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Vinylcarbonates as low-toxic monomers for digital ink-jet inks: Promising alternatives to acrylate based systems

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ABSTRACT

The last decade has seen a significant increase in research on UV curable digital inks for industrial printing applications with the focus to expand this technique into new markets. However, most of the commercially available inks are based on acrylic monomers, which provide a significant toxicological behavior limiting their applicability in promising fields, e.g. printing on food packaging materials. In this study, a variety of biocompatible monomers based on vinylcarbonate building blocks were evaluated regarding their application in UV curable digital inks. Although, the viscosity and surface tension of these monomers is appropriate for ink-jet printing, the curing speed is far too low for high speed printing processes. In order to circumvent this limitation, thiol-vinylcarbonate formulations were prepared that offer reactivities and double bond conversions (DBC) similar to those of acrylates. For that purpose, a multifunctional thiol was synthesized providing both, low odor and an appropriate low viscosity facilitating the formulation of basic ink-jet inks, which offer excellent jetting behavior, together with good film forming properties and adhesion on PET. Although there are some challenges regarding stability, in particular for pigmented formulations, this system represents a promising alternative to commercially available acrylate based inks.

1. Introduction

Ink-jet printing offers many advantages over traditional printing and coating methods such as lithography, flexography and screen printing [1–3]. Among these advantages are factors such as “digital printing” and “printing on demand”, which enable the realization of high quality prints without the need of individual printing plates or stencils, offering the utmost flexibility in the printing process. Recent years have seen a significant increase in research on digital inks for industrial graphic printing. The main focus of these efforts is to bring this technique into new markets. In this regard, many experts promise huge market potentials for digital inks for printing on food packaging, textiles and garments. For the time being, however, commercially available inks contain noxious substances or solvents, which limit or completely prevent their application in these specific fields. In particular, UV curable inks that offer unique advantages such as instantaneous drying, the absence of VOCs, good adhesion on substrates and excellent film forming properties consist of potentially harmful monomers and photoinitiators [1–3]. In general, such ink-jet inks are derived from the UV curing and surface coating technology, which has been well established for a number of decades and which is mainly based on acrylate building blocks [4,5]. These monomers and oligomers are polymerized and cross-linked via a free radical mechanism, which is initiated by appropriate photoinitiators. Although these acrylate based systems are exhaustively investigated and also well understood, there are several considerable drawbacks in terms of health, safety and environmental compatibility [6]. The predominant applied acrylic monomers are known to have high irritancy levels in their uncured state and can also cause sensitization after skin exposure [7–9]. This fact can be mainly deduced from the reactivity of the acrylate double bond toward amino- or thiol-groups of proteins within the human body via Michael addition reactions [10]. The use of high irritancy chemicals in ink-jet printing is not recommended as the inks are effectively being sprayed, producing vapors and aerosols that can cause health problems to the operator [11,12]. Moreover, the application of acrylate based inks for the printing onto food

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packaging poses a problem due to a possible migration of residual photoinitiator (PI), its cleavage products, as well as uncured acrylates in the eatables. Another mentionable drawback of free radical curing, which has to be taken into account is its sensitivity to oxygen [13]. Particularly in the curing of low-viscosity acrylate systems, as applied in UV curable ink-jet inks, oxygen inhibition poses an ongoing problem. The well-known oxygen inhibition decelerates the polymerization reaction, which increases the amount of residual acrylate monomers in the cured ink film. In the worst case, this effect can totally inhibit monomer curing. One possibility to overcome oxygen inhibition is to increase the amount of photoinitiator in the formulation explaining the high PI concentration (up to 15 wt%) in digital inks.

In the last years, alternative monomers to the well established (meth)acrylate building blocks have been investigated intensively by the group of Liska [14,15]. These monomers are mainly based on vinylcarbonates and vinylesters as reactive group, which can also be polymerized by free radical initiation using either thermal- or photoinitiators. This new generation of building blocks shows low cytotoxicity, has good storage stability and provides high biocompatibility in the cured state, making these monomers interesting candidates for the realization of medical implants such as bone scaffolds [15].

Besides these beneficial properties, the reactivity of these compounds in terms of curing speed after photochemical initiation is significantly slower than of acrylic monomers, which prevents their application for digital inks, where curing speed is a major cost factor. In particular, vinylcarbonates bearing easily abstractable hydrogens, e.g. oligo ethylene glycol units, are far less reactive. This might be explained by the fact that the vinylcarbonate monomer itself possesses low monomer reactivity due to the poor resonance stabilization of the subsequently formed radical. In contrast, the poor resonance stabilization leads to highly reactive vinylcarbonate based radicals, whereby hydrogen abstraction reactions, e.g. from ethylene glycol groups, results in a radical of low reactivity, which is slowing down the polymerization process [16].

