Macroporous Cross-Linked Poly(dicyclopentadiene)

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ABSTRACT: This article describes the preparation of macroporous cross-linked poly(dicyclopentadiene) by chemically induced phase separation. Dicyclopentadiene was polymerized and cross-linked by metathesis in the presence of 2-propanol, using a ruthenium-based catalyst, and then dried under vacuum. The resulting porous materials were characterized by SEM, density measurements, and mercury porosimetry. By varying the initial 2-propanol content, it was shown that closed or open cell porosity could be obtained, with narrow pore size distributions and micrometric average access diameters. A linear dependence of the pore volume fraction and the initial 2-propanol content was also observed, suggesting easy tailoring of the former.

Introduction

Monolithic macroporous polymers are widely used as light structural materials, damping elements, and thermal or electrical insulators. Other specific applications such as membranes, ion-exchange and chromatographic media, solid support resins, carriers, catalysts, and adsorbents take advantage of the high specific internal surface area or the tortuosity of the porosity in these materials.[1−15] In these applications, control of the pore content and size is normally desired. Moreover, most of them need surface functionality to promote appropriate interactions. Styrene−divinylbenzene is commonly used since it fulfills many of the requirements. However, it suffers from inherently low functionality.

Although the metathesis reaction had been discovered earlier,[16,17] the expression "ring-opening metathesis polymerization" (ROMP) was first used by Calderon in 1967[18] after he introduced "olefin metathesis" in the same year.[19,20] The ROMP of dicyclopentadiene (DCPD) has been widely studied since it was first reported in 1968−1969.[21,22] The main interest of this monomer is that it can be used to produce a range of different macromolecular architectures, from purely linear to highly cross-linked polymers, depending on the catalytic system used.[23−31] DCPD is also an economically interesting monomer since it is a byproduct in the petrochemical industry (C_5 fraction) and is cheap and readily available, at least as a technical grade. It has been used, for example, to produce objects by reaction injection molding.[32] For applications requiring a high degree of surface functionality, DCPD-based polymers are potentially interesting because of the large number of double bonds resulting from ROMP. Indeed, it is likely that dense grafting of functional moieties suitable for a given application can easily be performed on the double bonds present at the surface of such materials. Moreover, their purely hydrocarbon structure should be stable over a wide range of pH, despite the high degree of unsaturation, which will tend to promote oxidation.[27]

To produce macroporosity in thermosetting resins, chemically induced phase separation (CIPS),[33−36] also termed chemical cooling,[37] polymerization-induced phase separation,[38] or reaction-induced phase separation,[39−43] can be used. This approach, illustrated in Figure 1, consists of polymerizing a mixture of the polymer precursors and a nonreactive solvent, termed the porogen, that will template the porosity. The porogen must be a solvent for the precursors but a nonsolvent for the polymer. Thus, owing to the substantial decrease in the entropy of mixing on polymerization, the initially homogeneous solution separates into a solvent-rich phase and a polymer-rich phase. When polymerization and phase separation are complete, the solvent may be removed by drying, leaving a porous structure.

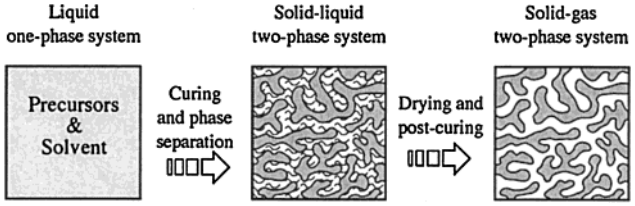

Figure 1. Principle of chemically induced phase separation.

The aim of the present work is to prepare macroporous cross-linked poly(dicyclopentadiene) (PDCPD) with controlled porosity via CIPS. Because of the potentially large change in entropy during polymerization and cross-linking, phase separation is envisaged to occur for a large range of porogen concentrations, resulting in a wide range of final morphologies. With the incorporation of suitable functionality, such materials could serve as base materials for functional beads and membranes in chromatography or as solid support resins. This report describes the synthesis and processing of macroporous cross-linked PDCPD and its characterization by scanning electron microscopy (SEM), density measurements, and mercury porosimetry.

