



# Interpenetrating polymer network systems based on poly(dimethylaminoethyl methacrylate) and a copolymer containing pendant spiroacetal moieties

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## ABSTRACT

The interpenetrating polymer networks (IPNs) are promising materials due to their unique properties. In this context, in the present study, new IPN structures based on poly(dimethylaminoethyl methacrylate) (PDMAEMA) and poly(itaconic anhydride-co-3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5] undecane) (PITAU) were synthesized. The double network was prepared by synthesizing and crosslinking (with *N, N'*-methylenebis(acrylamide)) PDMAEMA in the presence of a preformed PITAU network. The effect of the two components upon some properties such as: viscoelasticity, thermal stability and swelling behavior of the new prepared gels were deeply investigated. The viscoelastic parameters indicated stronger networks for PDMAEMA/PITAU hydrogels as compared with PDMAEMA.

The thermal parameters also indicate that the IPNs are more stable than PDMAEMA. The IPNs present an increased sensitivity to temperature and pH, the equilibrium swelling degree being strongly influenced by them. This behaviour highlights the possibility of controlling the release of therapeutic agents by swelling and deswelling cycles of the IPNs at different pH and temperatures, depending on composition and the application envisaged.

## 1. Introduction

The interpenetrating polymer networks (IPNs), as one of the most rapidly growing areas in the polymer science, present an increased interest from the viewpoint of preparation owing to the properties derived from the involved multicomponent polymeric systems. The IPN structures are considered "blends" formed by two or more polymer networks interlocked at molecular level, when one of which is synthesized and/or crosslinked in the presence of the other, but which cannot be separated without destroying their chemical structure [1–5].

IPN hydrogels are very promising materials due to the improved properties gained through this method of preparation [6–12]. Taking into consideration the method of preparation, the IPN hydrogels can be classified in (1) *simultaneous IPN* when two networks are synthesized simultaneously by two different chemical routes and they cannot interact, and (2) *sequential IPN (semi-IPN)* obtained by swelling a preformed network into a solution which contains monomer, initiator/activator necessary for the synthesis of the second network. If a cross-linking agent is present, *full-IPN structures* will result [13].

Semi- and full-IPN techniques are significant ways to obtain hydrogels with thermo- and pH-sensitivity [14–17], and with the possibility to have a better control of the chemical composition and final properties [18]. The methods present certain advantages: feasibility, the possibility to combine the pH or temperature sensitivity with other properties, the obtaining of interconnected porous network structures that allow the hydrogels to have a faster swelling/deswelling rate than nonporous hydrogels [19–24].

The most studied stimuli responsive hydrogels are those based on the polymer poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) [25] which has received substantial consideration for use in the controlled delivery of drugs [26], chemical sensors [27], support carriers [28] and gene transfer agents [29]. Even though numerous studies have been focused on the obtainment of responsive hydrogel based on PDMAEMA, their application is generally restricted in the biomedical fields because of their slow response rate to the change of an external parameter, of the overshooting phenomenon which appears during the swelling process, the poor dimensional stability and low mechanical strength [29].

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Related to this issue, this study introduces the preparation of a new sequential interpenetrating polymer networks where the first polymer network (I) is the synthetic copolymer, namely poly(itaconic anhydride-co-3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5] undecane) (PITAU) [30,31] followed by the *in situ* polymerization of DMAEMA along with initiator/activator and crosslinker swollen into the network I.

PITAU copolymer, synthesized through a radical polymerization process and previously characterized [31], presents sensitive character to pH and temperature changes. Also, the *in vitro* and *in vivo* studies confirmed the biocompatibility and versatility of this polymeric structure as network for pharmaceutical delivery systems or support for bioactive compounds [32].

In the present study, the rheological parameters, thermal stability and swelling behaviour of the new IPN PITAU/PDMAEMA structure, as “double network” gel system, in relation to its chemical composition were investigated.

## 2. Experimental part

### 2.1. Materials

(2-dimethylaminoethyl) methacrylate (DMAEMA) (Alfa Aesar) was purified by passing the monomer through a column of inhibitor removers (Sigma Aldrich).

The other chemical compounds: 3,9-divinyl-2,4,8,10-tetraoxaspiro [5.5] undecane (U; purity 98%, Sigma-Aldrich), itaconic anhydride (ITA; purity 98%, Aldrich), 2,2'-Azobis(2-methylpropionitrile) (AIBN; purity 98%, Sigma-Aldrich), *N,N'*-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), *N,N,N',N'*-tetramethylethylenediamine (TEMED, Merck) were used without further purification. The used solvents – 1, 4 dioxane ( $\geq 99.0\%$ ) and diethyl ether (for precipitation) – were purchased from Sigma-Aldrich. The water used in the experiments was purified using an Ultra Clear TWF UV System.

### 2.2. Hydrogel synthesis

#### 2.2.1. Copolymer synthesis

The synthesis and characterization of the PITAU copolymers was recently described [31,32]. Shortly, the copolymer was synthesized through a continuous radical process of polymerization of ITA/U comonomers (in 0.05/0.07 M ratio), in the presence of AIBN as initiator and 1, 4-dioxane as solvent, under nitrogen atmosphere, at 75 °C, in a constant temperature bath, with a stirring rate of 250 rpm; the reaction was carried out for 17 h. The copolymer, separated after solution precipitation in diethyl ether, was washed several times also with diethyl ether, and dried for 24 h in a vacuum oven at room temperature and 600 mm HG [31].

