Porous Polystyrene Monoliths Prepared from in Situ Simultaneous Interpenetrating Polymer Networks: Modulation of Morphology by Polymerization Kinetics

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Supporting Information

ABSTRACT: Semi-interpenetrating polymer networks (semi-IPNs) were prepared by in situ simultaneous orthogonal polymerizations, where the linear poly(ε-caprolactone) (PCL) was synthesized by ring-opening polymerization of ε-caprolactone and the poly(styrene-co-divinylbenzene) (PS) network was formed by free-radical polymerization of styrene/divinylbenzene. Semi-IPNs were used as the precursors for the preparation of porous PS monoliths. To this end, the PCL domains were selectively removed by hydrolysis under basic conditions. By changing the amount of organocatalyst used for the ring-opening polymerization of ε-caprolactone, the relative polymerization kinetics of both monomers was varied, which has a pronounced effect on the morphology of thus-obtained PS frameworks.

INTRODUCTION

Interpenetrating polymer networks (IPNs) consist of inter-twined polymer networks that are not covalently bound to each other. Two individually cross-linked networks form a full-IPN, whereas a semi-IPN is obtained when only one of the polymeric components is cross-linked.1,2 Entanglement of polymer chains within the IPN results in a forced miscibility of the otherwise immiscible polymers. The IPN morphology strongly depends on the synthetic conditions, affecting a phase separation process. Sequential IPNs are prepared by a two-step process, consisting of dissolving/swelling of a preformed polymer by a second monomer/cross-linker mixture that is subsequently polymerized, or by an in situ polymerization of a homogeneous mixture of both (macro)monomers where the polymerization of one (macro)monomer is finished before the second one starts to polymerize. On the other hand, when polymerizations of both (macro)monomers take place at the same time, an in situ simultaneous IPN is formed.3 During simultaneous IPN synthesis, the rate of polymerization of each (macro)monomer can differ. The majority of literature dealing with kinetic studies comprises the IPNs prepared by free radical polymerization of vinylic monomers and step-growth polymerization of polyether polyols and isocyanates to form polyurethanes (PU).5–9 Instead of polyether, polyisobutene,9,10 polysiloxane,11 and polycarbonate12 have been applied as the components of PU, and moreover PUs were combined also with epoxy13 or thiol–ene chemistry.14 The effect of the order of individual network formation on the IPN morphology was studied for the in situ full-IPNs, consisting of polystyrene (PS) and polyisobutene-based PU.10 For this purpose, the amount and type of the free-radical initiator were varied to form the PS network faster or slower than the PU network or to form it only after the PU network was almost fully formed. The interpenetration degree of both networks within the resulting IPNs was the highest when the PS network was formed last since in the opposite case the full (macro-)monomer conversion to PU was prevented by the PS network in the glassy state. Previous studies showed that relatively high molecular weight polyols, used for the PU network formation, enhance incompatibility between the two polymers, leading to early onset of the phase separation during IPN formation.5,6

The onset of network gelation, which locks in the structure, also plays an important role in morphology formation of the resulting materials. In general, the PU network should form first to achieve fine interpenetration of both networks,5,10,11,12 or the times of gelation of both networks should coincide.13 Polyurethane chemistry has also been used to cross-link the polyester polyols within the IPNs. Polysters are particularly interesting components since they can be selectively removed from the IPNs to prepare the porous polyom monoliths, as highly desirable materials for flow-through applications in chromatographic analysis, solid phase extraction, and heterogeneous catalysis,15,16 where a degree of phase separation determines the pore sizes.17 In situ sequential full-IPNs were prepared by dissolution of polyactide (PLA) polyl in a mixture of methacrylic monomers and subsequent in situ cross-
linking of PLA to form the PU network.\textsuperscript{18,19} Afterward, the methacrylate monomer and cross-linker were polymerized at high temperature to produce the full IPNs. Finally, the polyester network was hydrolyzed in the phosphate buffer/ EtOH to obtain the porous poly(methacrylate) (PMMA) frameworks. When the PLA had not been cross-linked, its removal by selective dissolution led to the porous PMMA of larger pore sizes.\textsuperscript{20} Similar porous morphology of PMMA was obtained when poly(e-caprolactone) (PCL) had been used as the sacrificial polyester.\textsuperscript{21} The pore sizes of different methacrylic and styrenic frameworks, obtained after dissolution of linear PLA or after basic hydrolysis of cross-linked PLA from the IPNs, were in a range of few tens to few hundreds of nanometers.\textsuperscript{22}