Experimental Section

Materials. Dicyclopentadiene ("Petroplast 94%" from Shell, 94% pure, and containing stabilizer, trimers, and other products) was degassed for 5 min under 1 mbar pressure, purged with N_2, and stored over 5 Å molecular sieves. 2-Propanol (purum) and dichloromethane, together with the trial solvents and toluene, were purchased from Fluka and used as received. The catalyst, $RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PCy_3)$

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Table 1. Sample Compositions

			2-propanol		
sample no.	DCPD (g)	Ru-cat (mg)	(g)	(wt %)	(vol %)
1	1.87	18.7	0.0976	4.91	6.54
2	1.93	19.2	0.215	9.93	13.0
3	1.70	16.9	0.301	14.9	19.2
4	1.96	19.6	0.489	19.8	25.1
5	1.48	14.8	0.493	24.8	30.9
6	1.41	14.1	0.604	29.8	36.5
7	1.31	13.1	0.702	34.7	41.9
8	1.19	11.8	0.791	39.8	47.2
9	1.09	10.9	0.896	44.9	52.5
10	1.01	10.1	1.00	49.6	57.2
11	0.921	9.12	1.13	54.8	62.2
12	0.811	8.03	1.23	59.8	66.8
13	0.669	7.10	1.30	65.8	72.3
14	0.403	4.03	1.60	79.7	84.2
ref	1.95	18.9	0	0	0

complex (Cy = cyclohexyl), was synthesized according to the procedure described by Bennett and Smith.[44]

Preparation of the Samples. A solution of 10 wt % of the ruthenium-based catalyst (Ru-cat) in dichloromethane was prepared for each set of samples (four or five samples per set). The DCPD, 2-propanol, and Ru-cat solution were then mixed in screw-cap disposable flasks. The amount of Ru-cat solution was calculated to give 1 wt % of Ru-cat in the DCPD. Thin needle syringes were used for high accuracy in weighing and handling the dichloromethane and the Ru-cat solution. All the sample compositions are given in Table 1. The 2-propanol weight percent was calculated without taking into account the weight of the dichloromethane. The 2-propanol volume percent was calculated using the density of the reference sample as the density of the DCPD and Ru-cat mixture. The flasks were hermetically sealed, and the mixture was homogenized by vibrating the flask with a Thermodyne type 16700 Max-Mix 1 mixer for a few seconds. The flasks were then placed in an oven, preheated at 80 °C, for 20 h. After polymerization, the flasks were broken to extract the samples. The samples were finally placed in an oven at 80 °C under vacuum for 20 h of drying.

Characterization Methods. Two samples of the reference were swelled by Soxhleting in toluene and 2-propanol until no further changes in the sample weight were observed. The degree of swelling and the sol and gel fractions were then determined by weighing after redrying at 140 °C under vacuum. The density of the porous samples was obtained by weighing them and determining their volume with a caliper after sandpapering to obtain regular cylinders. The density of the reference sample was measured using a Mettler density measurement kit adapted for a AT261 DeltaRange balance. The fracture surfaces, obtained by notching and fracturing at room temperature, were observed by SEM without gold sputtering using a Phillips XLF-30 microscope equipped with a field emission gun, operating at 2 kV. The mercury porosimetry was performed on a Porosimeter 2000 WS coupled to a Macropores Unit 120 from Carlo Erba Instruments, assuming a cylindrical pore shape for the pore size calculation. For these tests, the samples were fractured through their center. The number-average access diameters were calculated from the distributions given by mercury porosimetry. Thermal gravimetric analysis (TGA) measurements were performed on a Perkin-Elmer TGA7 equipment, using a 10 °C/min temperature scan up to 400 °C under nitrogen.

