

Macroporous Poly(dicyclopentadiene) Beads

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ABSTRACT: Macroporous poly(dicyclopentadiene) beads have been produced via chemically induced phase separation in suspension polymerization. Phase separation is promoted by the enthalpic and entropic changes induced by the polymerization of dicyclopentadiene. By using poly(1,2-butylene glycol) monobutyl ether (M_n 500 g/mol), which is not soluble in the suspending medium, as the porogen, the stabilized droplets of the monomer/porogen mixture can be considered microreactors in which both polymerization and phase separation occur, resulting in solid, biphasic microspheres. The porogen is then extracted with methanol and the particles are finally dried. The resulting macroporous

crosslinked poly(dicyclopentadiene) beads are analyzed by scanning electron microscopy, mercury intrusion porosimetry, and nitrogen adsorption and are compared with similar bulk samples. Materials containing isolated pores as well as microstructures built with agglomerated particles have been produced. The porous microspheres showed micrometric average pores' access diameters and specific surface areas ranging from 1.3 to 3.1 m²/g. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 407–415, 2005

Key words: beads; macroporous polymers; phase separation; ROMP; suspension polymerization

INTRODUCTION

Despite the recently growing interest in monolithic stationary phases,^{1–5} microspheres, or beads, are still the most widespread medium used for different types of supports and chromatography.^{6–13} For specific applications such as protein or lately the growing field of DNA chromatography, materials with pore diameters over the micrometer are required.^{14,15} Macroporous polymers show pore sizes adapted to the coil sizes of such molecules, allowing high flow rates associated with high separation efficiency.^{16,17} Nowadays, polystyrene-divinylbenzene macroporous beads are commonly used but they suffer from inherently low functionalization capability.

It has been shown that chemically induced phase separation (CIPS) can be used to produce monolithic and gradient porosity macroporous thermosets.^{18–22} This technique consists of polymerizing polymer precursors in presence of an initially miscible, nonreacting porogen. The enthalpic and entropic changes of

the system, due to the polymerization of the monomer, drive the phase separation of the porogen. Using dicyclopentadiene (DCPD) with a ruthenium-based catalyst promoting ring-opening metathesis polymerization (ROMP) in the presence of isopropanol, CIPS allows us to obtain macroporous poly(dicyclopentadiene) (PDCPD) with either closed-cell or open-cell morphologies, with porosities up to 80%. PDCPD polymerized by ROMP are interesting for applications requiring high surface functionality owing to the large number of double bonds and active catalyst molecules present at the surface of these materials. Thus, there are different possible functionalization routes, as recently demonstrated.^{23,24} Also, an initiator was grafted to their surface and atom transfer radical polymerization was performed to obtain a thick grafted layer of poly(methyl methacrylate).²⁵

Various methods exist to produce beaded polymers by heterogenous polymerization. Emulsion, dispersion, precipitation, and suspension polymerization, for example, can be used.^{26,27} But, to obtain microspheres with diameters of several micrometers, suspension polymerization is the most adequate technique, because the other techniques referred to usually lead to much smaller particles.²⁸

The aim of this work is to evaluate the feasibility of combining CIPS and suspension polymerization to obtain macroporous PDCPD microspheres. To couple these two techniques, several aspects must be considered. The choice of the porogen is critical and will be discussed. The catalyst must be resistant to the protic suspension medium, which is, in the present work,

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TABLE I
Sample Composition and Nomenclature^a

Sample	DCPD (g)	Ru-Cat II (mg)	Poly(1,2-butylene glycol) monobutyl ether		
			(g)	(wt %)	(vol %)
B0	2.0134	0.0201	—	—	—
B1	1.4004	0.0139	0.5989	30	32.2
B2	1.2012	0.0120	0.7998	40	42.5
B3	1.0024	0.0101	1.0023	50	52.6
B4	0.8034	0.0081	1.2006	60	62.4
M1	2.8027	0.0281	1.2029	30	32.2
M2	2.4009	0.0240	1.6002	40	42.5
M3	2.0118	0.0201	2.0044	50	52.5
M4	1.6033	0.0161	2.4023	60	62.4

^a Names starting with **B** stand for bulk samples. Names starting with **M** stand for microsphere samples.

water. These are requirements, additional to those of the bulk CIPS, that must be fulfilled to reach the desired product. The fraction of porosity is tailored by varying the amount of porogen. The beads are characterized by scanning electron microscopy (SEM), nitrogen adsorption, and mercury intrusion porosimetry and are compared with similar bulk samples.

