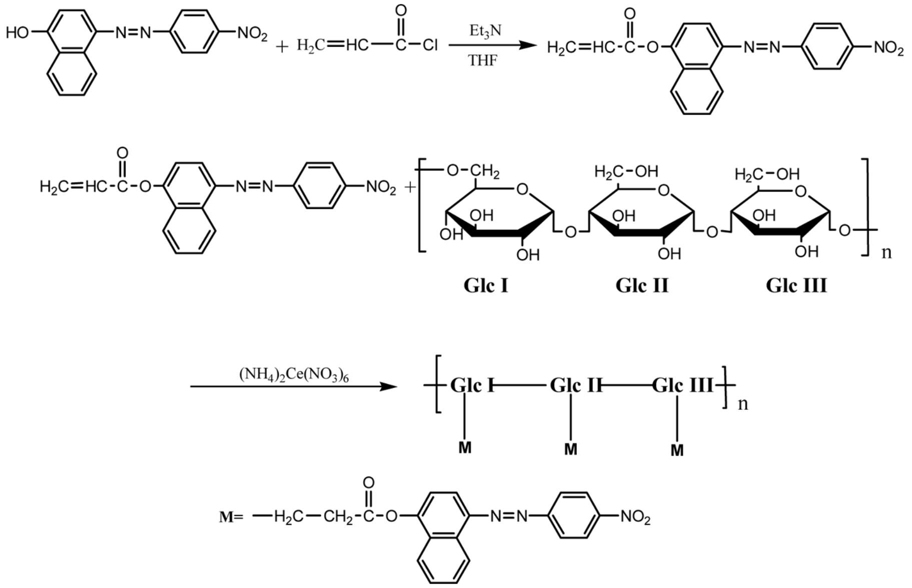
Received 23 February 2010; accepted 28 April 2010.
We gratefully acknowledge the Hexi University and Northwest Normal University for their financial support.
Address correspondence to Xinghai Yu, Hexi University, Zhang Ye, China 734000. E-mail: yuxinghai455@163.com

INTRODUCTION

Azoaromatic compounds have attracted much attention due to their novel photochromic properties [1–6]. The synthesis of a photochromic polymer containing azoaromatic chromophores has attracted interest in recent years, because it can be used as a material for optical data storage, information processing, holographs and electro-optic applications [7–11]. 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 [12–14]. 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 [15,16]. Unlike starch and cellulose, pullulan is easily soluble in water and dimethyl sulfoxide (DMSO), even though its molecular weight is higher, and consequently deemed to be a promising material for synthetic polymer. So much increasing attention has been paid to chemical modification of pullulan [17–21].

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 a 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 [22–24]. Micromolecular azobenzene



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

compounds generally have more excellent photochromism than macromolecular ones [25,26]. In our present experiment, the photochromism property of pullulan which grafted azobenzene compounds has been monitored by UV-vis spectroscopy in DMSO solution under 365 nm ultraviolet light irradiated. Surprisingly, the results showed that pullulan copolymer had a much better photochromism property than the corresponding vinyl monomer containing NPANO. We consider the results demonstrated pullulan's macromolecular backbone should exert an influence on the photochromism property of the copolymer in a dramatic way.

EXPERIMENTAL

Materials and Methods

Pullulan (M/W = 150,000) supplied by NWNU Bioengineering Lab (China), was dried at 40°C for 20 h before use. 4-(4-nitro phenylazo)-1-naphthol (Shanghai Chemical Co. Ltd, China) was dried over anhydrous $CaCl_2$ and stored in a refrigerator. The vinyl monomers were prepared according to the method described in the literature [27,28]. Ceric ammonium nitrate (CAN) (Beijing Chemical Co. Ltd, China) was dried in an air oven at 100°C for about 5 h, and 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 250 mL three-neck flask equipped with a stirrer and condenser. Pulluan 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 an initiator) were added in. The 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 70 W for 2 h at 60°C. After reaction, the crude products were extracted with benzene in a Soxhlets extractor for 24 h to remove the homopolymer and pure copolymer was 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 conditions. 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 cm^{-1}.

