Nanoporous Crosslinked Polyisoprene from Polyisoprene - Polydimethylsiloxane Block Copolymer

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Summary

The polyisoprene block of a polyisoprene-polydimethylsiloxane (PI-PDMS) diblock copolymer with 0.68 volume fraction of PI was tightly crosslinked with dicumylperoxide. The PDMS part of the obtained glassy material was subsequently quantitatively etched with anhydrous hydrogen fluoride or tetrabutylammonium-fluoride, in this way obtaining a nanoporous material. The fraction of the surviving double bonds was estimated by solid state NMR, while thermal analysis was used to characterize the glass transition temperature of PI as a function of crosslinking degree. Small angle x-ray scattering confirmed the existence of microphase separated cylinders of PDMS in a PI matrix and its conservation in the form of channels in the crosslinked matrix.

Introduction

Self-organization in block copolymers is very interesting in relation to active material nanostructuring [1]. Preparation of nanoporous materials (NPMs) by the specific removal of a minority block in a block copolymer has attracted the attention of many researchers and a number of more or less quantitative and specific cleaving schemes have been proposed [2-9]. Potential applications of NPMs include templates for electronics, special dielectric materials, substrates for catalysis, design of nano-reactors, micro-filtration membranes and use in medical diagnostics. The question of bulk stability combined with the possibility to prepare well-defined block copolymer precursors has limited the actually reported polymer based NPMs largely to polystyrene (glassy at room temperature). However, many possible applications of NPMs require the presence of solvents in which cases it is necessary to crosslink the matrix to a sufficient high degree before removing one of the blocks of the copolymer.
  A specific and quantitative method for preparing NPMs is the use of PDMS as a degradable block in a nanophase separated block copolymer, as recently demonstrated for the first time [9]. This procedure extends the range of possible NPM matrices, notably with the class of polydienes, which are easily amenable to crosslinking [10]. This is the subject of the present work. The most commonly used polydienes have glass transition temperatures below 0 °C and eventual cavities generated by etching PDMS in a polydiene-PDMS block copolymer would be unstable to collapse from surface tension at room temperature. Therefore, in order to stabilise the remaining matrix a high degree of crosslinking of the polydiene is necessary before the removal

of PDMS [9]. The high and controllable degree of cross-linking of the matrix permits the use of NPMs both in bulk and in solution and many interesting properties are expected from such materials [11]. Model polydiene-PDMS block copolymers are readily synthesized by living anionic polymerisation [12,13].

This is the first report on the preparation of a polyisoprene based NPM, derived from a PI-PDMS block copolymer. The resulting NPM retains a significant portion of the original double bonds of PI as shown by solid state ^{13}C NMR. The double bonds can be used subsequently to introduce functional groups for different applications.

Materials and experimental

A PI with molecular weight (MW) of 10 kg/mol, a polydispersity index (pdi) of 1.03 and a PI-PDMS diblock copolymer with a total MW of 12.3 kg/mol, a 0.68 PI volume fraction and pdi = 1.04 were prepared by sequential living anionic polymerisation [12,13]. The order to disorder temperature of the PI-PDMS was measured to 130 °C by rheology [13]. Dicumyl peroxide (*bis(α,α-dimethylbenzyl) peroxide*) (DCP) from Merck was used as is for the crosslinking of PI. Anhydrous hydrogen fluoride (HF) from Holz+Co or tetrabutylamonium fluoride (TBAF) from Aldrich were used as etching reactants for PDMS. The crosslinking reaction on 3-4 g samples was conducted under argon at 115 °C or at 105 °C in a gas-tight steel cylinder. DCP was dispersed on the surface of the polymer in portions of $2.5 - 10\%$ moles relative to the initial moles of double bonds in PI. Samples for characterisation were taken at different times for up to 230 h. Fresh portions of DCP were dispersed on the polymer film every approx. 20 h during the crosslinking reaction (DCP was measured to have a half-life of 15 h at 115 °C [10]). Five to six additions of DCP and a reaction time of about 100-120 h produced acceptable crosslinking degrees. The precursor materials and the gelation process were characterised by size exclusion chromatography. Swelling ratio measurements of crosslinked PI samples in toluene were used to monitor the network crosslinking degree after the gelling point. The swelling ratio was taken as the mass ratio between equilibrium-swollen and dry sample. The same crosslinking conditions were applied for the PI-PDMS diblock copolymer. The crosslinked PI-PDMS sample was etched either by HF for 0.5 h at 0 °C or by 1 M TBAF in THF for 30 h at room temperature. The materials were characterised by ^{1}H NMR, differential scanning calorimetry (DSC), solid state ^{13}C NMR and small angle x-ray scattering (SAXS).