EXPERIMENTAL

Materials

Poly(1,2-butylene glycol) monobutyl ether ($M_n \sim 500$ g/mol, from Fluka), dichloromethane and methanol (purum, from Fluka), and hydroxypropyl cellulose ($M_w \sim 80,000$ g/mol, from Aldrich) were used as received. The catalysts, $\text{RuCl}_2(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)(\text{PCy}_3)$, where Cy = cyclohexyl and further abbreviated Ru-Cat I, and $\text{RuCl}_2(\text{styrene})\text{P}(\text{i-Pr}_3)_2$, where i-Pr = isopropyl and abbreviated Ru-Cat II in the following, were kindly supplied by A. Mühlebach (Ciba Specialty Chemicals). DCPD ("Petroplast 94%" from Shell, 94% pure, mainly endo- and containing stabilizer, trimers, and other products) was degassed (5 min under 1 mbar pressure, then purged with N_2) and stored on 5-Å molecular sieves. When Ru-Cat II was employed, the DCPD was distilled with a rotary evaporator before use.

Preparation of the samples

Bulk samples

The catalyst was weighted directly into 10-mL disposable screw-cap flasks. Having dissolved the catalyst with a few drops of dichloromethane, the porogen and DCPD were added in the flasks. The latter were sealed and placed overnight in an oven at 80°C for polymerization. The flasks were then broken to recover the solid that was extracted overnight with methanol using a soxhlet extractor to remove the porogen, fol-

lowed by drying at 80°C under vacuum to constant weight.

Microspheres

The aqueous solution of stabilizer(s) was poured in a 500-mL three-neck, round-bottom flask and heated to 80°C with an oil bath. Rubber stoppers were fitted in the lateral necks of the round-bottom flask and a stirrer shaft, with a glass bearing and a flat Teflon stir blade, was fitted in the central neck. The solution was stirred with an overhead stirrer and degassed by bubbling argon through the solution during the stirring for about 15 min. While heating under nitrogen, the mixtures of DPCP precursors and porogen were prepared and then injected with a needle into the three-neck round-bottom flask under stirring. The suspension was allowed to polymerize overnight at 80°C. After polymerization, the particles were collected by filtration. The porogen was then removed by overnight extraction with methanol using soxhlet. The particles were finally dried, at 80°C under vacuum, to constant weight.

Sample compositions

The composition of the samples is given in Table I. The poly(1,2-butylene glycol) monobutyl ether wt % was calculated without taking into account the weight of the dichloromethane. The porogen vol % was calculated using the density of sample **B0** (1.055 g/cm^3) as the density of the DCPD and Ru-Cat II mixture.

Characterization techniques

The density of samples **B0** and **B1** was measured using a Mettler density measurement kit adapted to a AT261 DeltaRange balance. The density of samples **B2**, **B3**, and **B4** was obtained by weighing them and determining their volume with a caliper after sandpa-

pering to obtain regular cylinders. The beads were gold sputtered with a Bio-Rad Polar Division SEM Coating System, Sputter Coated E5400, operated at 1 kV with 20-mA current for 60 s to obtain a gold layer of ~ 20 nm. The gold-sputtered beads were observed by SEM using a Phillips XLF-30 microscope equipped with a field emission gun operating at 2 kV. The mercury intrusion 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. The specific surface area was measured by nitrogen adsorption using a Micromeritics Gemini 2375 and the BET model for the adsorption isotherm. The particle size distribution was measured by a laser diffraction method using a Malvern Mastersizer S.

RESULTS AND DISCUSSION

Choice of the porogen

To apply CIPS in suspension polymerization, the porogen must: (1) be soluble in the monomer, in this case DCPD, (2) separate upon polymerization of the monomer, and (3) not be soluble in the dispersive medium, because if it was, it would simply dissolve in the dispersive medium upon phase separation, resulting in nonporous PDCPD beads.

Among the possible porogens undergoing phase separation upon polymerization of DCPD, the easier to use and process were low-formula-weight substances. The best results were obtained using alcohols such as 2-propanol.²⁰ However, such porogens cannot be employed when the polymerizing mixture is suspended in aqueous medium because they are soluble in water. To find porogens not soluble in water, substances with a lower solubility parameter had to be investigated. However, low-molecular-weight solvents with low solubility parameters failed to undergo phase separation upon polymerization of the DCPD.

