

Communication

Photografting of Polystyrene: III. Preparation of Chemically Modified Polystyrene Containing Oxime-Ester Groups and its Photografting with Hydroxyethyl Methacrylate

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Special properties are required for the successful application of polymers to the fields of adhesion, biomaterials, protective coatings, microelectronics devices, and thin film technology. Polymers have excellent bulk physical and chemical properties, but they often do not possess the properties needed for such applications. For this reason, modification of polymers has become an important area in the polymer industry [1].

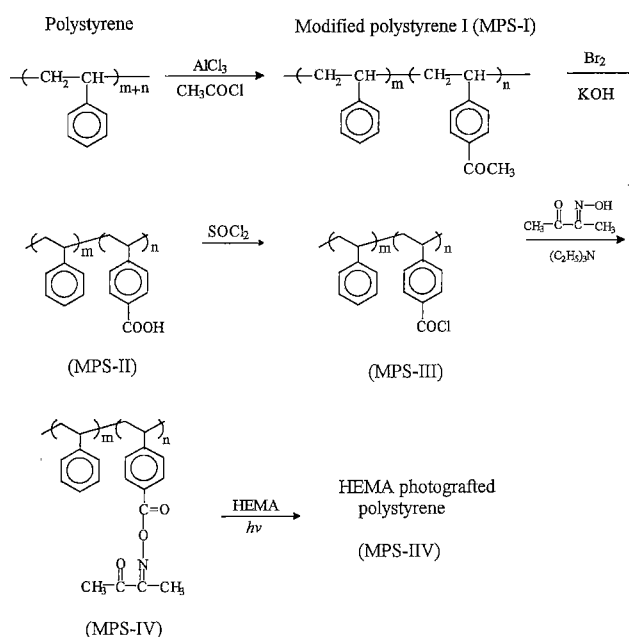
Many processes have been developed to modify polymers, including chemical, photochemical, plasma, corona and flame treatments, and surface grafting [2, 3]. UV irradiation is one of the simple, efficient, and inexpensive methods used in surface modification. Photochemical modification of polymers has been used for the introduction of functional groups [4, 5] and special compounds [6-9], immobilization of biomolecules [10], and for adhesion enhancement of metals [11]. UV irradiation of a polymer containing photosensitive groups induces an alternation of various physical properties of polymer surfaces such as wettability, bondability, solubility, and dyability, etc.

Polystyrene (PS) is widely used in packaging, housewares, appliances, and furniture, electrical and electronic parts, construction, transportation etc. because of its low cost and acceptable mechanical properties. Although the market finds excellent utilities for PS, PS has several limitations for special uses [11]. Among the important physical deficiencies are that PS is hydrophobic property which limit its biomedical applications.

In previous studies, we reported that a styrene copolymer containing oxime-ester groups [12] and a commercially available styrene-ethylene-butylene-styrene (SEBS) [13] rubber were photografted with the hydrophilic monomers such as 2-hydroxyethyl methacrylate (HEMA) or methacrylic

acid resulting in the hydrophilically modified PS. In this paper, we report on the preparation of a chemically modified PS containing oxime-ester groups and its photografting reaction with HEMA in order to prepare a hydrophilically modified PS.

Scheme 1 shows a synthetic route for the preparation of a chemically modified PS containing oxime-ester groups. A modified polystyrene-I (MPS-I), acetylated polystyrene was prepared by the Friedel-Crafts acylation of PS. A modified polystyrene-II (MPS-II) containing carboxylic acid groups was prepared by the bromoform reaction of MPS-I. Treatment of MPS-II with SOCl_2 resulted in the formation of a modified polystyrene-III (MPS-III) that contains benzoyl chloride groups. A modified polystyrene-IV (MPS-IV) bearing oxime-ester groups was prepared by the reaction of MPS-III with butanedione monooxime (BDMX) in the presence



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Scheme 1.

of triethylamine. The progress of reaction was monitored by the IR absorption spectroscopy.

A starting polymer, PS was prepared by polymerization of styrene (60 ml, 0.52 mole) in the presence of AIBN (0.25 g) as an initiator at 60 °C for 30 min, 65 °C for 1 hour, 70 °C for 2 hours, and 75 °C for 12 hours, consecutively. The resulting polymer was purified by precipitation twice in methanol with 60% yield. Number average molecular weight determined by GPC was 41,200 with polydispersity of 1.7.

A acetylated PS, MPS-I, was prepared as follows: PS (10 g) was dissolved in CS₂ by refluxing at 70 °C for 10 min. After cooling to room temperature, AlCl₃ (10 g, 0.074 mole) was added to the PS solution and the mixture was stirred for 1 hour at room temperature. Acetyl chloride (6.5 ml, 0.083 mole) in 20 ml of CS₂ was added to the reaction mixture and refluxed for 12 hours with stirring. The product was isolated by precipitation into water after washing twice with H₂SO₄/H₂O/dioxane (1/7/8, v/v) solution, followed by washing with water, dioxane, and methanol, consecutively. Yield of MPS-I was 95 %.

