Materials Today Communications 4 (2015) 1–5

Contents lists available at ScienceDirect

Materials Today Communications

journal homepage: www.elsevier.com/locate/mtcomm

Synthesis and characterization of simultaneous IPNs. Evidence of the IPN structure by selective chemical attack on the cross-linker

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ARTICLE INFO

Article history:
Received 11 February 2015
Accepted 23 February 2015
Available online 11 May 2015

Keywords:
IPN
Semi-hydrogel
Simultaneous photopolymerization
3-[Tris(trimethylsiloxy)silyl]propyl methacrylate
2,2,2-Trifluoroethyl methacrylate

ABSTRACT

Interpenetrating polymer network hydrogels based on fluoro-, siloxane-acrylates and N-vinylpyrrolidone were synthesized using simultaneous photopolymerization technique in presence of poly(ethylene glycol diacrylate) as cross-linker. These hydrogels were characterized by Fourier-transform infrared spectroscopy and by their swelling properties. Evidence of the semi-IPN structure was shown thanks to the selective chemical attack on the cross-linker. Poly(ethylene glycol diacrylate) crosslinks of prepared hydrogels were attacked by concentrated basic solution leading to the hydrolysis of the poly(ethylene glycol diacrylate) molecules and the degradation of the polymer network. The solid residue and the liquid phase after degradation were analyzed by gas chromatography with mass spectrometry analyzer and by FTIR spectroscopy. These analyses gave evidence of the presence of non-crosslinked poly(N-vinylpyrrolidone) chains in the acrylate network. Henceforth, the synthesized hydrogel should be associated to a semi-IPN structure.

1. Introduction

Hydrogels are polymeric materials containing a large number of hydrophilic groups, inducing their swelling in aqueous solutions. They are characterized by the presence of a large amount of water in their three-dimensional networks. Hydrated gels are soft, rubbery materials with a variety of application areas such as tissue engineering [1], medicine [2,3], pharmaceuticals [4]. An interpenetrating polymer network (IPN) [5] is defined as an intimate combination of two or more polymers, both cross-linked and at least one of the networks formed in the presence of the other. IPN may combine networks with different properties and structures that stimulate a particular interest for such structure. Materials with only one cross-linked component are called as semi-interpenetrating polymer network (semi-IPNs) [6]. From a synthetic point of view, IPN elaboration could proceed in sequential steps [7–9] involving the preparation of the first polymer network, its subsequent swelling in this second monomer solution and the in situ polymerization of the latter one [10,11]. However, the IPN could also be prepared in a one step-process, with the polymerization of two or more monomers at the same time following independent chemical reactions. The two separate steps of synthesis make the sequential technique less attractive for the industrial purpose than the simultaneous one. One of the common methods to prepare the simultaneous interpenetrating polymer network is focused on the hybrid radical/cationic photo-polymerization [12–14]. Furthermore, combination of the polyaddition and the free radical well known techniques is also applied for appropriate monomers [15]. Alternative polymerization techniques such as-polymerization initiated by donor/acceptor mechanism [16], “click chemistry” and the atom transfer radical polymerization (ATRP) [17] are also discussed in the literature.

Beside the different preparation routes, the phase morphology of bi-phasic IPNs may vary from isotropic structures associated to random, statistical polymers to more or less ordered anisotropic structures [18]. Hybrid IPN networks were also shown to be dependent on chemical composition of the initial monomers. As an example, Sangermano et al. [13] showed that the morphology evolves from a co-continuous IPN to complete phase separation simply depending on the monomer ratios.

The goal of this study is the semi-quantitative investigation of morphological structure presented by the simultaneous biphasic IPNs. Polymer networks were elaborated from the radical-cationic photo-polymerization of the hydrophilic 1-vinyl-2-pyrrolidinone (NVP) monomer and the radical photo-polymerization of the hydrophobic acrylate monomers: 2,2,2-trifluoroethyl methacrylate

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http://dx.doi.org/10.1016/j.mtcomm.2015.02.004
2352-4928/

(TFEM) or 3-[tris(trimethylsiloxy)silyl]propyl methacrylate (TRIS). Poly(ethylene glycol diacrylate) (PEGDA) is used as cross-linker. Since NVP can be polymerized through either a radical or ionic mechanism [7,19], two competitive reactions take place and may influence the IPN morphology. In order to characterize the final structure and morphology, several analytical techniques such as scanning electronic microscopy (SEM) [20–22], Fourier transform IR spectroscopy (FTIR) [16,23,24] and X-ray photoelectron spectrometry (XPS) [25,26] are usually applied for the investigation of IPN. In this paper, we also present another efficient and simple method for describing for the IPNs structure investigation. Such methodology coupled with size exclusion chromatography was shown to provide information about the crosslinking density of each network [27,28]. This method is based on the selective attack of the cross-linker of acrylate network (PEGDA) leading to the degradation of the polymer network. The resulting solid and liquid residues are therefore analyzed by FTIR and gas chromatography coupled with mass spectrometry (GC–MS) [29].