For this reason, other parameters influencing the behavior of the polymerizing mixture had to be considered. The rationale for the choice of a suitable porogen was based on the interaction parameter χ_i as defined by Flory,²⁹ on which the heat of mixing depends. χ_i is proportional not only to the energy of a pair contact Δw_{12} and to the number of these pair contacts z_{pc} , but also to the number of segments of the solvent molecule n_s :

$$\chi_i = (z_{pc} - 2) \cdot \Delta w_{12} \cdot n_s / kT. \quad (1)$$

If a defined amount of solvent, being short or long molecules, is introduced in the mixture, the number of pair contacts z_{pc} between the solvent molecule and the polymer, which is proportional to the volume fraction of solvent and polymer, is the same. Likewise, if a

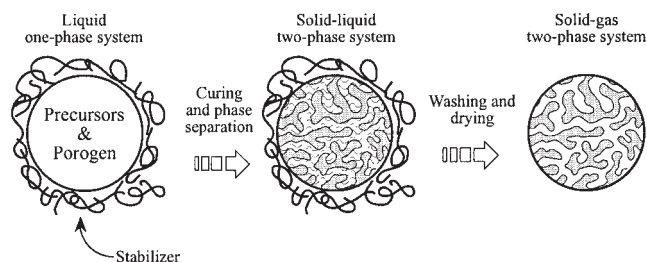


Figure 1 Phase separation occurring inside the suspended droplets.

particular type of solvent molecule is chosen (for example, di(ethyleneglycol) dimethyl ether and tri(ethyleneglycol) dimethyl ether could be an example of two molecules of the same type), the energy of a pair contact Δw_{12} is the same. However, to increase the interaction parameter, and thus promote the phase separation of the system, the number of segments n_s , i.e., the size, of the solvent molecule can be increased.

Moreover, the size of the molecule is also a factor influencing the change in the entropy of the system upon polymerization ΔS_{pol} . The latter can be expressed according to the Boltzmann equation, where k is the Boltzmann constant and W_0 and W_1 are the number of possible configurations of the molecules before and after polymerization, respectively:

$$\Delta S_{pol} = k \cdot (\ln W_1 - \ln W_0) \quad (2)$$

In this case, if the solvent molecules become trapped in the polymer network, their possible configurations can be regarded, for the clarity of the deduction, as being reduced to 1. But for molecules in solution before polymerization, the number of possible configurations being larger for a larger, flexible molecule, the entropy loss for such a larger molecule would be larger.

Both of these aspects suggested oligomeric porogens, rather than low-molecular-weight solvents, with solubility parameters lower than 2-propanol. This resulted in the choice of poly(1,2-butylene glycol) monobutyl ether with a M_n of 500 g/mol.

With the use of poly(1,2-butylene glycol) monobutyl ether, the suspended droplets consist only of substances of negligible water miscibility and these droplets, stabilized by hydroxypropyl cellulose, can be considered isolated microreactors. Indeed, the mixture of PDCPD precursors and poly(1,2-butylene glycol) monobutyl ether forming these droplets polymerizes and phase separates within these droplets, resulting in microspheres consisting of solid PDCPD and poly(1,2-butylene glycol) monobutyl ether domains. The only drawback with the use of such a high-molecular-weight porogen is the fact that a washing step (soxhlet extraction for solvent exchange) is needed before the

achievement of porous materials by drying. This is illustrated in Figure 1.

Preparation of the beads

A successful preparation of macroporous beads in the right bead diameter range was dependent on the catalyst used and on stabilizer type and amount. When 1 wt % (ratio to the weight of monomer) Ru-Cat II was used in distilled DCPD and the suspension medium consisted of 1 wt % hydroxypropyl cellulose in water, nicely solid, round particles were produced. Indeed, to find the optimal parameters to obtain microspheres of the desired size, several attempts (not indicated under Experimental) with different stabilizers, amounts of stabilizers, and catalysts were made.

First, the catalyst Ru-Cat I was not efficient in the suspension in aqueous medium. Indeed, the polymerization is relatively slow when catalyst Ru-Cat I is employed, due to the low rate of the initiation step since the active carbene must be formed first.³⁰ This allows time enough for interactions with water, promoted by the shearing of the droplets, even at low stirring speeds, to inhibit the catalyst's activity. Moreover, side reactions can take place within the time scale of the polymerization. For example, dissociation of the phosphine and arene from the catalyst, oxidation of the catalyst, and subsequent peroxide formation lead to the decomposition of the catalyst. It was therefore rejected.