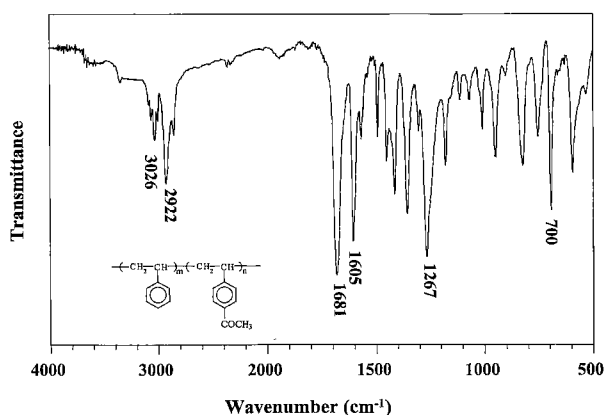


Figure 1. FT-IR spectrum of the MPS-I (KB pellet).

Figure 1 shows FT-IR spectrum of MPS-I. A new absorption band due to the formation of carbonyl group was appeared at 1681 cm⁻¹ indicating acetylation of benzene groups in the PS.

A carboxylated PS, MPS-II, was prepared by haloform reaction of MPS-I. MPS-I (6 g) was dissolved in dioxane (30 ml) by refluxing for 10 min. After being cooled to room temperature, a mixture of KOH (20 g), H₂O (30 ml), dioxane (130 ml), and Br₂ (6 ml) was added slowly to the MPS-I solution and maintained below 10 °C for 2 hours. After stirring overnight at room temperature, the reaction mixture was concentrated under reduced pressure and then precipitated into 0.2 N HCl solution. The precipitate was washed two or three times with water and then with methanol. Yield of MPS-II was 70 wt%. MPS-II was soluble in DMF, dioxane, THF, or DMSO, while insoluble in toluene, chloroform or benzene.

Figure 2 shows FT-IR spectrum of MPS-II. Appearance

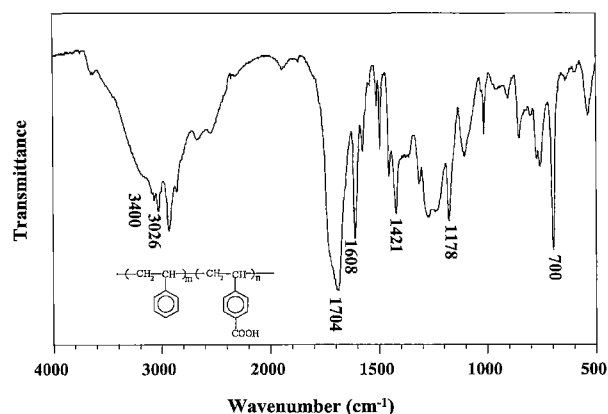


Figure 2. FT-IR spectrum of the MPS-II (KBr pellet).

of new strong absorption bands at 3400 and 1704 cm⁻¹ indicates the formation of -COOH groups by the haloform reaction of acetyl groups in MPS-I.

MPS-III that contains benzoyl chloride groups was prepared by chlorination of -COOH groups in MPS-II with SOCl₂. MPS-II (0.3 g) was dispersed in benzene (10 ml) and DMF (2 ml) mixture. SOCl₂ (0.5 ml) was added to the MPS-II solution slowly, and the reaction mixture was refluxed for one day. The solution was concentrated by simple distillation, and SOCl₂ and DMF were removed under reduced pressure. As the benzoyl chloride groups in MPS-III were too reactive to isolate, MPS-III was used for next step without further purification.

MPS-IV, a modified PS containing oxime-ester groups was prepared by the reaction of MPS-III with BDMX. BDMX (0.1 g) and triethylamine (0.1 ml) in THF (5 ml) was added dropwise to a solution of MPS-III (1.0 g) in THF (5 ml) with stirring for 3 hours at room temperature. The reaction mixture was maintained at 40 °C for 12 hours with stirring. MPS-IV was isolated by precipitation into methanol with 40 wt% yield.

Figure 3 shows FT-IR spectrum of MPS-IV. New absorption bands at 1717 and 1690 cm⁻¹ are due to the stretching

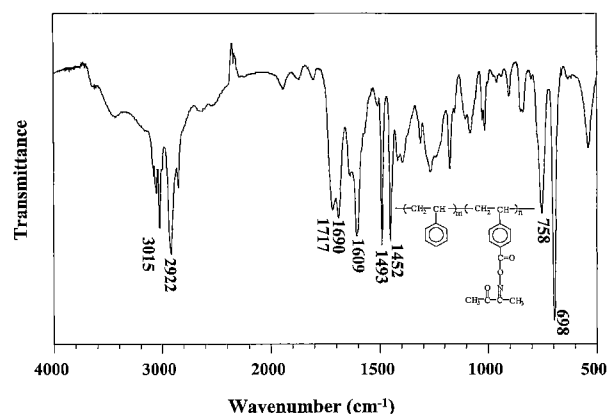


Figure 3. FT-IR spectrum of the MPS-IV (KBr pellet).

vibration of the carbonyl group of ester and BDMX moieties, respectively. The IR spectrum of MPS-IV is similar to that of the styrene - butanedionemonooxime vinylbenzoate copolymer [11] which was reported previously. These results indicate that the PS was chemically modified to have BDXM groups.