Very recently, Mautner et al. [16] showed that the addition of multifunctional thiols to vinylcarbonate monomers enhance the curing speed significantly up to values comparable to those of acrylates. In general, thiols are very susceptible to hydrogen abstraction under free radical conditions leading to the formation of thiyl radicals. This fact explains the enhancement in curing speed as the radicals formed during initiation preferably react with the thiol groups to form thiyl radicals that are able to propagate the polymerization. Besides an acceleration of curing speed, the conversion of the vinylcarbonates increases by adding multifunctional thiols leading to significant lower concentration of uncured monomers in the obtained polymer film [16].

One major challenge in the development and formulation of ink-jet inks is their very demanding requirements, such as long shelf life, good adhesive properties and proper curing behavior. Additionally, the ink must provide chemo-physical properties which are specific for the various printing devices [1,3]. By the choice of appropriate monomers, photoinitiators, pigments and additives the requirements for the used printhead and the used substrate have to be fulfilled. The viscosity and the surface tension of the ink have to meet the demands of the used printhead in order to obtain proper jetting and thus high quality printing performance. In comparison to dyes and varnishes of traditional printing and coating methods such as lithography, flexography and screen printing, ink-jet inks have to be very low in viscosity [17]. The viscosity limitation drastically reduces the fraction of viscous compounds and adhesives which can be included in the ink formulation. The viscosity range for ink-jet is very much dependent on the designated hardware. Desktop office printers can cope with inks of viscosities ranging from 1 to 5 mPa s, whereas industrial print-heads can process viscosities up to 30 mPa s [17,18]. Due to this fact UV curable ink-jet inks contain mainly mono- and bifunctional building blocks with contents of multifunctional acrylates mostly in the single digit range. Besides an appropriate viscosity, the surface tension is an extremely important physical parameter in ink-jet technology [19]. The surface tension dictates the position and the ink meniscus within the nozzle along with its droplet generation [20]. The surface tension must be high enough to hold the ink in the nozzles without dripping but low enough to guarantee an ejection of ink droplets.

In this study, we investigated the thiol-vinylcarbonate system for its applicability as “low-toxic” UV curable ink for digital printing. In previous studies [16,21] mainly commercially available thiol compounds such as pentaerythritoltetra(3-mercaptopropionate) (PETMP) were used in combination with vinylcarbonate monomers, which however, show too high viscosities for pigmented ink-jet inks. There is still an ongoing necessity to investigate and develop multifunctional thiol monomers with low viscosity and improved hydrolytic stability. Consequently, the multifunctional thiol tetra(3-mercaptopropyl)silane (**thiol-1**) was investigated that provides both, low odor and an appropriate viscosity allowing its application in ink-jet inks. The synthesis of **thiol-1** has previously been described in a patent dealing with novel thiol-ene based materials for augmentation of hard tissues [22].

Besides the reactivity, conversion and printability of the thiol-vinylcarbonate system, also application orientated considerations such as the pot life, the film forming properties and the adhesion behavior of pigmented formulations on plastic substrates have been evaluated in this study.

2. Experimental

2.1. Materials

All chemicals were commercially available and purchased at Sigma–Aldrich or TCI Europe unless otherwise mentioned. The thiols TMPMP and PETMP were obtained from Bruno Bock. (5-Ethyl-1,3-dioxan-5-yl)methanol acrylate was obtained from Sartomer.

2.2. Monomer synthesis

Several mono- and multifunctional monomers (depicted in Fig. 1) were synthesized using the well-reported reaction of the corresponding alcohols with vinyl chloroformate in the presence of pyridine as acid scavenger [23,24]. The monomers were obtained in good yields in the range of 66–85%. ^{1}H NMR, ^{13}C NMR and FTIR-spectroscopy are in accordance with the proposed structures and can be found in the Supporting Info alongside the detailed reaction procedure. Besides the vinylcarbonate monomers, **thiol-1** was synthesized in a high yield (63%) via a multistep reaction starting from tetraallyl silane as reported elsewhere [22].

2.3. Cytotoxicity tests (ISO 10993-5:2009)

The cytotoxicity experiments were conducted at Cytox (Bayreuth, Germany). For these tests mouse fibroblast cells (L929) were used. Cells were cultured for 24 h in Dulbecco’s modified Eagle’s medium (DMEM) with added antibiotics, supplemented with 10% fetal calf serum at 37 °C in an incubator with 5% CO_2. Four different concentrations of the examined substance (dissolved in DMSO) were applied onto the cells and incubated for 48 h at 37 °C with 5% CO_2. The final concentration of DMSO in all cavities in the cell culture medium was 1% (v/v). Triton X 100 was used as toxic positive control (final concentration 1% (v/v)) and the cell culture medium was used as non-toxic negative control. All experiments