When catalyst Ru-Cat II, which provides much faster polymerization, was used, the quality of the monomer as well as the quality and amount of the catalyst was critical to obtain solid microspheres. When the DCPD was stored for long times in bottles that were regularly exposed to light and air, the quality of this monomer was obviously altered and solid materials could not be obtained. The batch, first used as received, was therefore purified by distillation. The Ru-Cat I catalyst requires the presence of acetylenic impurities in the DCPD to form the active carbene *in situ*.³⁰ This is not the case when catalyst Ru-Cat II is used since it already possesses the active carbene, and thus utilizing a distilled DCPD that doesn't contain those impurities, is not an obstacle to the polymerization with Ru-Cat II. Moreover, the fact that the carbene-formation slow step is not required by this catalyst explains the higher polymerization rate it promotes. However, to assure the efficiency of the catalyst, it had to be handled and stored under a protective atmosphere. When exposed to air and light for periods longer than a few days, the activity of the catalyst decreased (probably due to oxidation) and could no longer generate solid microspheres.

The most efficient stabilizer was hydroxypropyl cellulose, which produced a fairly narrow range of bead sizes. Other stabilizers, such as poly(vinyl alcohol),

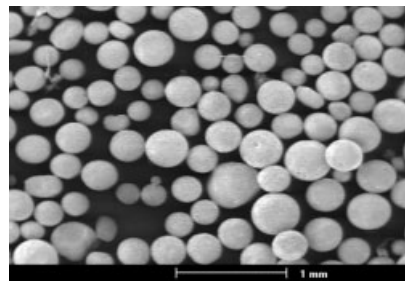


Figure 2 Scanning electron micrograph of sample M2.

were tested. These provided lower stabilization, even when high concentrations were used, and the final beads were excessively large. When high stirring speeds were investigated to reduce the bead size, poorly polymerized materials, sometimes not even solid, resulted. High stirring speeds generated too high shear stresses that tended to tear the droplets too much, resulting in too high water-polymer precursor interactions. These interactions obviously altered the catalyst's activity and arrested the polymerization.

On the basis of the combination of these parameters, it was possible to define a narrow but suitable processing window for the system. Once this processing window was established, the preparation of solid, opaque, phase-separated microspheres was very easy and batches of microspheres could be obtained with all the different initial amounts of porogen. Figure 2 shows a scanning electron micrograph of the obtained beads.

The produced beads were spherical with diameters in the 200–600 μm range. The bead diameter distributions measured by laser diffraction are given in Figure 3.

Samples M2, M3, and M4 show very similar bead diameter distributions. Only a slight increase in the width of the distribution, especially toward smaller diameters, can be noted with increasing initial porogen concentration. This can be explained by the higher porogen concentrations that cause gelation to occur later, thus allowing more time for the stirring to shear the polymerizing droplets. In the same manner, sample M1 not only has the lowest initial porogen concentration, but also is below the critical point, which is defined as the particular composition separating a compositions domain inside of which the porogen precipitates within a polymer matrix (low porogen concentrations) and a domain where polymer particles precipitate within the porogen (high porogen concentrations).^{19,20} In this case, gelation of the microsphere occurs even earlier since it corresponds to the gelation of the PDCPD matrix, while the gelation of the samples with porogen concentrations above the critical point corresponds to the moment where the primary particles (arising from the precipitation of PDCPD