Scanning Electron Microscopy

The surface morphology of the copolymer and pullulan samples was studied using a JSM-120 microscope (Japan). The specimens in the form of films were mounted on the specimen slabs and coated with thin film of gold by the ion sputtering method, then tested in 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°C with a heating rate of 10 K/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 Cu Kα radiation with a scanning angle (2θ) of 5–80° and a voltage and current of 40 kV and 100 mA.

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

RESULTS AND DISCUSSION

Infrared Spectra Analysis

The IR spectra of pure pullulan and the copolymer are shown in Figure 1. Both of the spectra had similar absorption peaks at 3450–3520 cm^{-1} due to O$-$H stretching and bending modes, respectively. Additional characteristic bands of pullulan appeared at 1108 cm^{-1} due to C$-$O stretching and bending vibration. The IR spectra of copolymer showed new absorption at 2925 cm^{-1} of $-CH_2$ stretching, 1655 cm^{-1} of C=O stretching, and 1545 cm^{-1} were related to stretching vibration of the phenyl groups. From the FTIR 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, the pullulan surface has 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°C, and it was a single-step degradation process (Figure 4). The rate of weight loss increased initially but after 80% weight loss,

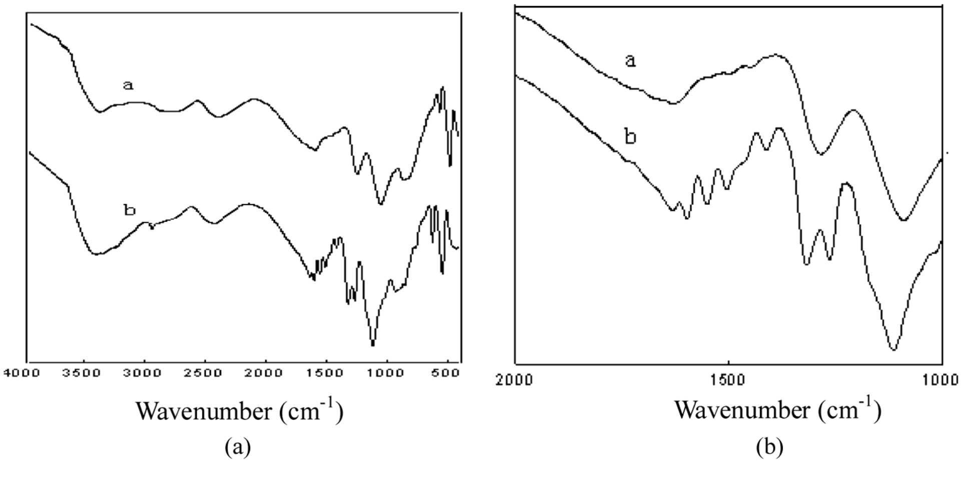


Figure 1: IR spectra of pullulan (a) and graft copolymer (b).

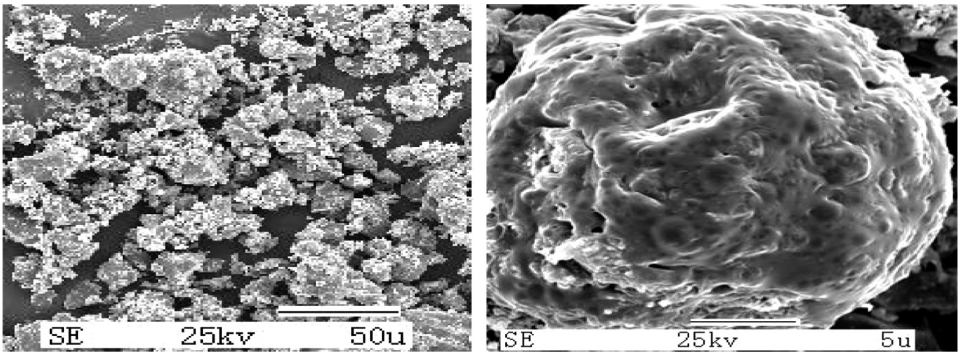


Figure 2: SEM photos of pullulan.