PLA has also been used as an etchable component in different copolymer systems, in which the microphase separation is a consequence of the incompatibility of covalently linked copolymer constituents. The domains and subsequently the pore sizes were in a range of few nanometers to few tens of nanometers. Nanoporous PS frameworks were prepared from the copolymer networks based on the telechelic hydroxyl-terminated PS and PLA, which were randomly end-linked with a tetrafunctional isocyanate.\textsuperscript{23} A cross-linkable block copolymer of PLA and PS with the incorporated epoxy groups was prepared by using a macromolecular chain transfer agent (macro-CTA) based on PLA. The copolymer’s disordered structure at high temperatures was kinetically trapped by a subsequent cross-linking through the epoxy groups to afford the nanoporous PS structure after PLA removal.\textsuperscript{24} The macro-CTA based on etchable PLA was also used for polymerization of multifunctional styrene monomers. Such block copolymers were cross-linked in the course of polymerization.\textsuperscript{25–27} Block polymerization of PLA and styrene/divinylbenzene (DVB) was performed also simultaneously from a heterofunctional initiator, so the use of macro-CTA was avoided.\textsuperscript{28} Furthermore, a hierarchical porosity, consisting of macro- and mesopores, was obtained when the polymerization of styrene/DVB from the PLA-based macro-CTA had been performed in the presence of a nonreactive poly(ethylene oxide),\textsuperscript{29} whereas the meso- and micropores were generated when the PS framework had been hyper-cross-linked\textsuperscript{30} or when the sterically hindered styrene monomers had been applied.\textsuperscript{31}

In the case of sequentially prepared semi-IPNs of PCL and cross-linked PS, the domain sizes were in a micrometer range due to the incompatibility of these two polymers.\textsuperscript{32,33} This is expected since the blends of PCL and high molecular weight PS, prepared by extrusion\textsuperscript{34} or solution casting,\textsuperscript{35,36} also reveal large tendency to phase separate over time due to absence of cross-linking. In this work, we aimed to control the extent of phase separation of the in situ simultaneously prepared semi-IPNs consisted of the immiscible PCL and PS by changing their relative polymerization rate, while locking in the morphology by cross-linking the PS phase. e-Caprolactone (CL) and styrene/DVB were polymerized in situ by the simultaneous orthogonal polymerizations, i.e., organocatalyzed ring-opening polymerization (ROP) and free-radical polymerization (FRP), respectively. The simultaneous formation of both polymers should improve their compatibility, leading to smaller domain sizes. After semi-IPNs formation, the PCL domains were selectively hydrolyzed to produce the porous poly(styrene-co-DVB) monoliths. A comprehensive study of the effect of the polymerization kinetics on the morphology of thus-obtained PS frameworks is reported herein.

## EXPERIMENTAL SECTION

### Materials

The chemicals 2,2′-azobis(2-methylpropionitrile) (AIBN, 98%, Fluka Chemika), 3-phenyl-1-propanol (PPA, 98%, Aldrich), diphenyl phosphate (DPP, 99%, Aldrich), and sodium hydroxide (NaOH, Honeywell) and solvents chloroform (Honeywell), methanol (Sigma-Aldrich), and toluene (Merck, anhydrous) were used as received. CL (97%, Aldrich) was dried over calcium hydride (95%, Sigma-Aldrich) overnight and distilled under vacuum. DVB (Merck) and styrene (99%, Sigma-Aldrich) were passed through a layer of active alumina (Al2O3, Merck) prior to use.