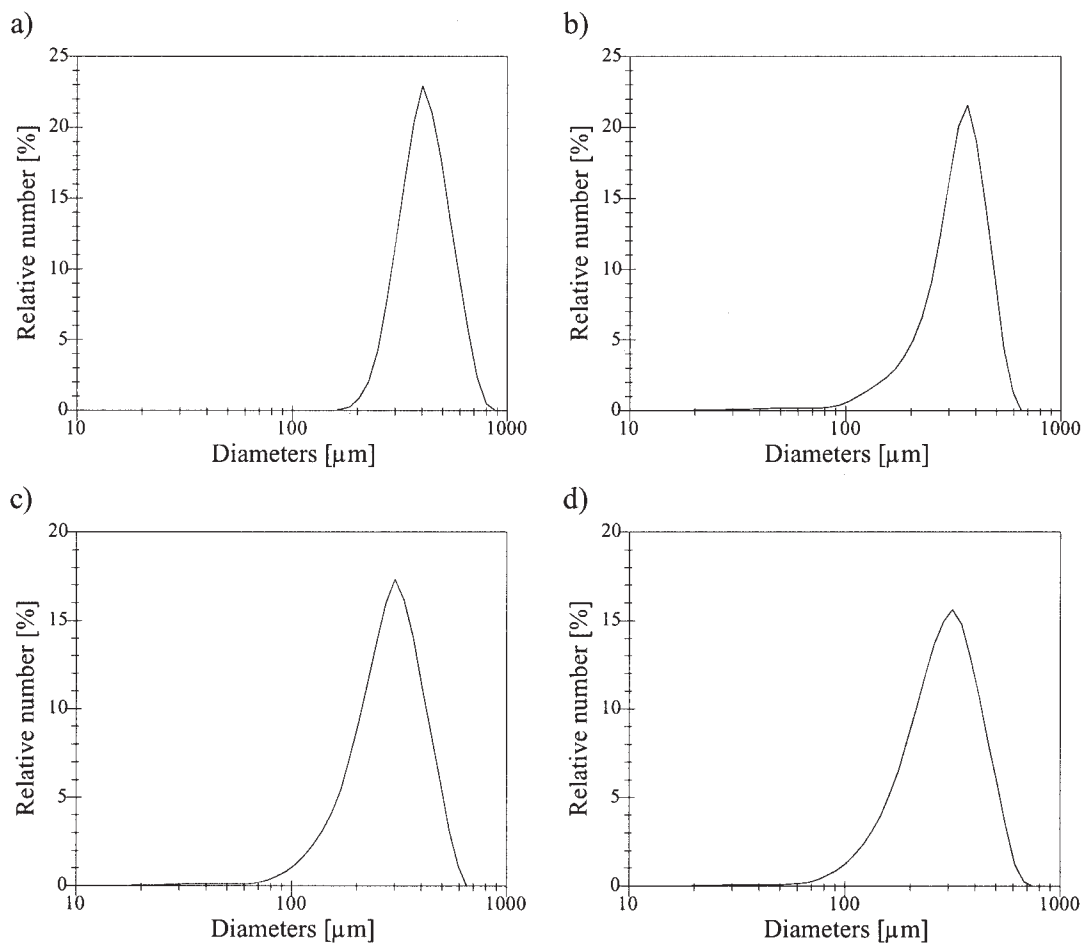


Figure 3 Bead diameter distributions: (a) M1, (b) M2, (c) M3, and (d) M4.

within the monomer/porogen mixture) agglomerate. This very early gelation explains the even narrower bead diameter distribution obtained for sample M1, which almost does not have any particles with diameters below 200 μm .

Prolonged stirring prior to polymerization would likely produce smaller particles and narrower size distributions. Ways to accomplish this would be of interest to explore in the future.

Microstructure and density of the beads

To compare the microstructure shown by the microspheres with reference materials produced as bulk samples, the bulk samples were characterized by SEM and their density was measured.

Like the beaded samples (Fig. 5), the final microstructure depends on the initial porogen concentration. Samples containing low initial amounts of porogen show isolated pores in a continuous PDPCD matrix resulting from the nucleation and growth of porogen-rich domains within a polymer-rich continuous phase (Fig. 4a, corresponding to sample B1, poro-

gen vol % = 32.2). Samples with porogen contents above the critical point are made of interconnected solid particles resulting from the nucleation and growth of polymer-rich domains within a porogen-rich continuous phase (Fig. 4b, c, and d, corresponding, respectively, to sample B2, porogen vol % = 42.5; B3, porogen vol % = 52.6; and B4, porogen vol % = 62.4). The cohesion between the primary particles forming this kind of microstructure arises from the fact that they grow until they come in contact while they are still not completely solid. Therefore, where they touch their interfaces melt together by diffusion and some crosslinking can occur between the polymer chains of the different particles. This occurs in the bulk for the bulk samples and within the droplets for the beaded samples.

The density results for the bulk samples are given in Table II. For this catalyst and this porogen, the final porosity of the samples with open porosity (i.e., samples B2, B3, and B4) is directly proportional to the initial amount of porogen; moreover, it is almost equal to the initial volumetric content of the latter. This indicates that the phase separation is almost complete.

