Mesoporous Polymeric Materials Tailored from Oligoester-Derivatized Interpenetrating Polymer Networks

*Géraldine Rohman, Daniel Grande**

Summary: The utilization of semi-hydrolyzable oligoester-derivatized Interpenetrating Polymer Networks (IPNs) as nanostructured precursors provides a straightforward and effective route to novel (meso)porous networks. In a first stage, different types of poly(D,L-lactide)/poly(methyl methacrylate)-based IPNs were synthesized by resorting to the so-called *in situ* sequential method. In a second stage, the quantitative hydrolysis of the polyester sub-network afforded porous structures with pore sizes ranging from 10 to 100 nm. The potentialities offered by this versatile approach were discussed, and the porosity of the resulting methacrylic networks was examined by Scanning Electron Microscopy (SEM) and thermoporometry using Differential Scanning Calorimetry (DSC).

Keywords: crosslinking; degradation; hydrolyzable polyesters; interpenetrating polymer networks (IPNs); (meso)porous polymers

Introduction

Over the last decade, the design of porous polymeric materials has attracted much interest as they find a large variety of applications in many areas, including separation and filtration techniques, enzyme immobilization, supported catalysis, as well as controlled drug release.[1] Obtaining mesoporous polymeric materials with controlled porosity is not a trivial task. In this context, the preparation of ordered mesoporous polymers through the selective degradation of one block from self-organized annealed block copolymers has largely been established by many groups.[2] However, an alternative approach for generating (meso)porous crosslinked materials has been put forward only by a handful number of research teams through the utilization of partially degradable IPNs as nanostructured precursors.[3,4]

This work shows how IPNs based on an hydrolyzable polyester, such as poly(D,L-lactide) (PLA), and a polymer containing a non-hydrolyzable skeleton, such as poly(methyl methacrylate) (PMMA), can be used as effective precursors for the formation of (meso)porous networks, through the selective hydrolysis of the polyester sub-network, under mild conditions.

Experimental Part

Materials

Dihydroxy-telechelic PLA ($M_n = 1{,}700$ g·mol^{-1}; $M_w/M_n = 1.2$) was synthesized by ring-opening polymerization of D,L-lactide initiated by the ethylene glycol/tin (II) octanoate system, according to a literature method.[5] Dibutyltin dilaurate (DBTDL, Fluka) was used as received. 4,4′,4″-triisocyanato-triphenylmethane (Desmodur® RU, 1.25 mol·L^{-1} in dichloromethane solution) was provided by Bayer. Methyl methacrylate

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Equipe « Systèmes Polymères Complexes », Institut de Chimie et des Matériaux Paris-Est, UMR 7182 CNRS – Université Paris XII, 2, rue Henri Dunant, 94320 Thiais, France
E-mail: grande@icmpe.cnrs.fr

(Aldrich) was dried over CaH_2, and distilled under vacuum prior to use. Bisphenol A dimethacrylate (BADMA) and diurethane dimethacrylate (DUDMA) were purchased from Aldrich and used as received. AIBN (Merck) was purified by recrystallization in methanol.

Synthesis of PLA/PMMA IPNs

IPNs constituted of PLA and PMMA sub-networks (50/50 wt %) were synthesized by the *in situ* sequential method, *i.e.* by mixing all the precursors homogeneously, and then forming both networks *via* two successive and non-interfering crosslinking processes.[6] Hence, the PLA sub-network was first generated at room temperature for 20 h by a DBTDL-catalyzed end-linking reaction involving a dihydroxy-telechelic PLA oligomer and Desmodur® RU as a triisocyanate cross-linker. Subsequently, the methacrylic sub-network was created at 65 °C by AIBN-initiated copolymerization of MMA and a dimethacrylate (2 h), and finally cured at 110 °C for 2 h. It is noteworthy that the $[NCO]_0/[OH]_0$ and $[DBTDL]_0/[PLA]_0$ ratios were constant and equal to 1.4 and 0.44 respectively, while the ratio $[AIBN]_0/([MMA]_0 + 2 \cdot [dimethacrylate]_0)$ was maintained constant to 0.02.