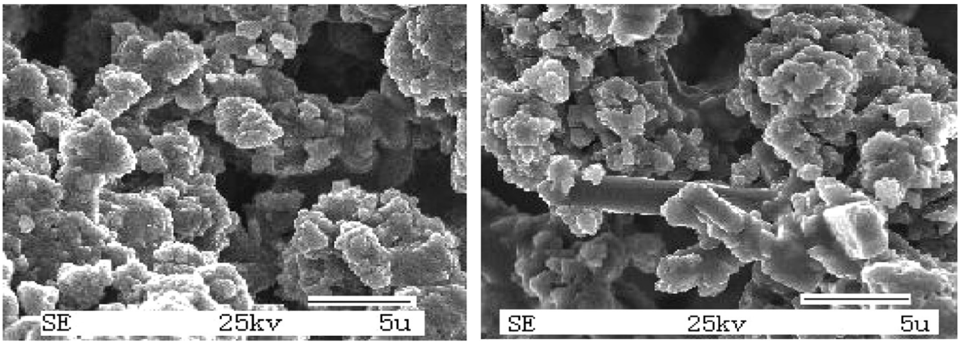


Figure 3: SEM photos of graft copolymer.

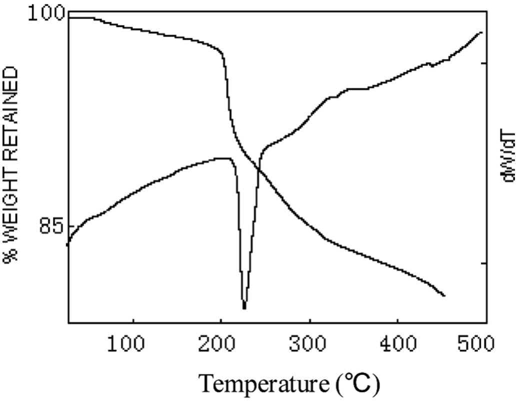


Figure 4: TGA curves of the pullulan.

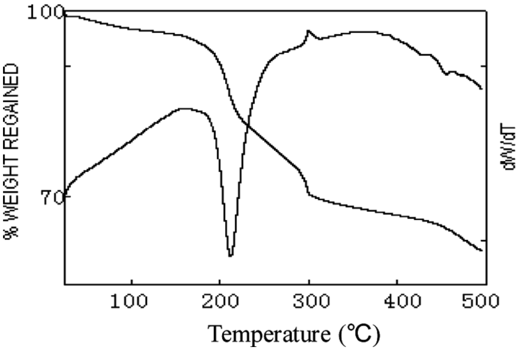


Figure 5: TGA curves of the graft copolymer.

the rate was found to decrease. It was considered that the endothermal behavior 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 the 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 2θ range of 24–60°. However, in the grafted products, some crystalline peaks of pullulan disappeared but other new crystalline peaks

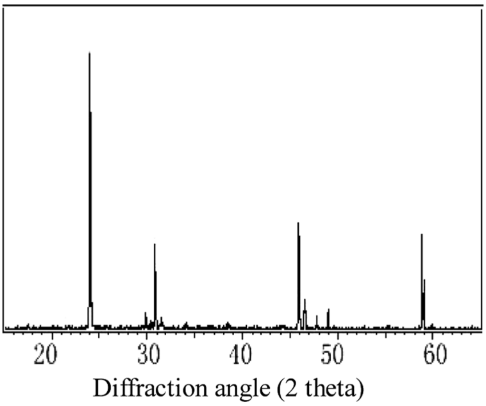


Figure 6: XRD spectra of pullulan.

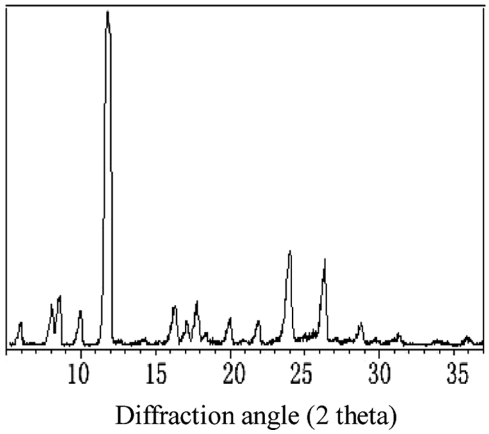


Figure 7: XRD spectra of graft copolymer.

($2\theta = 8°, 10°, 12°, 25°$) appeared. It may be concluded that grafting leads to disruption in the crystalline structure of pullulan, and a new crystalline peak came into being.