Results and Discussion

System Design and DCPD Polymerization. An appropriate choice of solvent is one of the keys to successful CIPS. Prediction of which solvents will give the desired behavior is nevertheless difficult and has to be complemented with experimental verifications. Solvents less polar than PDCPD were first tried. Toluene, hexane, and decane failed to promote phase separation, even at 50 wt % loading. Solvents more polar than PDCPD were therefore tested. Although aprotic solvents such as acetone and dimethylformamide did not work, protic solvents, and alcohols in particular, were found to be suitable, with 2-propanol providing the best results among the solvents surveyed.

Scheme 1. Polymerization and Cross-Linking of Dicyclopentadiene Using [Ru(arene)$Cl_2(PCy_3)$]

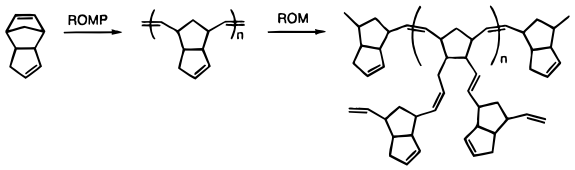

Table 2. Extraction Results

	sample swelled in toluene	sample swelled in 2-propanol
initial weight	0.2361 g	0.7200 g
swollen weight	0.4471 g	0.7156 g
redried weight	0.2202 g	0.6926 g
swelling ratio	2.03	1.03
gel fraction	93.3 wt %	96.2 wt %
sol fraction	6.7 wt %	3.8 wt %

To be used for CIPS, the catalyst has also to fulfill a number of requirements. It has, for example, to be soluble. Common catalysts known to be efficient for polymerizing a given monomer are usually soluble in that monomer, but they need not be soluble in the monomer/porogen mixture. In the present case, where a protic solvent was used as the porogen, a catalyst combining adequate reactivity with good resistance to protic solvents was necessary. For this reason many metathesis catalysts systems (W- or Mo-based) were unsuitable.[28] Moreover, the system should be relatively latent at room temperature, allowing for mixing and homogenization before polymerization.

With the appropriate choice of ligands, ruthenium-based catalysts can possess remarkable tolerance toward most functional groups,[28,45−47] which make them suitable candidates. They are also known to be very efficient catalysts for the polymerization of technical grade DCPD at temperatures of 80 °C and higher,[27−29,31] and at room temperature, DCPD/[Ru(arene)$Cl_2(PCy_3)$] is sufficiently latent for processing. For CIPS, the lowest temperature in this range (80 °C) was chosen in order to give slow polymerization, allowing for phase separation.

As stated in the Introduction, the mechanisms and the products of polymerization of DCPD depend on the catalytic system and on the conditions used. The same is true of cross-linking, which can occur via an addition reaction of the pendant cyclopentene double bonds[23] or via a second ring-opening metathesis[7] of the pendant cyclopentenyl ring. In the present system, ^{13}C solid-state NMR has shown that cross-linking via ring-opening metathesis (ROM) (Scheme 1) is the dominant mechanism.[28]

Two polymerized and cross-linked samples were subjected to extraction using 2-propanol and toluene (a poor and a good solvent, respectively). The results of these measurements are given in Table 2.

Toluene swelled the samples to twice their initial weight, but 2-propanol only entered to a level of 3 wt %. Extraction by toluene gave a gel fraction of 93.3 wt %, indicative of a high degree of conversion, taking into account the use of a technical grade (94%) of DCPD.

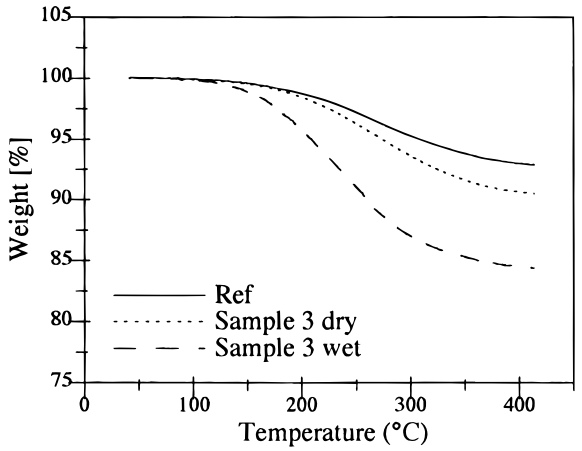

Figure 2. TGA performed on the reference (Ref), on sample **3** prior to drying (Sample 3 wet), and on sample **3** after drying at 80 °C under vacuum for 20 h (Sampe 3 dry).