Photografting of MPS-IV with HEMA was carried out as following procedure: A mixture of MPS-IV (0.1 g), HEMA (0.9 ml), and THF (4 ml) in a quartz tube was irradiated with 254 nm UV light after bubbling N₂ for 20 min. The photografted copolymer was isolated by precipitation from the irradiation mixture into methanol, and purified by extraction with methanol for one day in the Soxhlet extractor to remove the homopolymer of HEMA.

Figure 4 shows FT-IR spectrum of the HEMA photografted PS. Two broad absorption bands at 3400 and 1730 cm⁻¹ are due to the -OH and carbonyl groups of PS photografted with HEMA.

Table 1 shows the physical properties of the modified PS and PS photografted with HEMA. The contact angle of PS

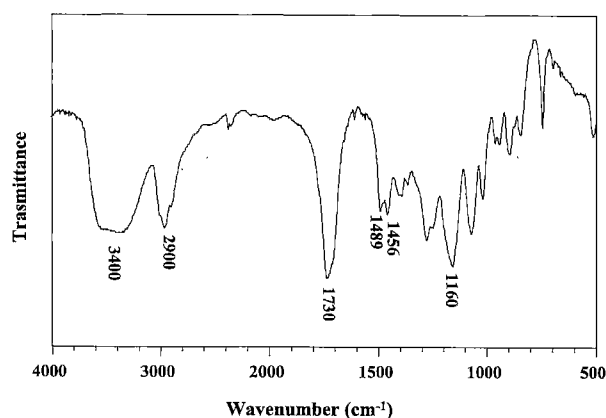


Figure 4. FT-IR spectrum of PS photografted with HEMA (KBr pellet).

and poly(HEMA) is 91 and 60°, respectively. The contact angle of MPS-1 is similar to that of an unmodified PS, while that of MPS-II is greatly reduced after introduction of -COOH groups. The contact angle of MPS-IV, a modified PS which contains oxime-urethane groups is again increased upto 104.5°. The contact angle of PS photografted with HEMA lies between that of unmodified PS (91°) and poly(HEMA) (60°).

The absorption band at 1730 cm⁻¹ increased with the content of the grafted poly(HEMA). The photografting yield of MPS-IV with HEMA was determined from the IR absorption spectra. Figure 5 shows photografting yield of MPS-IV as a function of irradiation time upon irradiation with 254

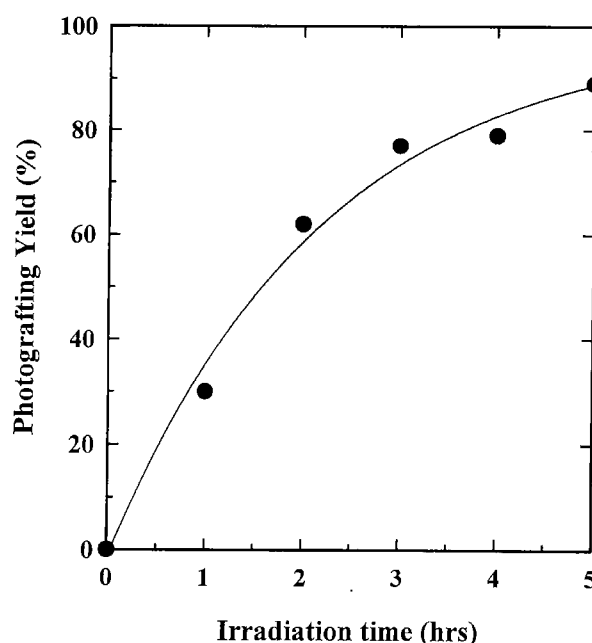


Figure 5. Effect of irradiation time on photografting yield of HEMA on MPS-IV upon irradiation with 254 nm UV light.

Table 1. Physical Properties of Modified PS.

Compounds	Solubility			η_{inh}^a	Contact angle (θ)
	Soluble	Moderately soluble	Insoluble		
MPS-I	THF, DMF, dioxane, chloroform	acetone	benzene, toluene, CH ₃ CN	0.568	93.6 °
MPS-II		DMF, dioxane, THF, DMSO	CH ₃ CN, chloroform, toluene, benzene	0.208	0-6 °
MPS-IV	DMF, DMSO	THF, chloroform	CS ₂ , CH ₃ CN, diethyl ether, benzene, toluene, dioxane	0.266	104.5 °
HEMA-g-PS	DMF, DMSO	THF, dioxane, chloroform	acetone, CH ₃ CN, benzene, toluene	0.342	85 °

^a Inherent viscosity was measured in DMF at concentration of 0.5 g/dl.

nm UV light. The photografting yield was increased with irradiation time, and it reached to 90 % at 5 hours of irradiation time.

In conclusion, we prepared a chemically modified polystyrene bearing oxime-urethane groups and it was successfully photografted with HEMA resulting in the change of the hydrophobic property of polystyrene to hydrophilic. A more detailed study on the surface modification of PS by photografting will be in progress.

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