### Methods

\textsuperscript{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova 300 MHz spectrometer (Varian, Inc., USA). All measurements were performed in CDCl\textsubscript{3} at room temperature in the pulse Fourier transform mode. Tetramethylsilane (TMS, δ = 0) was used as an internal chemical shift standard.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed on a Bruker UltraflexXtreme MALDI-TOF mass spectrometer (Bruker Daltonik, Germany). Samples were dissolved in tetrahydrofuran (THF) (10 mg mL\textsuperscript{-1}), and mixed with a solution of 2,5-dihydroxybenzoic acid in THF (30 mg mL\textsuperscript{-1}) as a matrix and sodium trifluoroacetate in THF (10 mg mL\textsuperscript{-1}) as a cationizer in a volume ratio of 1:10:3. A 0.4 μL of thus-prepared solution was spotted on the target plate (dried-droplet method). The reflective positive ion mode was used to acquire the samples’ mass spectra. Calibration was performed externally with a mixture of PMMA standards dissolved in THF (MALDI validation set PMMA, Fluka Analytical), covering the measured molecular weight range, and using the nearest-neighbor position method.

Size-exclusion chromatography coupled to a multilength light-scattering photometer (SEC-MALS) was performed on a modular liquid chromatograph consisting of an Agilent Technologies 1260 series pump and a degasser (Agilent Technologies, USA) coupled to a Dawn Heleos-II multangle light-scattering photometer with a GaAs linearly polarized laser (λ\textsubscript{e} = 661 nm) and to an Optilab rEX interferometric refractometer (RI), operating at the same wavelength as the photometer (both instruments are from Wyatt Technology Corp., USA). A MesoPore column (Agilent Technologies, USA) was used for sample separation by size. THF was used as the solvent (100 μL, 1 mg mL\textsuperscript{-1}) and eluent at a flow rate of 1 mL min\textsuperscript{-1}. For the data acquisition and evaluation the Astra 5.3.4 software (Wyatt Technology Corp., USA) was utilized.

Fourier-transform infrared (FT-IR) spectra were collected using a Spectrum One FT-IR spectrometer (PerkinElmer, UK). FT-IR spectra were recorded in an attenuated total reflectance (ATR) mode in a spectral range of 650–4000 cm\textsuperscript{-1}.

Nitrogen sorption measurements were performed on a TriStar II 3020 (Micromeritics, USA) sorption analyzer. The samples were outgassed at 40 °C. The specific surface areas (SSAs) were determined by means of the nitrogen sorption data in the relative pressure range from 0.05 to 1 using the Brunauer–Emmett–Teller (BET) method. Pore size distributions of samples were determined based on the Barrett–Joyner–Halenda (BJH) analysis of the nitrogen sorption isotherms.\textsuperscript{39}

Scanning electron microscopy (SEM) was used to investigate the morphology of porous samples. Sample surfaces were sputtered with a
6 nm layer of gold using a Gatan PECS 682 (Gatan, USA) sputter coater. SEM images were taken on a HR-SEM Zeiss Ultra plus instrument (Carl Zeiss, Germany).

Mercury intrusion porosimetry was performed on an AutoPore IV 9500 instrument (Micromeritics Instruments, USA). The samples were evacuated at 50 μmHg and room temperature prior to mercury intrusion. Samples were analyzed under the following parameters: contact angle = 130°, mercury surface tension = 480 mN m⁻¹, and maximum intrusion pressure = 441 MPa.

### RESULTS AND DISCUSSION

Acid-catalyzed ROP of CL using DPP as a catalyst and FRP of styrene/DVB using AIBN as an initiator were chosen as the orthogonal polymerizations for the simultaneously prepared semi-IPNs of PCL/poly(styrene-co-DVB) (50/50 wt %) with a styrene/DVB composition of 90/10 mol % (Scheme 1). The DPP catalyst offers a high degree of control over ROP of CL in solution as well as in bulk. Under the conditions we had used in this work, ROP and FRP did not appear to interfere with each other significantly and no copolymerization or grafting was observed. Soluble fractions obtained during extraction of the crushed IPNs in chloroform contained linear PCL chains and unreacted styrene monomer in trace amounts as determined by H NMR (Figure S3). FT-IR spectra of the remaining cross-linked PS frameworks after removal of PCL from the IPNs by extraction showed only the bands characteristic of PS (Figure S4).