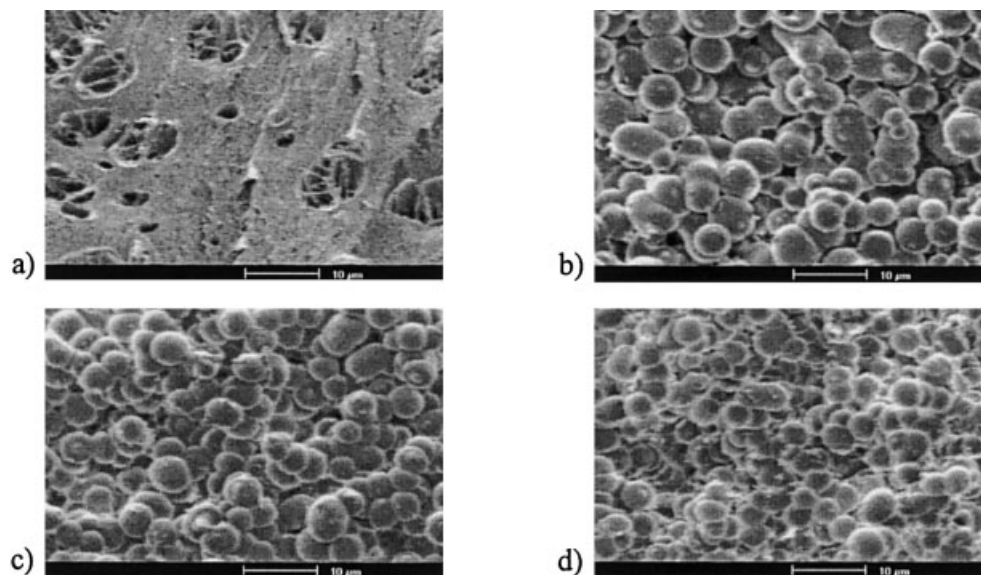


Figure 4 Scanning electron micrographs of the microstructure of samples: (a) **B1**, (b) **B2**, (c) **B3**, and (d) **B4**.

Sample **B1**, on the other hand, shows a rather limited porosity. The high rate of polymerization generated using catalyst Ru-Cat II traps an important fraction of the porogen in the matrix. The poly(1,2-butylene glycol) monobutyl ether, owing to its high molecular weight, might tend to phase separate earlier than lower molecular weight molecules. However, the competing effects of its lower diffusion rate, also due to its higher molecular weight, and the faster polymerization promoted by catalyst Ru-Cat II resulted in final porosities similar to those found in a previous work where macroporous PDPCD monoliths were produced with catalyst Ru-Cat I and 2-propanol as the porogen.²⁰

It can be seen from Figure 5 that the same type of morphologies are formed, in suspension and in bulk polymerizations, when the same amounts of porogen are used (i.e., isolated pores for both samples **M1** and **B1** and a microstructure consisting of agglomerated particles for samples **M2** and **B2**; **M3** and **B3**; **B4** and **M4**).

However, the final porosity of sample **M1** is clearly higher than that of sample **B1** due to slower polymerization in water suspension than in bulk, which allows more time for the porogen to diffuse out of the polymerizing PDPCD matrix. This tends to corroborate the idea that the catalyst's activity is hampered by the interactions with the aqueous medium in suspension polymerization, as stated in the previous section. In-

deed, it was observed that gelation for the suspended particles took about an hour, while it took only a few minutes for the equivalent bulk sample.

For the porogen concentrations above critical point, the microstructures are very similar, for in both suspension and bulk polymerizations, diffusion of monomer for nucleation and growth of polymer particles within a porogen-rich matrix is not limited by increasing degree of polymerization as observed for the samples below critical concentration. This was demonstrated by the final porosity achieved with the bulk samples (those with faster polymerization), which was very close to the initial volumic fraction of porogen (Table II).

However, it can be seen that the size of the particles forming the microstructure of the beaded samples (**M2**, **M3**, and **M4**) is slightly smaller than that of the corresponding bulk samples (**B2**, **B3**, and **B4**). This can also be explained by the faster polymerization obtained in bulk compared to the polymerization in the suspended droplets. The nucleation of these particles is driven by the supersaturation of the forming polymer in the porogen/monomer mixture. When a certain supersaturation is reached, nucleation starts. The phase separation of these nuclei reduces the supersaturation and when it is reduced below the equilibrium concentration between polymer, monomer, and porogen, the nucleation stops.³¹ The higher the polymerization rate, the higher the molecular weight of the polymers forming these nuclei will be. When higher molecular weight polymers phase separate to form the nuclei, the decrease in supersaturation is more important than when lower molecular weight polymers form these nuclei, thus arresting the nucleation earlier. For this reason, in the present case, fewer nuclei are

