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Modified polyglycidol based nanolayers of switchable philicity and their interactions with skin cells

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ABSTRACT

Temperature-responsive polymer surfaces based on modified high molar mass polyglycidol were obtained via the “grafting onto” technique. The solid support (glass or silica) was modified to introduce reactive anhydride groups. The covalent bonding of the temperature-responsive poly(glycidol-co-ethyl glycidyl carbamate) to the base support was obtained by the chemical reaction between reactive functional groups on the support and on the polymer. The surface properties, such as the composition, morphology, thickness and wettability, and their changes with the temperature were investigated using Fourier Transform Infrared Analysis, Atomic Force Microscopy, ellipsometry and contact angle measurements, respectively. The attachment of the hydrophobically modified polyglycidol derivatives produced a polymer layer with a thickness of 20–60 nm and a changeable philicity due to the temperature alterations. This unique behavior was applied to the investigation of the interaction of polymer nanolayers with skin cells (fibroblasts and keratinocytes). The skin cells adhesion to the poly(glycidol-co-ethyl glycidyl carbamate) surface was possible at temperatures above the phase separation temperature, when the polymer layer was hydrophobic.

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1. Introduction

Temperature-responsive polymer materials, such as gels, micro- and nanogels, micelles and surfaces, have gained a significant interest in recent decades [1]. Such systems recognize changes of temperature as a signal and undergo large changes of their properties over a narrow range of temperatures [2]. The temperature-dependent conformational changes of these polymer systems appear above a certain value, called the cloud point (T_{CP}) (or phase separation temperature), and are reversible.

Recently, attention has been directed toward smart, temperature-responsive surfaces. Covalently attaching a thermo-responsive polymer to a solid substrate leads to stable polymer layers with temperature-dependent

properties. Below the T_{CP} of the thermo-responsive polymer, the layer formed by this polymer exhibits hydrophilic properties – it is hydrated and its polymer chains adopt an expanded state. However, phase separation occurs as the temperature increases. Above the T_{CP} , the polymer chains collapse due to dehydration and the surface becomes hydrophobic [3].

Temperature-responsive *N*-substituted acrylamide surfaces have been the most widely investigated system. Studies have focused mainly on poly(*N*-isopropylacrylamide) (PNIPAM) [4–7] and its copolymers with *N*-tert-butylacrylamide [8], ethylene glycol [9], dimethylaminoethyl methacrylate [10], *n*-butylmethacrylate [11], acrylic acid [12], *N*-acryloxysuccinimide [13], 1-vinylimidazole [14] and vinylidene fluoride [15]. Temperature-responsive surfaces based on oligo(ethylene glycol) methacrylates [16,17], copolymers of ethylene oxide and propylene oxide [18] as well as poly(2-oxazolines) [19] have also been explored.

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Different approaches have been used to obtain temperature-responsive surfaces. In particular, the majority of studies use the “grafting from” and “grafting to” methods [20]. In the “grafting from” (also referred to as “surface-initiated polymerization”), the polymerization is initiated from the surface by attached initiating groups. Surface-initiated polymerization is compatible mostly with a radical polymerizations [16,21,22] but also with cationic polymerization [23]. The “grafting from” method leads to a surface made of functional polymer brushes of large thickness (up to 100 nm) and high density in a controllable manner [24]. However, this approach is technically demanding and the obtained polymer brushes can be quite inhomogeneous due to differences in the polymer chain lengths.