2. Experimental part

2.1. Materials

The hydrophobic monomers, 3-[tris(trimethylsiloxy)silyl]-propyl methacrylate] (TRIS) and 2,2,2-trifluoroethyl methacrylate (TFEM) (Sigma–Aldrich, Europe) were used after purification on the dry Al_2O_3 column. The hydrophilic monomers, 1-vinyl-2-pyrrolidone (NVP), poly(ethylene glycol) diacrylate (PEGDA) (Sigma–Aldrich, Europe) were used as received.

The free radical photo-initiator, 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173, Sigma–Aldrich, Europe) and the radical-cationic initiator, 4,4-dimethyl diphenyl iodonium hexafluorophosphate (DDIP, Sigma–Aldrich, Europe) were used without any purification.

2.2. IPNs synthesis

Weight percentages of monomers used in each composition are reported in Table 1. The radical polymerization of the acrylate was initiated by UV light ($\lambda = 280$ nm) in the presence of Darocur while the ionic polymerization of NVP is initiated by UV irradiation in the presence of DDIP. Acrylate chains were cross-linked with PEGDA. Initiators concentrations were fixed at 0.5 wt% for Darocur and for DDIP in all compositions, PEGDA content was fixed at 0.3 wt%. The mixture of each formulation was introduced into the round polypropylene mold and kept in a closed glass box under inert atmosphere of nitrogen for solution deoxygenating (10 min). At the last step, the mixtures were cured under UV irradiation ($\lambda = 280$ nm) for 1 h and then at 80 °C for 1 h without irradiation.

2.3. IPN degradation

Water-swollen samples (0.7 g) were dipped into sodium hydroxide solution ([NaOH] = 5 mol/L) and heated for 48 hours at 70 °C. After reaction, solid residues mostly composed of NVP polymer fragments were filtered, washed, weighed and analyzed by FTIR. The liquid residues partially composed of fragments of acrylate networks were extracted by dichloromethane and then analyzed by GCMS.

2.4. Swelling properties of IPN

The samples were weighed (W_d), and then swollen in distilled water for 24 h at 37 °C before being weighed in a swollen state (W_s). The equilibrium water content (EWC) was evaluated as follows:

$$\mathrm{EWC} = \frac{W_s - W_d}{W_s} \times 100\%$$

2.5. FTIR spectroscopy

The FTIR spectra were performed on Bruker IFS66 spectrometer (Globar source, 32 scans, DTGS detector, resolution 2 cm^{-1}) in transmission mode on KBr pellets prepared including ≈2% of powdered dry hydrogel or solid residue.

2.6. Gas chromatography–mass spectrometry (GC–MS)

The GC-MS analysis was carried on Agilent Technologies 7890B GS system equipped with Agilent Technologies 5977A MSD system for fragments of acrylate networks extracted by dichloromethane from the liquid phase obtained after the IPN degradation. Samples of 1 ml were prepared for the analysis. Splitless mode was chosen for the chromatography in order to increase the signal intensity.

2.7. Differential scanning calorimetry (DSC)

Samples of dry hydrogels (10–15 mg) were weighted in an aluminum pan. The measurements were performed using DSC Q100, TA Instruments differential scanning calorimeter. The samples were first heated to 200 °C and equilibrated for 5 min and then cooled to −40 °C at rate of 5 °C/min and equilibrated for 5 min. Then, the samples were heated to 200 °C at rate of 5 °C/min. Glass transition (T_g) is associated to a drastic change in the base line, indicating a change in the heat capacity of the polymer.

3. Results and discussion

3.1. IPN synthesis and characterization

The hydrogels were synthesized following the formulations described in Table 1. Such formulations were chosen to study the IPN structure and properties depending on the ratio of hydrophilic and hydrophobic components. These compositions could illustrate all morphological schemes from a complete phase separation to a co-continuous IPN phase morphology depending on this ratio and the miscibility of the monomers. However, deeper microscopic investigation should be required to prove this statement. It must be noted that all of the synthesized TFEM-based hydrogels are completely transparent while TRIS-based hydrogels are opaque or even white, while TRIS/NVP 35/65 sample is semi-transparent. The FTIR spectra of TRIS-based compositions show the presence of TRIS characteristic bands of $Si(CH_3)_3$ (stretching, 845 cm^{-1}), Si—O (stretching, 1050 cm^{-1}), Si—CH_3 (stretching, 1256 cm^{-1}) and carbonyl of ester group (stretching, 1748 cm^{-1}) [30]. In case of TFEM-based IPN, characteristic absorption bands of TFEM were observed: C—F stretching at 650 cm^{-1} and 1140–1160 cm^{-1} and carbonyl stretching of ester group at 1748 cm^{-1} [26]. For both of IPN, bands at 1683 cm^{-1} and at 1289 cm^{-1} were assigned to PVP characteristic bands of respectively carbonyl group stretching and C—N stretching [16]. Ratio of the characteristic TFEM (1140–1160 cm^{-1}) or TRIS (1050 cm^{-1}) and NVP (1683 cm^{-1}) band area are given in Table 1. In both cases, increase of characteristic peaks intensity with the part of acrylate monomer in composition has almost linear behavior.

Water content measured at equilibrium (EWC) is another parameter which also depends on the monomers nature and the cross-linking density. EWC was measured (Table 1) and significant correlation with polyvinylpyrrolidone (PVP) content was