Results and Discussion

The gelling point of PI was reached after 10 h at 115 °C. Samples of crosslinked PI showing a swelling ratio in toluene smaller than 10 were characterised by DSC [10]. The DSC thermograms for three crosslinked samples together with the initial PI are shown in Figure 1. A summary of the characterization data on these four samples is given in Table 1. As the degree of crosslinking increases the segmental motion becomes more constrained, resulting in a diminished glass transition enthalpy [14]. It was not possible to measure a glass transition for the sample with highest degree of crosslinking, which was taken to indicate an average network strand length comparable to the monomeric unit. It is possible to estimate the crosslinking degree from the swelling data by using the model of Flory [15] adapted for a bulk crosslinked network:

$$M_c = -\rho \, [V_1 \, (v_2^{1/3} - \omega v_2)] \, / \, [\ln (1-v_2) + v_2 + \chi_{12} \, v_2^2] \qquad (1)$$

where M_c is the number average molar mass per network strand, ρ the overall density, V_1 is the solvent molar volume, v_2 the volume fraction of polymer at swelling equilibrium, χ_{12} the solvent-polymer interaction parameter and ω is twice the inverse of the crosslink functionality. The M_c values listed in tab. 1 were obtained from relation (1) substituting the following values for the parameters: $\rho = 0.90$ g/cm^3, $\chi_{12} = 0.36$ [16], $\omega = 0.50$, $V_1 = 107$ cm^3/mol for toluene; the polymer volume fractions v_2 were calculated from the swelling ratios in tab. 1. The M_c values for the networks with increasing crosslinking degree correspond to average monomer unit numbers of 53, 14 and 0.8 respectively. Thus the estimated number of crosslinks is comparable to the number of monomers for the tightest crosslinked PI. In the above estimation the chain ends were neglected (on average there are 147 monomer units per initial PI chain) which is expected to be a questionable assumption for the loosest network but not for the other two networks.

Table 1. Summary of conditions and data on precursor and prepared materials

Precursor	x-linking T/°C	x-linking time/h	Tg [b] °C	Swelling ratio [d]	M$_c$ [e] g/mol	Etching reagent	% double bonds [f]
PI	-	-	-65	∞	∞	-	100
	115	20	-58	4.40	3590	-	n.m. [c]
		30	-53	2.50	971	-	n.m. [c]
		120	not possible to detect	1.14	53	-	n.m. [c]
PI-PDMS	-	-	n.m. [c]	∞	∞	-	100
	115	120	n.m. [c]	n.m. [c]	-	-	35
					-	HF	25
						TBAF	28
	105&115[a]	120	n.m. [c]	n.m. [c]	n.m. [c]	TBAF	n.m. [c]

[a] Crosslinked at 105 °C for the first 20 h with two additions of DCP and at 115 °C for additional 100h; [b] DSC temperature gradient 10 °C/min; [c] not measured; [d] Mass ratio between equilibrium-swollen and dry network; [e] Number average molar mass of network strands calculated from relation (1); [f] double bonds present in % relative to the initial double bonds in PI as measured by solid state ^{13}C NMR.
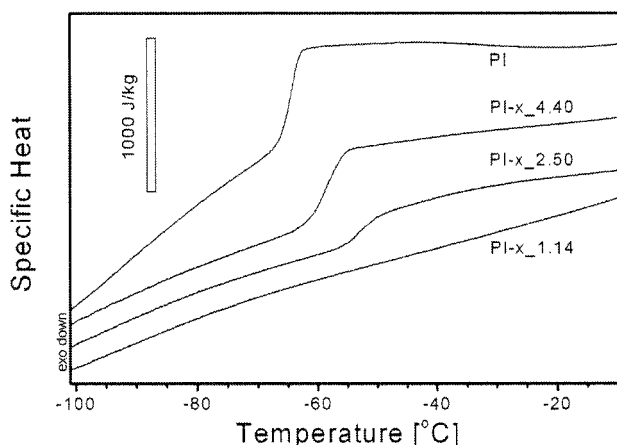