Samples Preparation. Since the polymerization and cross-linking of DCPD are very slow at room temperature with the present catalytic system (gelation takes several hours), the components can be added to the reaction mixture in any order, although care should be taken to add the correct proportion of catalyst. Hermetically closing the flasks is also important for polymerization temperatures above the boiling points of 2-propanol and dichloromethane, as solvent loss or macroscopic pore formation inside the samples is to be avoided.

On polymerization, the initially transparent single-phase solution turns opaque, owing to phase separation and the formation of a light scattering morphology. After polymerization, all the samples except sample **14** (80 wt % 2-propanol) were solid. In sample **14**, phase separation and precipitation occurred before gelation, resulting in a sedimentation of the polymer-rich phase. Sample **1** and the reference remained transparent, suggesting a lack of porosity and hence that 5 wt % 2-propanol is below the solubility limit for 2-propanol in PDCPD or that a non-light-scattering morphology was present in sample **1**. All the other samples were uniformly opaque.

The final porous samples were obtained by drying in a vacuum oven at 80 °C for 20 h. This temperature was chosen to be well below the glass transition of the PDCPD matrix, thus avoiding softening which could result in collapse of the structures. To verify the efficiency of drying, TGA analysis was performed on sample **3**, prior to and after drying, and on the reference. Sample **3** was chosen since it is a sample with a high closed porosity, assumed to be among those requiring the longest drying times. The TGA curves are given in Figure 2.

The weight losses at 300 °C were of 4.7% and 6.4% respectively for the reference and for sample **3** after drying, with an onset at about 180 °C. This weight loss corresponds to the evaporation of the unreacted DCPD, which has a boiling point of 170 °C, suggesting the conversion of the DCPD to be about 95% for the reference and a little lower for sample **3**. Above 300 °C, the PDCPD starts to degrade, and at 400 °C the weight losses were 7% and 9.5% for the reference and sample **3** after drying, respectively. This difference is probably due to the increased surface area of sample **3**. The curve for sample **3** prior to drying showed an onset of weight loss at about 120 °C, corresponding to the evaporation of the 2-propanol, with an acceleration in weight loss at 180 °C, the curve finally becoming parallel with the reference curve above 280 °C. These features were not observed after drying, confirming the success of the drying procedure.

Characterization. *Scanning Electron Microscopy.* All samples, except sample **14**, were investigated by SEM. Four representative morphologies are shown in Figure 3, ranging from isolated pores (a), open porosity (b), fused large spheres (c) to fused small spheres (d). Care should be taken though in interpreting Figure 3c and especially Figure 3d. Electron beam damage during the observation caused a certain amount of collapse of the microstructure, which in these cases consists of fused spheres. Thus, sample **13** appears to be quite dense in Figure 3d although, as will be shown below, it was initially approximately 80% porous.

As shown in Figure 3a, for low porogen concentrations, we observe solvent-rich droplets precipitation in the continuous phase during CIPS, resulting in a solid continuous PDCPD matrix with isolated pores typical of a nucleation and growth mechanism.[33,36] At higher solvent contents, closer to the critical point, precipitation of solvent-rich droplets was also though to take place, but the overall porosity was increased, and the pores were interconnected, suggesting some coalescence of the droplets, as can be seen in Figure 3b. Phase separation was observed (i.e., the solution turned translucent and then opaque) relatively early in the solvent-rich compositions, indicating the cloud point to correspond to a relatively low degree of polymerization. At 30 wt % 2-propanol and above, the final structures consisted of agglomeration of roughly spherical PDCPD particles (Figure 3c,d), from which it was inferred that the critical point concentration was between 25 and 30 wt % 2-propanol. This type of structure is very interesting for applications as ion-exchange media for example, owing to the large extent of open macroporosity allowing high flow rates. Detailed discussion of the general principles of morphological development during CIPS is given elsewhere.[36,37] The behavior described above is typical of an addition polymerization reaction, as illustrated schematically in Figure 4. The phase diagram in this case has three components because monomers are present in the system until the last stages of polymerization.