Hydrolysis of Polyester Sub-Network in IPNs

In different vials containing 3 mL of a phosphate buffer solution (pH = 8.2) and 3 mL of ethanol, 0.2 g of network samples were immersed at 60 °C. After a given period of time, the reaction medium was neutralized by a 0.1 mol $\cdot$ L^{-1} NaOH aqueous solution, and the residual network was rinsed with distilled water up to neutral pH. Two characteristic parameters were assessed, namely mass loss (Δm) and water absorption (Q_{H2O}), as follows: $\Delta m = (m_0 - m_d)/m_0$ and $Q_{H2O} = (m_w - m_d)/m_d$, where m_0, m_d, and m_w stand for the initial mass of the samples, their residual mass after vacuum drying, and their wet mass after wiping, respectively.

Instrumentation

^1H NMR spectra were run using a Bruker AC 200 spectrometer at resonance frequencies of 200 and 50 MHz, respectively. Solid-state ^{13}C NMR spectra were recorded with a Bruker Avance 300 spectrometer at a resonance frequency of 75 MHz. The Size Exclusion Chromatography (SEC) equipment comprised a Spectra Physics P100 pump, two PL gel (polystyrene–divinylbenzene) columns, and a Shodex RI71 refractive index (RI) detector. The eluent was tetrahydrofuran (THF) at a flow rate of 1 mL $\cdot$ min^{-1}; the calibration was effected with polystyrene (PS) standards. Fourier Transform Infra-Red (FTIR) spectra were recorded between 450 and 4000 cm^{-1} with a Bruker Tensor 27 DTGS spectrophotometer. Glass transition temperature (T_g) and thermoporometry analyses were performed by Differential Scanning Calorimetry (DSC) with a Perkin Elmer DSC 4 calorimeter. The scans were run from −50 to 250 °C for T_g analyses and from −50 to 5 °C for thermoporometry, at a heating rate of 20 °C $\cdot$ min^{-1} and 1 °C $\cdot$ min^{-1} respectively. Scanning Electron Microscopy (SEM) analyses were performed with a LEO 1530 microscope equipped with a high-vacuum (10^{-10} mmHg) Gemini column. The accelerating tensions ranged from 1 to 5 kV. Prior to analyses, the samples were cryo-fractured and coated with a Pd/Au alloy.

Results and Discussion

IPNs represent an intimate combination of two independently crosslinked polymers, at least one being obtained in the immediate presence of the other.[7] Such complex polymer structures are of particular interest when they arise from the association of two components that exhibit a contrasted degradability under specific conditions. Indeed, (meso)porous networks can be designed from such IPNs by resorting to selective degradation methods.[3,4] In this context, IPNs based on an hydrolyzable polyester, such as PLA, and a polymer containing a non-hydrolyzable skeleton, such as PMMA, can be considered as appropriate precursors. Furthermore, PMMA is a rigid matrix with a high T_g, while PLA has a lower T_g, and both polymers are characterized by a low interaction parameter ($\chi = 0.017$), which ensures a good compatibility.

In this work, IPN systems constituted of PLA and PMMA sub-networks were prepared by the *in situ* sequential method as explained in the Experimental Section. For the PMMA sub-network generation, two different dimethacrylates were employed: BADMA, a "rigid" dimethacrylate, and DUDMA, a "softer" one.[8] The influence of crosslink density on the structure and properties of the resulting networks was also probed by varying the initial dimethacrylate content from 1 to 10 mol %. All IPN samples were subjected to a dichloromethane extraction for 24 h at 40 °C; the amounts of soluble fractions were lower than 10 wt % as long as the crosslinking of dihydroxy-telechelic PLA oligomer was carried out with a 40 mol % excess of isocyanate functions compared to alcohol functions. It is most noteworthy that IPNs were transparent, before and after extraction, suggesting good chain interpenetration of both constitutive sub-networks. Indeed, considering that the difference between the refractive indices of both partners is significant (n_D^{25} (PLA) = 1.46, n_D^{25} (PMMA) = 1.49), the transparency is at least indicative of microdomain sizes smaller than about 150 nm, according to Okay.[9]