UV-vis Absorption Spectroscopy

Figure 8 and Figure 9 illustrated the behavior of photoisomerization at 365 nm 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 467.0 nm. With the increase of irradiation time, the λ_{max} position didn't shift, and the cis isomers

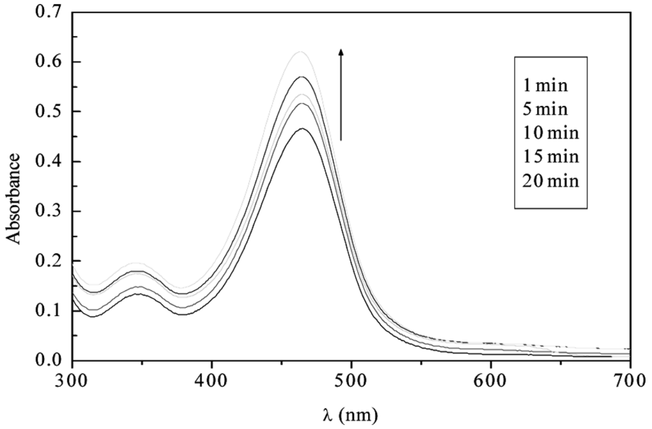


Figure 8: UV spectra of azo monomers sample for different irradiation times in ethanol solution at 25°C.

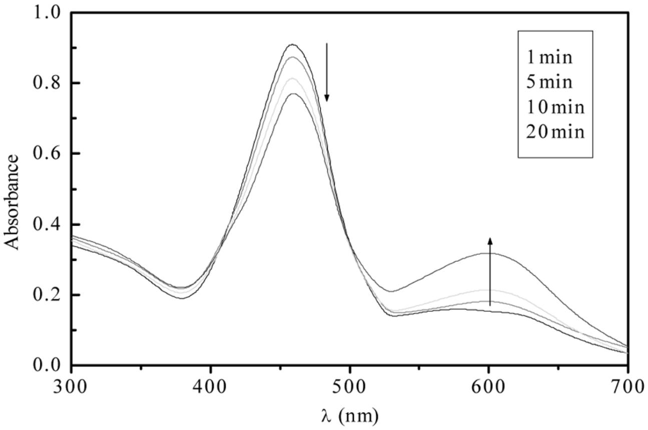


Figure 9: UV spectra of graft copolymer sample for different irradiation times in ethanol solution at 25°C.

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 467.0 nm, and the cis isomer absorption peak around at 600 nm. As the solution was irradiated, the intensity of absorption at 467.0 nm (λ_{max}) decreased, which is due to the π-π^* transition, while the cis isomer absorption at 600 nm increased, which is due to the n-π^* transition. We can also observe two isobestitic points at 419.9 nm and 485.0 nm, indicating that the photoisomerization is only a chemical transformation without other side reactions, such as photodegradation [29,30].

As described above, the pullulan copolymer has a 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 λ_{max} position, so the conformation of the macromolecular backbone must be a key factor in the photoisomerization process. We consider the effect of macromolecular conformation as having two facets; usually, one is positive, the other is negative. The negatively effect might always hinder the photoisomerization process of the azobenzene compounds, even impair or balance out completely the appearance of absorption spectra and displacement completely [31,32]. However a positive effect may strengthen and promote the photoisomerization process. Based on the available evidence revealed in our present work, we deduced that the pullulan macromolecule backbone is normally coiled, and may be made to overcrowd by binding azobenzene compounds in the trans form, and therefore the pullulan macromolecule backbone has a trend to relax into its neutral coil conformation. Upon irradiation by 365 nm UV light, if the trans form turn into the cis form, azobenzene compounds could not bind 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 a 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 a better photochromism property than the corresponding vinyl monomer containing NPANO. We considered that the macromolecular backbone of pullulan should have an active effect on the photochromism property of the copolymer.

REFERENCES

[1] Grebenkin, S. Y., and Bol'shakovb, B. V. *J. Photochem. Photobiol. A* **122**, 205 (1999).

[2] Cimiraglia, R., and Hofmann, H. *Chem. Phys. Lett.* **217**, 430 (1994).

[3] Grebenkin, S. Y., and Bol'shakov, B. V. *J. Photochem. Photobiol. A* **184**, 155–162 (2006).

