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Radiation grafting of oligo(ethylene glycol) ethyl ether methacrylate on polypropylene

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HIGHLIGHTS

- Irradiation was used to obtain polypropylene grafted by thermosensitive polymer.
- Formation of thermosensitive layer was indicated by FT-IR and contact angle.
- Grafting degree can be controlled by dose, monomer concentration and reaction time.
- Thermosensitive layers may find application as substrates for skin cell culturing.

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ABSTRACT

Oligo(ethylene glycol) ethyl ether methacrylate (OEGMA) can be grafted onto polypropylene (PP) films by post-irradiation grafting, forming a thermosensitive polymer layer, as indicated by FT-IR and contact angle measurements. In the first step, PP foils are irradiated by electron beam (5.5 kGy/min, up to 300 kGy) in the presence of air. Subsequently, the irradiated foils react with the monomer in oxygen-free solutions in isopropanol (up to 2 M of monomer) at 70 °C. Degree of grafting of OEGMA can be controlled by proper selection of absorbed dose, monomer concentration and reaction time. This work is a part of a broader project on thermosensitive materials facilitating cell growth and detachment for optimizing cell layer engineering techniques in the treatment of burn wounds.

1. Introduction

In cell layer engineering, in particular in cultivating skin cell layers for treatment of large-surface skin burns, there is a need for a suitable polymer substrate. An ideal case would be a substrate to which the cells adhere well, proliferate and form fully confluent, continuous layers, but then upon applying some simple stimulus, safe for the living cells, a complete and relatively rapid detachment of whole cell layer could be achieved. Since most cells can survive short-term lowering of temperature (e.g., from the standard 37 °C used in cell cultures to room temperature or even to 10–15 °C), it seems logical to design the substrate as a two-layer composite, where the bottom layer provides the mechanical strength and easy handling, while the upper layer is thermosensitive, i.e., attracts the cells at 37 °C (in general by providing partially hydrophobic character) while it repels them at a lower temperature (by becoming much more hydrophilic and water-swollen). This property can be achieved by grafting the surface of a neutral substrate, e.g., a polystyrene dish or vessel, with a thin layer of a thermosensitive polymer, the most typical (and almost solely used so far) being poly(*N*-isopropylacrylamide), PNIPAAm, cf. (Heskins and Guillet, 1968; Gil and Hudson, 2004). The phase transition temperature (Lower Critical Solution Temperature, LCST) of the latter in water is ca. 32 °C, rendering the grafting layer hydrophobic at 37 °C, and hydrophilic at R.T. While in fact such PNIPAAm-based materials have been developed and tested (Yamada et al., 1990; Yang et al., 2005,2007; Tang et al., 2012), and are even commercially available, this solution is still not fully satisfactory (problems with cell layer detachment at the stage of full confluence, lack of universal applicability to various kinds of cells of interest). Therefore attempts are being made to broaden the spectrum of thermosensitive cell substrates suitable for problem-free cell sheet culturing for burn wound treatment (see for instance (Chen et al., 2006)). The current study is a fragment of a project aimed at providing alternative materials for this purpose, by using biocompatible, thermosensitive materials other than PNIPAAm.

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In this work we investigated the possibility of classical post-irradiation grafting of oligo(ethylene glycol) ethyl ether methacrylate (OEGMA) (Structure 1) onto polypropylene. POEGMA, cf. (Han et al., 2003; Lutz et al., 2006; Ishizone et al., 2008), is a polymer of confirmed biocompatibility. In general, LCST values for polymers based on oligo(ethylene glycol) ethyl- and methyl-methacrylates vary greatly with the number of ethylene glycol units and kind of terminal group in the side chains as well as with polymer chain length. For the structure shown in Structure 1 a literature-reported LCST value in water is ca. 26 °C (Ishizone et al., 2008), while the actual monomer used in this work yields a polymer of LCST at 22 °C in water and 19 °C in typical DMEM medium used for fibroblast culture (Utrata-Wesolek and Dworak, private communication), i.e., in a suitable range for the envisaged application.

2. Experimental

2.1. Materials

Polypropylene (PP) foil (La-Mar, Poland) of 40 μm thickness was soaked in acetone for 15 min and dried at 40 °C overnight. Oligo(ethylene glycol) ethyl ether methacrylate (OEGMA monomer, Structure 1); $M=246$ g mol^{-1}, containing 100 ppm MEHQ as inhibitor (Sigma Aldrich), and isopropanol (Baker, HPLC Analyzed, 99.7%) were used as received. Water purified by MicroPure setup (TKA, Germany) had a specific resistivity of 18.2 MΩ cm. Argon (Ar BIP Plus Air Products) used to saturate the samples before grafting reaction was of $>99.95\%$ purity.