Mercury Porosimetry. All the samples were analyzed including those that did not show open porosity when observed by SEM. However, in the following discussion, only results from samples with open porosity will be referred to since the technique is intrinsically limited to the investigation of such porosity.[48] We also refer to the pore "access diameters" rather than the more common "pore size", owing to the obviously noncylindrical morphology of the observed porosity. The samples were broken into two pieces instead of being crushed into a fine powder. Indeed, crushing would have led to destruction of the fused particulate morphology and hence loss of the interstitial porosity. A typical pore access diameter distribution for a sample with this type of morphology is shown in Figure 5.

The pore access diameter distributions are narrow and situated in the 1−10 μm range. Surprisingly all samples showed similar distribution and similar average access diameters, as shown Figure 6. This can be explained in terms of the differences in different sample and morphologies. Samples with a relatively low initial 2-propanol content consist of large connected particles

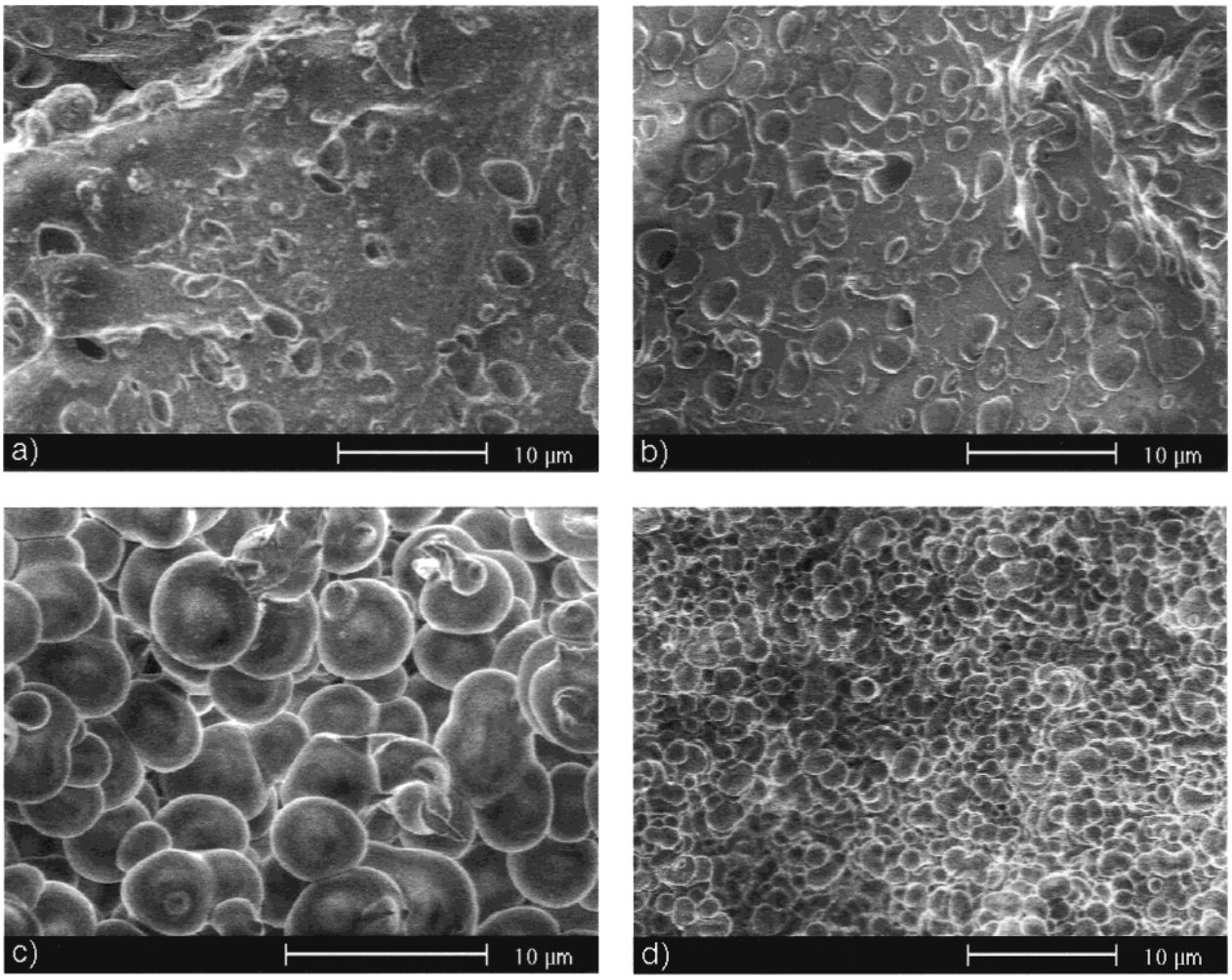

Figure 3. SEM of samples (a) 4, (b) 5, (c) 8, and (d) 13.

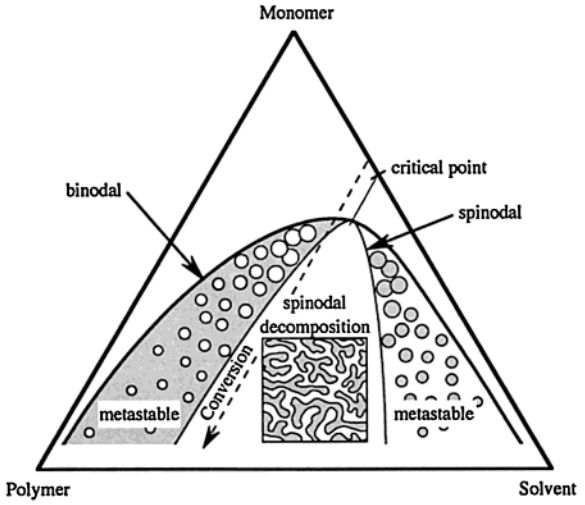

Figure 4. Schematic phase diagram for CIPS by addition polymerization.

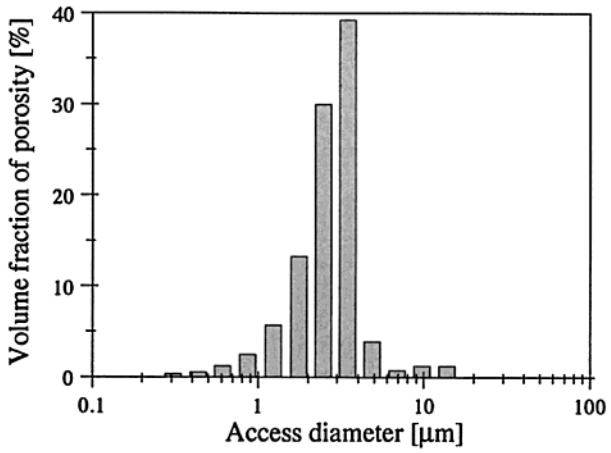

Figure 5. Distributions of the pore access diameters for sample **12**. This graph gives the volume fraction with respect to the total pore volume, for different ranges of pore access diameter (for example, 30 vol % of the pores have an access diameter between 2 and 3 μm).

(Figure 3c), and the packing defects and interstices are commensurate with the particles. On the other hand, samples with a high initial 2-propanol content are assumed to consist of smaller particles (Figure 3d) but with two levels of organization, i.e., the particles and particle agglomerates. The interstices between individual particles are smaller, but those between the agglomerates are approximately the same size as the interstices in the denser samples and tend to dominate the measured distributions. This suggests it may be possible to tailor the density independently of the effective pore size in these materials.