The kinetics of simultaneous ROP of CL and FRP of styrene were studied to evaluate the influence of relative polymerization rate on the IPN morphology. The polymerization rate of CL is governed by the DPP concentration, and thus it can significantly and break apart; however, they did not dissolve completely, which clearly indicates the formation of a chemically cross-linked gel. The time of phase separation was determined visually by noting the onset of turbidity. Approximate conversions of monomers at the times of gelation and phase separation were calculated from the corresponding polymerization kinetic study, assuming the first-order kinetics.

### Table 1. IPN Characteristics: Remaining Monolith Mass after PCL Hydrolysis, Densities before and after Hydrolysis, Specific Surface Area, Gelation Time, and Onset of Turbidity

| sample | w_DPP (%) | w Framework (%) | \( \rho_1 \) (g cm⁻³) | \( \rho_2 \) (g cm⁻³) | SSA_BET (m² g⁻¹) | gelation (min) | turbidity (min) |
|--------|-----------|-----------------|----------------------|----------------------|------------------|---------------|----------------|
| IPN0.1 | 5.0       | 40              | 0.98                 | 0.37                 | 4.8              | 12            | 2              |
| IPN0.5 | 5.0       | 40              | 0.90                 | 0.31                 | 2.9              | 16            | 10             |
| IPN1.0 | 2.0       | 39              | 0.92                 | 0.35                 | 4.1              | 22            | 19             |
| IPN1.5 | 1.5       | 40              | 1.02                 | 0.44                 | 22.7             | 23            | 22             |
| IPN2.0 | 1.0       | 44              | 1.05                 | 0.49                 | 47.6             | 27            | 28             |
| IPN3.0 | 0.5       | 46              | 1.06                 | 0.50                 | 70.3             | 26            | 45             |
| IPN5.0 | 0.3       | 48              | 1.08                 | 0.55                 | 46.5             | 29            | 70             |

*Remaining monolith mass after PCL hydrolysis. †Density determined by mass and geometry of IPN before hydrolysis. ‡Density determined by mass and geometry of IPN after PCL hydrolysis. ††Time of gelation determined by vial inversion method. ‡‡Onset of turbidity determined visually.
DPP concentration. The kinetics experiments were performed in the absence of DVB cross-linker to determine the conversion of both monomers by $^1$H NMR of aliquots taken from the reaction mixture during polymerization. The polymerization rates of CL and styrene are not significantly affected by the addition of DVB cross-linker until the gelation point is reached; however, after the system gelation the styrene/DVB polymerization rate rapidly increases due to the increase in viscosity and entanglement degree induced by cross-linking. The conversion of CL was determined from the integrals of signals of CL (4.22 ppm, $-\text{CH}_2\text{CH}_2\text{O}^-$) and PCL (4.06 ppm, $(\text{−CH}_2\text{CH}_2\text{O}^-)_n$), while the conversion of styrene was determined by comparing the integral of styrene signal (5.22 ppm, $\text{Ph−CH}═\text{CH}_2$) with that of CL (4.22 ppm) at $t = 0$, since a broad signal of the PS aromatic ring (7.2−6.3 ppm, aromatic) is overlapping with the signals of styrene and DPP (Figure S5). The relative polymerization rate was varied by the amount of DPP added, while keeping all the other polymerization conditions constant. The polymerization rate of styrene in bulk was found to be unaffected by the addition of DPP (5.0 wt %) (Figure S6). When lowering the amount of DPP in the mixture of CL and styrene from 5.0 to 0.5 wt %, the rate of ROP of CL slowed down significantly (Figure 1). However, a small change in polymerization rate of styrene was also observed, which could be ascribed to the autoacceleration effect caused by increase in viscosity of the reaction mixture. At 5.0 wt % DPP, the CL was rapidly consumed while the polymerization kinetics of styrene resembled that in the bulk. By lowering the concentration of DPP and slowing down the PCL formation, the polymerization rate of styrene was approximately the same as if it were only diluted in CL (0 wt % DPP), indicating that the change in styrene polymerization rate could also be connected with a phase separation process and corresponding changes in the local styrene concentration.