2.2. Irradiation and grafting

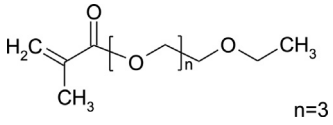
Samples of PP foil (2 × 9 cm size, total grafting area of 36 cm^2), were irradiated by electron beam in the presence of air using an ELU-6e linear electron accelerator (Elektronika, Russia, cf. (Karolczak et al., 1992)), generating pulses of 6 MeV electrons of 4 μs duration at a frequency of 20 Hz. Samples to be irradiated were mounted vertically at a distance of 160 cm from the exit of a horizontal electron beam. Absorbed doses have been determined by alanine dosimetry on a Bruker e-scan device, using Alanine Pellet Dosimeter pellets (Bruker). Average dose non-uniformity (defined as a ratio of maximum to minimum dose at various locations at the sample surface) was lower than 1.1.

Directly after irradiation, each sample was transferred to a separate glass vessel (150 ml) containing 120 ml of Ar-saturated OEGMA solution in isopropanol, and grafting reaction was carried out at 70 °C under constant Ar flow.

After grafting, each sample was washed in water for 72 h with frequent water exchange to remove unreacted monomer and free polymer, and dried at 37 °C to constant weight.

2.3. Characterization

Degree of grafting, defined as a percent of weight increase caused by the grafting procedure, has been determined gravimetrically. On that basis, grafting density was calculated (in miligram of grafted polymer per cm^2 of the substrate).



Structure 1. Chemical structure of oligo(ethylene glycol) ethyl ether methacrylate (OEGMA).

FT-IR spectra of non-grafted and grafted PP foils have been obtained using Thermo Nicolet Avatar 330 spectrophotometer (Thermo Electron Corporation, USA). Samples were mounted vertically in perpendicular direction to the analyzing light beam. Spectra were recorded in the transmission mode with 4 cm^{-1} resolution and averaged from 64 individual scans. Spectra of the (liquid) monomer were recorded on the same apparatus in the HATR mode on a Ge crystal.

Contact angle of a drop of water on the sample surface was determined using Phoenix Alpha 1000 (SEO, Korea) apparatus, at two temperatures 15 °C and 40 °C. Before measurement samples were conditioned in water for 1 h at the respective temperatures.

3. Results and discussion

Grafting has been performed by irradiating the PP foil samples in air at two doses, 150 kGy and 300 kGy, followed by reaction with OEGMA in oxygen-free solutions in isopropanol at 70 °C. Two monomer concentrations, 1 M and 2 M, have been used and the reaction time varied from 1.5–5 h. Observed increase in sample weight indicates successful grafting. Dependence of grafting degree and grafting density on experimental parameters is illustrated in Fig. 1.

As expected, the grafting degree is increased by doubling the dose, as well as by doubling the monomer concentration. Grafting increases with reaction time within the studied range of reaction time, while for the highest dose and concentration it seems to level off after ca. 2 h.

Irradiation of PP leads to the formation of alkyl radicals. Some of them react with oxygen yielding transient peroxyl radicals and subsequently labile peroxides and hydroperoxides, while a part of the initially formed radicals becomes trapped within the crystalline PP regions. Preliminary ESR observations for samples used in this work (data not shown) indicate slow decay of radical concentration within hours at R.T. One may expect that once the sample is placed in deoxygenated, hot monomer solution several processes take place side-by-side. Peroxides and hydroperoxides decompose forming oxyl radicals which react with monomer thus initiating graft polymerization. There is some diffusion of the reaction medium to deeper layers of the foil. This can gradually increase the number of active peroxide/hydroperoxide sites being exposed to monomer and probably also release and make available for reaction some of the trapped alkyl radicals.

In general, the higher the dose, the more active sites (radicals, peroxides, hydroperoxides) are available at the surface and within

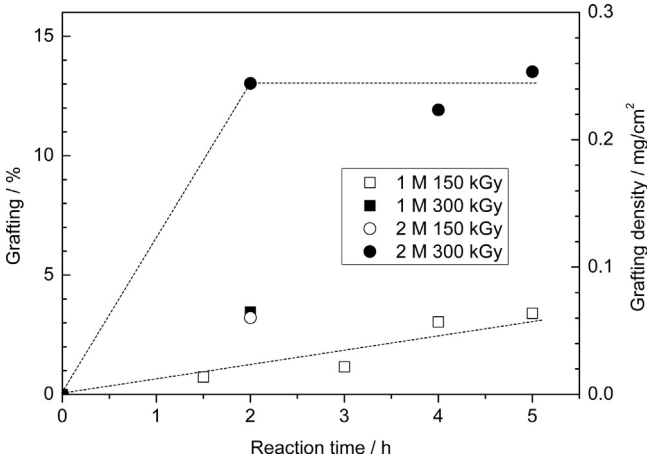


Fig. 1. Grafting percentage and grafting density in mg/cm^2 of OEGMA on PP foil as a function of reaction time for total absorbed doses: 150 kGy and 300 kGy and two different monomer solution concentration 1 M and 2 M.