Figure 1. DSC thermograms of (from above): PI, crosslinked PI with swelling ratio 4.40 (PI-x_4.40), PI-x_2.50 and PI-x_1.14. The glass transition temperature increases and the transition intensity decreases in the above order. For the sample PI-x_1.14 it was not possible to measure a glass transition. Samples were heated at a rate of 10 °C/min.

The overall expected reaction for the free radical crosslinking of PI can be schematised as follows [17]:
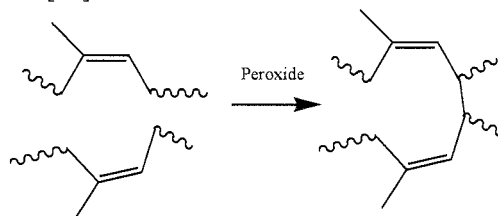
The thermally generated free radicals from the peroxide cleave allylic hydrogens from the PI chain, forming free radicals and the combination of two such radicals from different chains produces a crosslink. The double bonds remain intact in the above scheme. Other reactions that convert the double bonds into single bonds and/or crosslinks become important at high degree of crosslinking [10,17]. Solid state ^{13}C NMR was used for the characterisation of the tightly crosslinked PI and PI-PDMS. Figure 2 illustrates the findings for the precursor diblock (PI-PDMS), the crosslinked sample (PI-PDMS-x) and the crosslinked and etched sample (PI-PDMS-x-TBAF). Roughly 35% of the original PI double bonds in the diblock survived after crosslinking at 115 °C for 120 h. Between 25 and 28% of the starting double bonds were found present in the final NPMs with slightly higher survival for the TBAF-etched than for the HF-etched sample. Another important information from the NMR spectra of fig. 2 is the quantitative removal of PDMS, as seen from the disappearance of the signal at 0 ppm in the bottom plot.

The morphology of the prepared materials was studied by SAXS, as illustrated in Figure 3 for the untreated PI-PDMS, the crosslinked PI-PDMS and the crosslinked and etched sample. Notice the significant increase in scattering intensity for the NPM relative to the unetched samples. This is due to the increased electron density contrast as a result of PDMS removal [5]. As can be seen from fig. 3 the position of the main peak q* is displaced towards higher values for the NPM as compared to both the original and to the crosslinked PI-PDMS. Apart from this slight shrinkage the morphology of the crosslinked PI-PDMS is fully conserved after the removal of the PDMS block. The SAXS profiles of the HF-etched and TBAF-etched samples in fig. 3 are virtually identical.
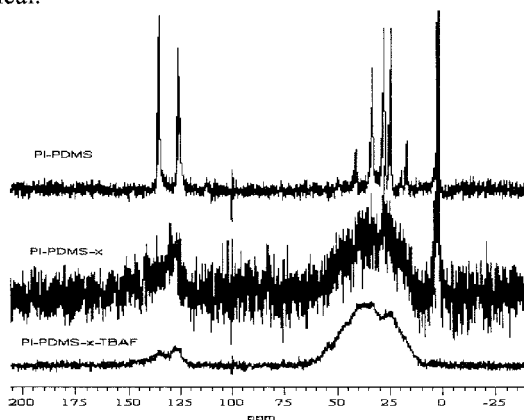

Figure 2. Solid state ^{13}C NMR of PI-PDMS, PI-PDMS-x and PI-PDMS-x-TBAF. The signal at 0 ppm is due to the PDMS and disappears completely for the etched sample. The group of signals around 130 ppm is due to the unsaturated carbons and the fraction of survived double bonds after crosslinking and etching is about 0.3 (see Table 1).