During the IPN synthesis, the phase separation and gelation onset times were monitored. Phase separation of PCL and PS is expected due to their incompatibility (solubility parameters of PCL and PS are 20.2 and 19.3 MPa$^{1/2}$, respectively$^{42, 10, 43−45}$). The phase separation causes the sample to become opaque due to a large difference in the PCL and PS refractive indices (1.47 and 1.59 for PCL$^{46}$ and PS,$^{47}$ respectively). Therefore, we considered the appearance of turbidity of reaction mixture as the onset of phase separation. The conversions of monomers at the times of onset of gelation and turbidity were calculated using a linear fit equation obtained from the polymerization kinetic study of the corresponding blend of linear polymers with the same amount of added DPP. The relative polymerization kinetics of the blends together with the onset points of gelation and turbidity are presented on the conversion−conversion plots in Figure 2.

In terms of relative polymerization kinetics, the polymerization of CL was faster compared to that of styrene when >0.5 wt % DPP had been used. Apparently, the differences in the kinetics of polymerizations of both monomers play a fundamental role in the time order of gelation versus phase separation. At 5.0 and 2.0 wt % (IPN5.0 and IPN2.0) of DPP used, the PCL formed rapidly, prompting the phase separation to occur before gelation. By reduction of the DPP amount to 1.5 wt % (IPN1.5), the turbidity appeared just before the gelation, whereas in the case of 1.0 wt % DPP (IPN1.0) the gelation occurred just before the sample turned turbid. By reduction of

![Figure 2](image-url)
the DPP further to 0.5 and 0.3 wt %, the phase separation in IPN0.5 and IPN0.3 occurred after gelation, since the polymerization of CL became slower than that of styrene. The gelation of the system seems to be independent of the CL polymerization rate and occurs at approximately the same conversion of styrene, while the onset of turbidity is delayed when the CL polymerizes more slowly.

The extent of phase separation in IPNs was studied after the removal of PCL within the PS networks. Extraction of PCL from the IPN monoliths by a solvent was proved to be less efficient since solvent diffusion slows down when both polymeric networks extensively interpenetrate, and furthermore, cracks occurred in the monolith as a result of swelling of PS network. To avoid significant morphological changes of the monoliths and to ensure a complete PCL removal, it was hydrolytically degraded in a basic aqueous/methanolic solution. The size and shape of the monoliths before and after PCL hydrolysis did not change significantly. The mass fractions of the samples after hydrolysis were below 50 wt % (Table 1), suggesting a complete polyester removal as supported by a disappearance of the carbonyl stretching band at 1720 cm$^{-1}$ in the FT-IR spectra of the resulting PS frameworks (Figure 3).

Because the onset of gelation and phase separation are suggested to play a vital role in the morphology formation of IPNs, the morphology of obtained PS frameworks was studied by SEM (Figure 4 and Figure S7). The samples where the phase separation occurred before gelation (IPN5.0 and IPN3.0) show much larger pores than the samples where the rate of CL polymerization was slowed down to postpone the phase separation to meet the gelation point (IPN1.5 and IPN1.0) or even to surpass it (IPN0.5 and IPN0.3). Moreover, the IPN5.0 shows visible defects most likely due to the autoacceleration effect, resulting in lower framework density. Among the IPN1.0, IPN0.5, and IPN0.3, no significant morphological differences were observed. As a reference, IPNseq was prepared sequentially, where the PCL was synthesized beforehand and subsequently dissolved in a styrene/DVB mixture. To ensure the same reaction conditions for the IPNseq as for the simultaneously prepared IPNs, the DPP was also added to the reaction mixture. However, the results show no influence of DPP on the morphology of IPNseq.