[4] Balcerzak, E. S., Sobolewska, A., and Miniewicz, A. *Opt. Mater.* **31**, 405 (2008).

[5] Han, M., Ishikawa, D., Muto, E., and Hara, M. *J. Lumin.* **129**, 1163 (2009).

[6] Masuda, T., Asari, S., Tamagaki, S., and Nagasaki, T. *Tetrahedron. Lett.* **41**, 2411 (2000).

[7] Ravi, P., Sin, S. L., Gan, L. H., Gan, Y. Y., Tam, K. C., Xi, X. L., and Hu, X. *Polym.* **46**, 137 (2005).

[8] Beattie, M. S., Jackson, C., and Jaycox, G. D. *Polym.* **39**, 2597 (1998).

[9] Pourjavadi, A., Mirjalili, B. F., Entezami, A. A., and Mehr, M. J. Z. *Eur. Polym. J.* **37**, 2111 (2001).

[10] Mooter, G. V., Samyn, C., and Kinget, R. *Int. J. Pharm.* **87**, 37 (1992).

[11] Bhatnagar, A., Schroder, A., and Mohanty, D. K. *Polym.* **36**, 3019 (1995).

[12] Kim, H. T., Lee, J. W., Sung, S. J., and Park, J. K. *Liq. Cryst.* **27**, 1343 (2000).

[13] Niemann, M., and Ritter, H. *J. Markromol Chem.* **194**, 1169 (1993).

[14] Balcerzak, E. S., Sapich, B., and Stumpe, J. *Polym.* **46**, 49 (2005).

[15] Lazaridou, A., Biliaderis, C. G., and Kontogiorgos, V. *Carbohydr. Polym.* **52**, 151 (2003).

[16] Seo, H., Son, C., Chung, C., Jung, D., Kim, S., Gross, R., Kaplan, D., and Lee, J. *Bioresour. Technol.* **95**, 293 (2004).

[17] Mocanu, G., Vizitiu, D., Mihai, D., and Carpov, A. *Carbohydr. Polym.* **39**, 283 (1999).

[18] Hasudaa, H., Kwonb, O. H., Kangc, I. K., and Itoa, Y. *Biomater.* **26**, 2401 (2005).

[19] Mihai, D., Mocanu, G., and Carpov, A. *Eur. Polym. J.* **37**, 541 (2001).

[20] Souguir, Z., Roudesli, S., Picton, E. L., Cerf, D. L., and Jaudet, E. A. *Eur. Polym. J.* **43**, 4940 (2007).

[21] Bruneel, D., and Schacht, E. *Polym.* **36**, 169 (1995).

[22] Fischer, E., and Frei, Y. *J. Chem. Phys.* **27**, 328 (1957).

[23] Fischer, E. *J. Am. Chem. Soc.* **82**, 3249 (1960).

[24] Hermann, R., and Shen, Y. Q. *J. Photochem. Photobiol. A* **42**, 321 (1988).

[25] Domenico, A., Eugenio, A., Valeria, B., and Simona, C. *Macromo.* **37**, 6418 (2004).

[26] Rachkov, A., Minoura, N., and Shimizu, T. *Opt. Mater.* **21**, 307 (2002).

[27] Khalil, A. A., Moustafa, H. Y., and Arief, M. M. H. *Eur. Polym. J.* **32**, 647 (1996).

[28] Fu, Z. S., Sun, B. B., Chen, J., and Yuan, L. *Dyes Pigm.* **76**, 515 (2008).

[29] Buruiana, T., Buruiana, E. C., Airinei, A., and Grecu, I. *Eur. Polym. J.* **37**, 343 (2001).

[30] Ankur, R., Sudeshna, B., Subir, G., Tapan, G., and Anup, B. *Tetrahedron Lett.* **48**, 8078 (2007).

[31] Sacarescu, L., Sacarescu, G., Simionescu, M., and Hurduc, N. *J. Inorg. Organomet. Polym. Mater.* **19**, 348 (2009).

[32] Jin, M., Lu, R., Yang, Q. X., Bao, C. Y., Sheng, R., Xu, T. H., and Zhao, Y. Y. *J. Polym. Sci. A: Polym. Chem.* **45**, 3460 (2007).