In order to design mesoporous networks with a narrow pore size distribution, we resorted to an original approach through the selective hydrolysis of the PLA subnetwork associated with partially hydrolyzable PLA/PMMA IPNs. Advantage of the well-known hydrolytic degradability of PLA was thus taken. As specified in Figure 1, this degradation was conducted at 60 °C using a mixture of a phosphate buffer (pH = 8.2) and ethanol. It has to be stressed that the hydrolysis was performed at intermediate temperature between the T_g of PLA single network (40 °C) and those of PMMA single networks (110–160 °C) to avoid the collapse of the residual porous methacrylic structures, while allowing for an efficient degradation of PLA.

Extracted IPNs as well as the corresponding single networks were subjected to hydrolysis under the same conditions, and the variations of mass loss were monitored as a function of the hydrolysis time (Figure 2 as an example). The PLA-based single network was completely degraded after 48 h. We observed a decrease of pH, due to the release of carboxylic acid functions in the hydrolysis medium. According to ^{1}H NMR and SEC analyses, the degradation products were constituted of oligolactides, lactic acid, and crosslinker residues, indicating that the hydrolysis affected both ester and urethane functions. As for IPN samples, regardless of the dimethacrylate nature and content, mass loss values higher than or close to 50 wt % were reached only after 285 h, and such

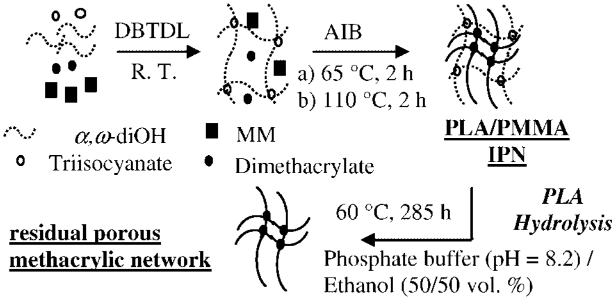

Figure 1.
Design of mesoporous networks from PLA/PMMA IPNs.

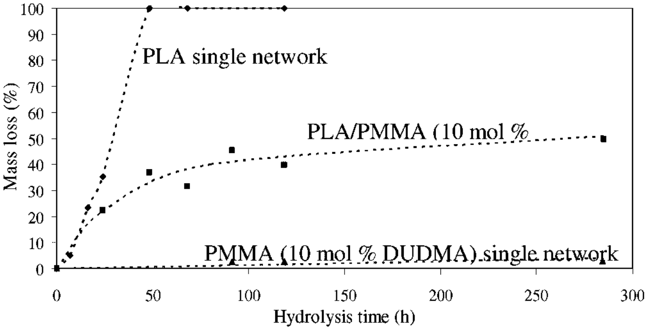

Figure 2.
Dependence of mass loss on hydrolysis time for PLA- and/or PMMA-based networks.

values were associated with the quantitative degradation of PLA sub-network. The total disappearance of the characteristic bands associated with PLA sub-network (urethane and carbonyl groups) in the FTIR and solid-state ^{13}C NMR spectra of residual networks after hydrolysis confirmed their pure methacrylic structure. Furthermore, the T_g values of hydrolyzed IPNs were very close to those of corresponding PMMA single networks (110–160 °C). In order to understand how the conditions of PLA degradation affected the structure of PMMA sub-networks during the partial hydrolysis of IPNs, PMMA-based single networks were analyzed after undergoing the same experimental conditions. Even though mass loss decreased significantly when increasing dimethacrylate composition, values as high as 15 wt % were assessed for single networks based on 1 mol % dimethacrylate. On the other hand, water absorption increased when decreasing dimethacrylate content. Therefore, the concomitant variation of both parameters indicates a non-negligible degradation of PMMA which may be ascribed to the partial hydrolysis of side-chain ester groups into carboxylic acid groups.