The main SAXS peak for the sample crosslinked at 115 °C is broader than that of the PI-PDMS precursor, while no additional significant broadening is observed for the etched samples. This peak broadening may be due to two effects: Firstly, the temperature for the crosslinking reaction is only 15 °C beneath the order to disorder transition temperature (ODT) of the PI-PDMS polymer. Therefore it is possible that the boundaries between the mesophases become more diffuse at such a temperature. Secondly, the crosslinking agent can act as a solvent at the temperature of crosslinking, which would cause a fall of the ODT, therefore amplifying the boundary blurring effect of the first point. Indeed, the broadening of the main peak was significantly reduced for a PI-PDMS sample crosslinked at a lower temperature (105 °C) and with smaller portions of crosslinker added stepwise in the crosslinking procedure. This is shown in Figure 4. Although the samples were not aligned, in this last case it is possible to see higher order reflections shown by the arrows in fig. 4, which are consistent with hexagonally packed cylindrical cavities.
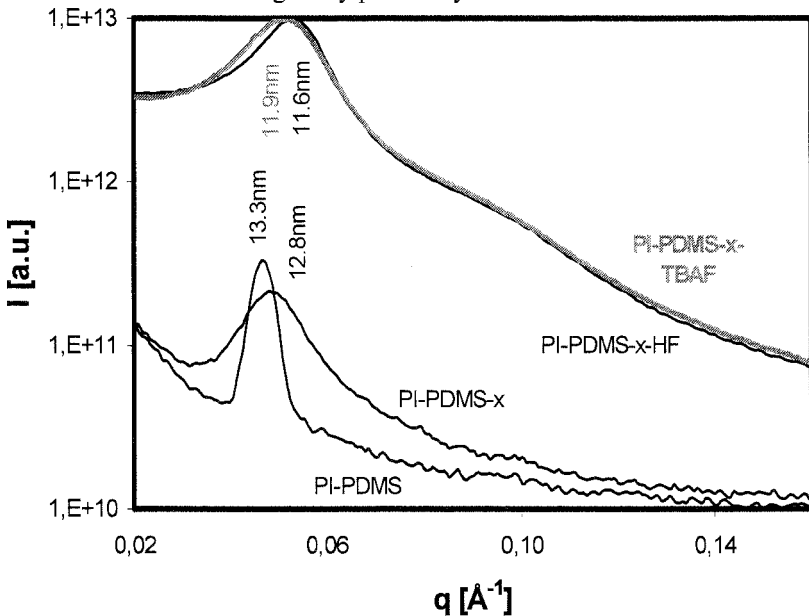

Figure 3. SAXS profiles of PI-PDMS, PI-PDMS-x, PI-PDMS-x-HF and PI-PDMS-x-TBAF. The broadening of the main peak is mostly due to the crosslinking stage. The HF- and TBAF-etched samples that were crosslinked at 115 °C show almost identical profiles with an intensity enhancement of almost a factor of 60 relative to the not etched samples. The peak displacement to higher q-values for the NPMs indicates a slight shrinkage of the matrix relative to the not etched materials.

In a previous work [9] it was demonstrated that there is a very good accordance between the structures deduced by SAXS and by direct space imaging (AFM, SEM, TEM). Therefore it is expected that such direct space imaging will confirm the hexagonal packing structure of the cavities in the final NPM. Such measurements are in progress.
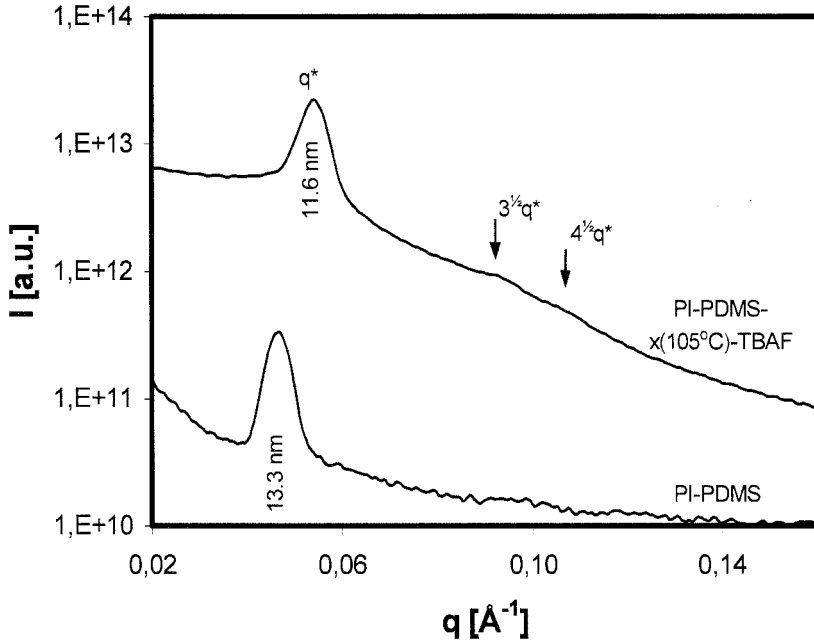
Figure 4. SAXS profiles of PI-PDMS and PI-PDMS-x-TBAF crosslinked at 105 °C. The broadening of the main peak is significantly reduced in this case. This is probably due to the combination of a lower initial crosslinking temperature (105 °C instead of 115 °C, therefore deeper in the segregation regime) and a lower amount of crosslinker (DCP) added at more steps, therefore reducing an eventual solvent effect of DCP during crosslinking.