TABLE II
Density Results for the Bulk Samples

Sample	B1	B2	B3	B4
Initial porogen content (vol %)	32.2	42.5	52.6	62.4
Final density (g/cm ³)	0.985	0.655	0.538	0.421
Final porosity (%)	6.64	37.9	49.0	60.1

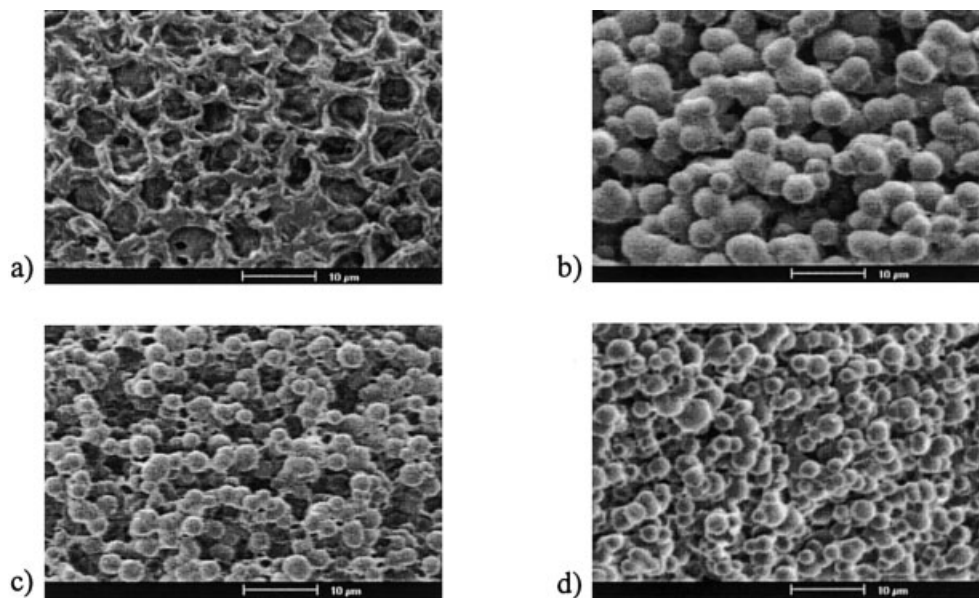


Figure 5 Scanning electron micrographs of the microstructure of samples: (a) M1, (b) M2, (c) M3, and (d) M4.

formed in the faster polymerization obtained in bulk. Finally, for the same amount of monomer in the initial monomer–porogen mixture, if there is a lower concentration of nucleated particles, these will grow larger to absorb more monomer than when a higher concentration of nuclei is produced, resulting in bulk samples with microstructures consisting of fewer, larger agglomerated particles.

Pore size and specific surface area

The beaded samples pores' access diameters distributions are given in Figure 6. The distributions of the pores' access diameters obtained on the particles are not very sharp. Mercury first needs to penetrate between the particles and the instrument considered these interstices between particles as porosity. These interstices represented a significant volume and the subsequent relative volume of the actual porosity inside the particles was small relative to the interstices. To obtain representative distributions of the pores' access diameters, the relative volume of pores' access diameters above 10 μm were, on the basis of the scanning electron micrographs (Fig. 5), which didn't show such porosity, attributed to the interstices between the particles and thus excluded.

Sample M1 pores' access diameters (Fig. 6a) are definitely smaller than those of samples M2, M3, and M4. This is easily understandable, because this is the only one among the four beaded samples showing a microstructure resulting from precipitation of porogen in the PDCPD matrix. As can be seen in Figure 5a, sample M1 possesses pores of a few micrometers in diameter, possibly interconnected by smaller win-

dows through the PDCPD matrix walls. The mercury intrusion porosimetry measures only the size of these windows. This is the reason why the discussion is based on the pores' access diameters rather than on the more common pore size. Samples M2, M3, and M4, which are composed of interconnected particles, show almost similar curves and peaks (diameters around 2–3 μm). However, the distributions seem to be slightly shifted toward larger sizes with increasing initial amount of porogen. This is understandable since the particles building the microstructure of those samples are smaller (see Fig. 5b, c, and d) and the overall porosity is larger, so the pores between those particles aggregates must be larger. These pores cannot, however, be observed in the micrographs of Figure 5 due to electron beam damage during the observation, which probably caused some collapse of the microstructure.

The specific surface areas measured by nitrogen adsorption are given in Table III.

Surprisingly, the sample showing the highest specific surface area is sample M1, the sample with the microstructure resulting from the precipitation of porogen in the PDCPD matrix. However, looking more closely at the micrographs shown in Figure 5, it becomes evident that the surface of sample M1 is rougher than that of samples consisting of interconnected particles (samples M2, M3, and M4), resulting in a higher specific surface area.