In the “grafting to” approach, a previously synthesized polymer reacts with the appropriate functional groups located on the surface. This reaction can be conducted by the surface-termination of living polymer chain ends [20]. The resulting brushes are frequently more homogeneous compared with those obtained by the “grafting from” approach, if a polymer with low molar mass dispersity is used [24]. A high grafting density can be difficult to obtain due to the steric screening of the surface reactive sites by the already bonded polymer chains. Furthermore, only thin layers (approximately 10 nm) can be obtained [20]. Alternatively, a simpler method for a “grafting to” surface preparation is a temperature-induced chemical reaction between the polymer and the surface, called a “melt reaction” [25,26]. Here, functionalized polymer reacts with complementary functional groups located on the surface. This method can be performed relatively easily because casting the polymer solution or spin coating is only required to cover the substrate. The covalent bonds between polymer chains and the surface are formed merely under the influence of temperature, what greatly simplifies the protocol for polymer layer preparation. The simplicity of this coating method is greatly appreciated. This process was used by Yang et al. [27] to develop temperature-responsive nanofilms of *N*-isopropylacrylamide copolymers onto hydroxylated glass surfaces. Following this approach, Montagne et al. [28] reported PNIPAM films grafted onto modified gold wafers and showed dependence of polymer chains conformation on the surface with the temperature. Using the “melt” process, Yim et al. [29] prepared temperature-responsive surfaces through the reaction of COOH-terminated PNIPAM with the hydroxyls on the substrate. Hirata et al. [30] applied temperature-induced immobilization of PNIPAM copolymers to hydroxylated wafers through a urethane bond to obtain thermoresponsive surfaces of different thicknesses.

To date, the interesting behavior of thermoresponsive surfaces has been exploited in a wide range of applications, including drug delivery systems [31], bioseparation [32], immobilization of biomacromolecules [33], antibacterial systems [34] and cell sheet engineering [35].

In this work, we report an easy method for obtaining temperature-responsive surfaces based on polyglycidol derivatives with well-defined surface properties and describe their interactions with skin cells. So far, mostly the PNIPAM brushes were well developed for interaction with

cells. However, the PNIPAM layers have some disadvantages. The aggregation of PNIPAM chains sometimes irreversible, influencing the transition behavior. Moreover, in order to optimize the properties, especially the surface-cell interactions, the surface may need to be modified, also with biologically active species. As PNIPAM is not a reactive polymer, its chemical modification is challenging. This may set limits to its applications and justifies the search for other biocompatible polymer layers containing reactive functional groups. Polyglycidol, a hydrophilic, water-soluble, nontoxic and biocompatible polyoxirane [36] can be a good candidate. The presence of one primary hydroxyl functional group per monomeric unit enables its hydrophobic modification into temperature-responsive polymers [37]. Temperature-responsive polyglycidol derivatives with different structures and topologies, including block [38], star-block [39] and random copolymers [37] with T_{CP} ranging from 21 to 86 °C were obtained. Temperature-responsive polyglycidol-based materials, including aqueous solutions [37], self-assembled structures [40], superabsorbing hydrogels [41] and cryogels [42] were also studied.

Here, we report the synthesis and characterization of polyglycidol-based surfaces made by the chemical reaction between the polymer and the activated solid substrate. Covalent bonds were formed as a result of the reaction between the polyglycidol hydroxyl groups and the anhydride groups located on the surface at increased temperature. The surface morphology, wettability and thickness, as well as their changes with temperature are described.

The studies concerning the effective support for the skin cell culture are of potential great therapeutic importance for treatment of difficult to heal wounds (burns or diabetes caused injuries). Nowadays the best solution to this problem are skin grafts or skin-cell grafts, as many conventional treatments (hydrogel dressing, allografts or xenografts) are costly, slow and not always effective. However the cell culture procedures used to obtain large-surface grafts have still to be optimized. In this work, the influence of surface properties on the skin cells (fibroblasts and keratinocytes) attachment and growth is examined.

2. Experimental

2.1. Materials

Ethoxyethylglycidyl ether (EEGE) was obtained by reacting 2,3-epoxypropanol-1 (glycidol) (96%, Aldrich) with ethyl vinyl ether (Aldrich) catalyzed with *p*-toluenesulfonic acid (98.5%, Aldrich), according to the procedure described in [43]. The obtained product was fractionated under reduced pressure. Fractions of 99.8% (GC) purity were used for the polymerizations. DMF (POCH, Poland) was dried over CaH₂, distilled under a dry argon atmosphere and was then dried over P₂O₅ and distilled again. Ethyl isocyanate (98%, Aldrich) was distilled under argon atmosphere. Diethyl zinc (1 M solution in hexanes, Aldrich), dibutyltin dilaurate (DBTL) (95%, Aldrich), H₂SO₄ (95%, POCH, Poland), hydrogen peroxide (30%, Chempur, Poland) and (3-aminopropyl)triethoxysilane (APTES) (99%, Aldrich) were used as received. Poly(ethylene-

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