Conclusions

In conclusion we have demonstrated the feasibility of creating nanoporous materials from a PI-PDMS block copolymer after crosslinking of the PI block and the subsequent etching of the PDMS block. The PI block was crosslinked with DCP. Anhydrous HF or TBAF in THF were used as etchants for PDMS. The precursor materials and the gelation process were characterised by size exclusion chromatography, extraction and swelling experiments, NMR and DSC. The PDMS was cleaved quantitatively and roughly 30% of the original PI double bonds survived both crosslinking and etching, as shown by solid state ^{13}C NMR. The morphology of the crosslinked material was largely conserved after PDMS cleaving as ascertained by SAXS.

References:

1. Park C, Yoon J, Thomas EL (2003) Polymer 44:6725
2. Lee J-S, Hirao A, Nakahama S (1988) Macromolecules 21: 276
3. Hashimoto T, Tsutsumi K and Funaki Y (1997) Langmuir 13:6869
4. Park M, Harrison C, Chaikin PM, Register RA, Adamson DH (1997) Science 276:1401
5. Chan VZH, Hoffman J, Lee VY, Iatrou H, Avgeropoulos A, Hadjichristidis N, Miller RD, Thomas EL (1999) Science 286:1716
6. Thurn-Albrecht T, Schotter J, Kästle GA, Emley N, Shibauchi T, Krusin-Elbaum L, Guarini K, Black CT, Tuominen MT, Russell TP (2000) Science 290:2126
7. Thurn-Albrecht T, Steiner R, DeRouchey J, Stafford CM, Huang E, Bal M, Tuominen MT, Hawker CJ and Russell TP (2000) Adv Mater 12:787
8. Zalusky AS, Olayo-Valles R, Wolf JH and Hillmyer MA (2002) J Am Chem Soc 124:12761
9. Ndoni S, Vigild ME, Berg RH (2003) J Am Chem Soc 125:13366
10. Hansen MS (Jan 2003) Polyisoprene Glass with Nanopores. Diplom K Thesis, Technical University of Denmark, Dept of Chemical Engineering, Lyngby, Denmark
11. Misner MJ, Skaff H, Emrik T, Russell TP (2003) Adv Mater 15:221
12. Ndoni S, Papadakis CM, Almdal K, Bates FS (1995) Rev Sci Instrum 66:1090
13. Vigild ME (1997) Mesomorphic Phase Behaviour of Low Molar Mass PEP-PDMS Diblock Copolymers Synthesized by Anionic Polymerization. PhD thesis, Risø National Laboratory
14. Pechhold W, Grassl O and von Soden W (1990) Colloid Polym Sci 268:1089
15. Flory PJ (1953) Principles of Polymer Chemistry. Cornell University Press, Ithaca New York
16. Van Krevelen DW (1990) Properties of Polymers. Elsevier, Amsterdam Oxford New York Tokyo
17. Mark et al (1988) In: Encyclopedia of Polymer Science and Engineering, Vol. 14, John Wiley & Sons, New York