#### 2.2.2. Interpenetrating polymer network synthesis

The synthesis of the IPN hydrogels was made by free radical polymerization process of DMAEMA into the preformed PITAU solution (Scheme 1) by using ammonium persulphate (APS)/*N,N,N',N'*-tetramethylethane-1,2-diamine (TEMED) as initiator/activator system and *N,N'*-methylene bis(acrylamide) (MBAAm) as crosslinking agent, respectively.

Table 1 presents the ratios between DMAEMA and PITAU used for IPNs preparation. For the second network formation, the *in situ* polymerization of DMAEMA is taking place following the next recipe: 2 ml of DMAEMA monomer (11.83 mmol) and *N,N'*-methylenebis(acrylamide) crosslinker (MBAAm) (0.65 mmol) were solved in 10 ml aqueous solution with initiator (APS–0.877 mmol) and activator (TEMED–0.0172 mmol), slowly mixed under  $N_2$  atmosphere for 2–3 min, and after that the mixture was added in PITAU dioxane solution (20% concentration) in correspondingly ratio (Table 1). Meanwhile, PDMAEMA synthesized accordingly to the presented recipe

constitutes the control sample in the further investigation. The gelation took place within 5 min, and the system was kept for 24 h at room temperature for completion of polymerization and maturation. Further, the synthesized gel compounds were purified *via* dialysis (cellulose membrane,  $M_w = 14.2$  kDa) against distilled water for 4 days to remove the residual unreacted monomers until the pH and the conductivity of the dialyzed water reached the values of distilled water [33]. Then, the synthesized IPN hydrogels were lyophilized for 72 h.

### 2.3. IPN hydrogels characterization

#### 2.3.1. FTIR spectra

The dried hydrogels were mixed with potassium bromide (KBr) powder and compacted into a disc for analysis on the Bruker spectrometer using a Vertex mode absorption ranging from 400  $cm^{-1}$  to 4000  $cm^{-1}$ . The FTIR spectra were obtained at 4  $cm^{-1}$  resolution as the average of 64 scans. The FTIR spectra of the IPN hydrogels are depicted in Fig. 1.

The characteristic bands of PITAU from 1000 to 1200  $cm^{-1}$  (C–O–C) are overlapped over the characteristic bands of PDMAEMA not being able to be detected. The absorption characteristic bands of ITA appear at  $\sim 1780$   $cm^{-1}$  and belong to the symmetric stretching of carbonyl (C=O). This peak is characteristic for the 5-member anhydride unit and indicates not disruption of the ITA moieties during polymerization and crosslinking processes. Other characteristic peaks of the anhydride group from  $\sim 1216$ – $1164$   $cm^{-1}$  (cyclic C–O–C) present an increase of the intensity in relation to the chemical composition of the IPN. The band from 2943  $cm^{-1}$  corresponding to PDMAEMA is due to the  $CH_2$ -CH group conjugated with the carbonyl group. The strong peak from 1718  $cm^{-1}$  is assigned to the ester carbonyl group, and this peak decreases with the introduction of PITAU showing the existence of the potential intermolecular physical bonds between the networks. The same explanation can be assumed for the decreasing of the intensity of the band from 2780  $cm^{-1}$  ( $NCH_3$ ), which demonstrates the obtainment of the IPN structure. The exposure of hydrogels to ambient medium (22 °C, relative humidity  $\sim 55\%$ ) is responsible for the broad peak from 3367  $cm^{-1}$  (characteristic for  $H_2O$ ), which overlaps to the characteristic C–H bond peaks.

#### 2.3.2. Thermal analysis

The thermal properties of the IPN gel samples were determined on a Jupiter STA 449 F1 (Netzsch) instrument. The samples were previously maintained in a controlled humidity atmosphere, respectively, in the presence of  $CaCl_2$  inorganic salt. 7.5–8 mg samples were heated in an open  $Al_2O_3$  crucible, under 50 ml/min $^{-1}$  nitrogen flow rate. Runs were performed in dynamic mode from room temperature up to 600 °C with a heating rate of 10 °C/min. The IPN<sub>2</sub> sample was also studied by thermogravimetric analysis connected with FTIR spectrophotometer and mass spectrometer (TGA-FTIR-MS), on the temperature range 30 °C–600 °C for analysis of gases evolved by thermal decomposition. The FTIR spectrum of the evolved gases by thermal degradation of IPN<sub>2</sub> was continuously recorded during the dynamic heating experiments with a heating rate of 10 °C min $^{-1}$ .

#### 2.3.3. Rheological measurements

The rheological investigations were performed by using a MCR 302 Anton-Paar rheometer equipped with plane-plane geometry (the diameter of the upper plate of 50 mm) with a gap of 500  $\mu m$ , and Peltier device for a rigorous temperature control. An anti-evaporation device, which created a saturated atmosphere near the sample, was used for limiting the water evaporation. The viscoelastic properties of the hydrogels were followed at 37 °C through oscillatory shear experiments with oscillation frequency ranging from 0.1 rad/s up to 100 rad/s in the linear domain of viscoelasticity. The elastic ( $G'$ ) and loss ( $G''$ ) moduli, as well as the complex viscosity ( $\eta^*$ ), were measured as a function of the oscillation frequency,  $\omega$ .  $G'$  gives information about the energy stored

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