



Macromolecular Nanotechnology

Semi-interpenetrating polymer networks by cationic photopolymerization: Fluorinated vinyl ether chains in a hydrogenated vinyl ether network

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ABSTRACT

Semi-interpenetrating polymer networks (semi-IPNs) were obtained by the cationic photoinduced polymerization of a hydrogenated difunctional vinyl ether (DVE3) and a fluorinated monofunctional vinyl ether (FVE). By analyzing the kinetics of polymerization and the thermal properties of the crosslinked networks, it was demonstrated that the molecular architecture of the photopolymers could be tuned by varying the amount of the fluorinated additive. When the weight content of FVE exceeded 15 wt.%, the monofunctional fluorinated monomer homopolymerized forming linear chains that were dispersed in the hydrogenated matrix composed by the DVE3 crosslinked network, thus generating a semi-IPN structure. Both bulk and surface properties of the resulting photopolymers were influenced by the addition of the fluorinated product. Fluorinated semi-IPNs were biphasic, displayed good thermal resistance both in air and under nitrogen ($T_{10} > 200$ °C, $T_{50} > 380$ °C) and showed a surface energy as low as 26 mN m^{-1} .

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1. Introduction

Vinyl ethers (VEs) represent a wide family of monomers, which are, in principle, easily accessible from acetylene and the appropriate alcohol. The synthesis of VEs can follow different strategies [1]: (i) elimination reaction from ethers that bear an efficient leaving group (e.g., halogen atoms, alkoxides, silyloxides), (ii) olefination of a carbon–oxygen double bond via phosphorus, silicon or sulfur reagents, and (iii) addition reaction on alkynes or dicarbonyl substrates. VEs react through a cationic mechanism and their polymerization has been known since a long time [2]. The discovery of living cationic polymerization, in 1984, by the pioneering work of Higashimura and Sawamoto [3], followed by Webster and coworkers [4], then led to the preparation of interesting polymeric structures. The living character of this polymerization is obtained if the counterion has the right nucleophilicity so that an equilibrium is established between the carbenium species and the unreactive covalent species (dormant species). The fast equilibrium controls the growth of the chains, which on average lengthen at the same rate, and thus the MW distribution. Moreover, the active chain-ends could be modified into functionalized end-groups by end-capping with a functional nucleophilic terminating agent [5]. Hence, the living character of the cationic polymerization

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allows to synthesize controlled structures, such as block copolymers and end-functionalized polymers. In addition, vinyl ethers have been successfully copolymerized with electron-withdrawing monomers, such as fluorinated alkenes [6].

Cationic polymerization can be easily triggered by a radiation. Preferably, multifunctional systems have been investigated and VEs demonstrated to be more reactive than epoxides [7–9]: their reactivity arises from the resonance stabilization of the carbocation and is often comparable to acrylate monomers, which polymerize by a radical mechanism. With respect to the radical route, the cationic polymerization of VEs is advantageous because it does not suffer of oxygen inhibition. Moreover, VE systems combine low toxicity together with good mechanical properties, low shrinkage and high adhesion [10]. VEs are thus used in various UV curing applications, in particular as protective coatings [11].

A wide variety of functionalized vinyl ethers was synthesized containing ether, ester, urethane and siloxane structures and were photopolymerized [10,12–15], leading to crosslinked networks. The performance of VE photocured polymers were mainly determined by the nature of the alkyl or aryl group; the introduction of fluorinated chains [16] is thus interesting, as reported in the authors' review on the use of fluorinated monomers in photopolymerization [17]. For instance, perfluoroalkylethyl vinyl ethers were homopolymerized and also copolymerized with a mesogenic vinyl ether [18,19]; the comonomers were employed with ethylene to form random copolymers [20], while alternated copolymers were synthesized with 2-trifluoromethylacrylate [21], vinylidene cyanide [22,23], chlorotrifluoroethylene [24]. Moreover, a previous work [25] reported the synthesis of fluorinated VE monomers, which were then copolymerized with fluorine-free vinyl ethers, not exceeding 3 wt.%. The presence of fluorine imparted valuable surface characteristics to the UV cured networks, such as hydrophobicity, oleophobicity, and low surface energy.

The present work aims at studying the copolymerization, initiated by UV light, of a hydrogenated vinyl ether with a fluorinated vinyl ether, introduced up to 20 wt.%. Complex morphologies are obtained and can be identified as copolymeric structures or semi-interpenetrating polymer networks (semi-IPNs). Moreover, besides the peculiar surface characteristics, even the bulk properties of the resulting photopolymers can be tuned by the addition of the fluorinated product.

2. Materials and methods

2.1. Materials

The photopolymerizable hydrogenated oligomer used is triethyleneglycol divinylether, kindly supplied by ISP Europe (DVE3, MW = 202 g mol⁻¹, Fig. 1). The fluorinated comonomer is 1H,1H,2H,2H-perfluorodecyl vinyl ether (FVE, MW = 490 g mol⁻¹ Fig. 1), which was synthesized as described in the Supporting Information (and further supplied by Unimatec, Japan).

Triarylsulfonium hexafluorophosphate (50% w/w solution in propylene carbonate, from Sigma-Aldrich) was chosen as cationic photoinitiator (PI). All the other chemicals were obtained from Sigma-Aldrich and used as received.

2.2. Photopolymerization process

DVE3 oligomer was copolymerized with different amounts of FVE, after addition of 2 wt.% of PI. The composition of the different reactive mixtures, which were prepared without the use of any solvent, are reported in Table 1.

The reactive UV curable formulations were spread on a substrate (Si wafer or PP sheet) using a bar coater, forming 150 μm thick films, and then cured by means of a 200 W high pressure mercury arc lamp Helios Italquarz (using a light intensity of 60 mW cm⁻²).

For studying the kinetics of photopolymerization and the monomer conversion, the reaction was monitored by real time Fourier Transform-Infra Red (FT-IR) analysis. Simultaneously with the UV irradiation of thin films (i.e., about 50 μm) of the reactive monomeric mixtures, FT-IR scans were acquired using a FT-IR spectrometer (Thermo-Nicolet 5700 instrument). A UV Hamamtsu LC8 lamp, provided via an optical fiber, with an intensity of irradiation of 12 mW cm⁻² was employed. The double bond conversion, χ , was calculated monitoring the decrease of the area of the absorption band of the reactive functionality (C=C peak at approximately 1635 cm⁻¹) with irradiation time. The area was normalized by a constant signal in the spectra (C–O peak at approximately 1100 cm⁻¹). Percent conversion of the double bond is given by the following equation:

$$\chi(\%) = \left(1 - \frac{A_t}{A_0}\right) \times 100 \quad (1)$$

where A_t indicates the ratio between the area of the C=C peak and that of the C–O peak at time t , and A_0 the peak ratio at time $t = 0$ s.

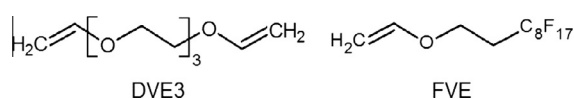


Fig. 1. Chemical structures of the hydrogenated telechelic (DVE3) and the fluorinated monofunctional (FVE) vinyl ether comonomers.

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