![Figure 3. FT-IR spectra of IPNs before and after hydrolysis together with FT-IR spectra of PCL synthesized in solution and cross-linked PS synthesized in bulk.](image)

![Figure 4. SEM micrographs of sequential IPNseq and in situ simultaneous IPNs, together with a photograph of monoliths obtained after removal of PCL from IPNs. The third row represents micrographs at higher magnification of samples IPN1.5, IPN0.5, and IPN0.3.](image)
The morphological features of the IPN seq resemble those of the IPN5.0, and the domain sizes correspond to those reported for the PCL/PS blends. Both samples also reached the onset of turbidity before gelation, indicating that the phase separation, dictating the final morphology, is truly limited if gelation of the network occurs first. The early onset of phase separation is ascribed to the high content of PCL already at the beginning of styrene polymerization, which thus resembles early phase separation observed in the simultaneously prepared PU-based IPNs. The faster is the CL polymerization, the faster is the phase separation in the PCL/PS system and the larger are the growing PCL domains within the PS matrix, resulting in the larger pores of PS framework after PCL removal. Thus, a decrease in the pore sizes of the IPNs when going from 5 to 0.3 wt % of DPP is a result of different relative kinetics of the CL and styrene polymerizations.

Pore size distributions of PS frameworks obtained by mercury intrusion porosimetry are shown in Figure 5. The IPNseq, IPN5.0, and IPN2.0 reveal the macroporous structures with pore sizes around 2–3 μm, which is consistent with a large domain spacing observed by SEM. The pore sizes of PS frameworks prepared by 1.0 wt % or less of DPP were shifted to much smaller pores with a majority of them smaller than 50 nm and with some also below 10 nm. The change in monoliths’ pore size distribution as a function of DPP amount is rather sharp, so this transition can be observed in a fairly narrow window of relative polymerization rates only, as indicated by the IPN1.5 monolith with the pore sizes between 100 and 400 nm.

The porous PS frameworks were further characterized by nitrogen sorption measurements. The pore size distribution as determined by BJH analysis is in relatively good agreement with data obtained by mercury intrusion porosimetry (Figure S9). SSAs were calculated using the BET theory (Table 1). The nitrogen sorption isotherms of the IPN seq, IPN5.0, and IPN2.0 revealed no accessible micro- or mesoporosity (Figure 6). Instead, an increase of N2 sorption uptake at \( p/p_0 \approx 1 \) indicates the presence of macropores, reflecting the low SSA of around 4 m² g⁻¹. The IPN1.5 sample shows larger SSA of 20 m² g⁻¹ due to smaller pore sizes of 100–400 nm. On the other hand, the IPNs where the amount of DPP was \( \leq 1.0 \) wt %, the pore sizes decreased even further, with majority below 50 nm, reflecting in type IV isotherms with the hysteresis loops that are typical for mesoporous solids. In this case, the SSA increased up to \( \sim 70 \) m² g⁻¹. These results are thus in a good agreement with the mercury intrusion porosimetry data.

### CONCLUSION

We have studied one-step, in situ simultaneous synthesis of semi-IPNs based on PCL and cross-linked PS with emphasis on the polymerization kinetics of CL and styrene and its effect on the IPN morphology. Semi-IPNs served us as the precursors for the preparation of porous PS frameworks, which were obtained after removal of PCL from the IPNs. By variation of the amount of the DPP organocatalyst, the relative polymerization rate was tuned, which in turn influences the time order of gelation versus phase separation. This plays a fundamental role in the final morphology of the porous network. Macroporous PS frameworks were obtained when the phase separation occurred substantially before gelation. On the contrary, when the phase separation was delayed, the PS frameworks reveal significantly smaller pores. The change in monoliths’ pore size distribution as a function of DPP amount is rather sharp since the transition from \( \sim 2 \) μm pore size to <80 nm was observed in a fairly narrow window of relative polymerization rates.

This work demonstrates importance of the kinetics of simultaneous and orthogonal polymerizations since it governs the time order of system gelation and phase separation, which in turn also dictates the IPN morphology and, after the removal of the PCL domains, also the pore sizes within the PS frameworks.
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