Density Measurements. The total porosities obtained from density measurements for all the samples are shown in Figure 7, together with the porosities given by mercury porosimetry for the samples with fully open porosity. The porosities from density measurements are

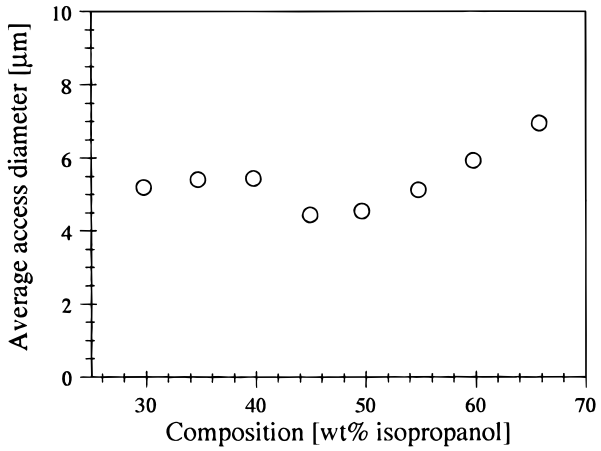

Figure 6. Average access diameters for samples with fully connected porosity.

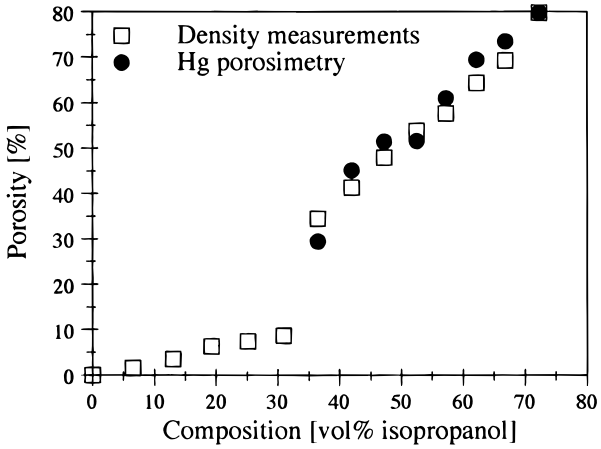

Figure 7. Comparison between total porosities obtained by mercury porosimetry and density measurements.

calculated using a reference density of 1.064 g/cm^3 for the sample containing no 2-propanol initially. The two techniques are in good agreement and, for the samples with open porosity, are roughly proportional to the initial 2-propanol content (indeed, over most of the range they are nearly equal).

The porosity of the samples with a low initial 2-propanol content is significantly lower than the latter. This is due to retention of 2-propanol in the PDCPD-rich phase up to high degrees of conversion. Indeed, bearing in mind experimental error, the similar densities of sample **1** and the reference are consistent with the lack of phase separation, inferred from the SEM results. On the other hand, sample **2**, which initially contained 13 vol % 2-propanol, shows a porosity of around 3%. The solubility limit is thus estimated to be below 10 vol %. Moreover, further increases in porosity with 2-propanol content below the estimated critical point are relatively small. This is because phase separation took place at relatively high degrees of conversion as also inferred from the very high viscosities at the cloud point (by inspection) and possibly gelation. Phase separation in this regime may therefore be impeded for kinetic reasons. Similarly, any resulting phase-separated microstructures may be very fine and hence undergo collapse during drying. This contrasts with the behavior at high 2-propanol contents where phase separation occurs at low conversions and the phase purity may be assumed to be high when conversion is complete. This is consistent with the low solubility of the PDCPD in the 2-propanol implied by the extraction experiment.

Conclusion

Dicyclopentadiene, polymerized and cross-linked with a ruthenium-based catalyst, has been successfully used to prepare macroporous materials via chemically induced phase separation. The resulting materials show micron-sized morphologies ranging from dispersed pores in a continuous matrix to low-density structures consisting of interconnected particles. Samples with fully connected porosity showed narrow pore access diameter distributions, and porosities up to 80% could be achieved at comparable initial solvent volume fractions. The potential ease with which the surface chemistry of these materials can be modified suggests them to have great possibilities for functional applications.

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