The morphologies of IPNs, before and after hydrolysis, were examined by SEM (Figure 3). Regardless of the dimethacrylate nature and content, the non-degraded

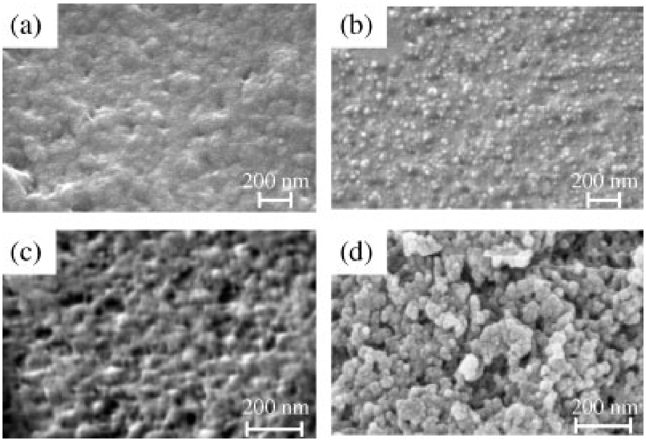

Figure 3.
SEM micrographs of different PLA/PMMA (50/50 wt %) IPN systems: before hydrolysis: (a) 10 mol % DUDMA-based sample, (b) 10 mol % BADMA-based sample; after hydrolysis: (c) 10 mol % DUDMA-based sample, (d) 10 mol % BADMA-based sample.

Table 1.
Pore Diameters (D_p) of Porous Methacrylic Networks as Determined by SEM and Thermoporometry

initial MMA/dimethacrylate composition (mol %)	D_p (nm) SEM **BADMA/DUDMA**	D_p (nm) thermoporometry **BADMA/DUDMA**
90/10	10–100/10–60	30–100/20–80
95/5	10–50/10–50	15–60/15–60
97/3	10–50/10–50	15–60/15–60
99/1	10–50/10–50	15–50/15–50

samples displayed compact and non-porous structures. This might arise from the good chain interpenetration of both constitutive sub-networks, as indicated by the transparency of IPN precursors. The corresponding PMMA single networks, after hydrolysis, did not exhibit a porous structure either, indicating a high compacity in this type of networks. In sharp contrast, the residual networks, after the hydrolysis of the PLA sub-network, exhibited porous structures with pore sizes ranging from 10 to 100 nm for BADMA-containing systems, and from 10 to 60 nm for their DUDMA-derivatized homologues. Pore sizes minimally decreased when decreasing the dimethacrylate content (Table 1). Thus, in such nanoporous materials, the dependence of pore size on dimethacrylate nature and content is not very significant.

Moreover, we determined pore sizes by thermoporometry through DSC measurements using water as the penetrant solvent. Thermoporometry has proved to be a reliable quantitative technique for the determination of pore size distributions in a wide range of (meso)porous materials, including porous silica, cellulose membranes, and hydrogels.[10] It relies on the depression of melting temperature (T_m) and the Gibbs-Thompson effect shown by a solvent constrained within the pores. This technique is sensitive and precise to measure pore diameter smaller than 200–300 nm. As a matter of fact, from the melting thermograms of water contained in the porous methacrylic networks, the T_m depression could be correlated to the pore diameter D_p as follows:[10] $D_p = 2 \cdot [0.68 - 32.33/(T_m - T_{m0})]$, where T_m and T_{m0} are the melting temperatures of confined and bulk water, respectively. The pore sizes thus determined are reported in Table 1. We clearly observed relatively narrow pore size distributions, regardless of the dimethacrylate nature and content. Overall, the results of pore diameters obtained by SEM and thermoporometry were in reasonable agreement. In these systems, the relatively small pore sizes and narrow pore size distributions of the methacrylic porous networks actually mirrored the good degree of chain interpenetration and small micro-domain sizes in IPN precursors.

Conclusion

A straightforward and versatile route toward mesoporous networks has been developed through the hydrolysis of the polyester sub-network from partially hydrolyzable PLA/PMMA-based IPNs as precursors. Thus, crosslinked PLA sub-chains may effectively serve as porogen templates for the generation of such porous polymeric materials. The mesoporosity of residual methacrylic networks can be attributed to the good degree of chain interpenetration of both PLA and PMMA sub-networks in IPN precursors conferred by their peculiar interlocking framework. The potential applications of such porous networks are mainly expected in the areas of separation techniques and chemistry in confined medium.

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