CONCLUSIONS

The feasibility of producing beaded macroporous polydicyclopentadiene has been demonstrated. Understanding of the phase separation principles al-

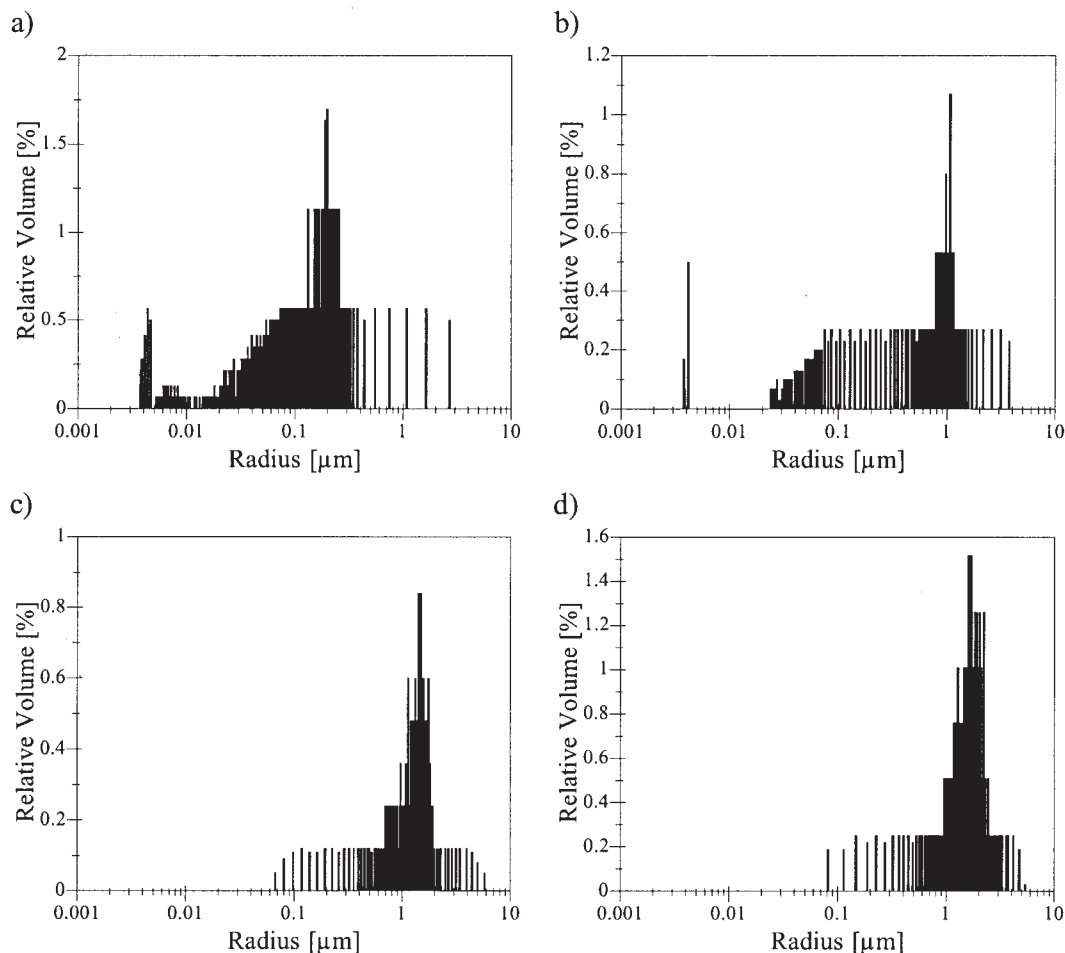


Figure 6 Distributions of the pores' access diameters of samples: (a) M1, (b) M2, (c) M3, (d) M4.

lowed the choice of a suitable porogen to be used in aqueous suspension. By adjusting the monomer purity and the type and quantity of catalyst, a processing window could be defined that allowed easy production of PDCPD microspheres with different initial porogen concentrations. The bead batches showed narrow diameter distributions with average diameters between 300 and 400 μm . Obtaining smaller bead sizes as well as narrower bead-size distributions should be possible when using longer stirring times, to reach an equilibrium suspended droplets size, before polymerization. The obtained microspheres showed porosity similar to that found for equivalent samples produced in the bulk and average pores' access diameters in the micron range. These beaded macroporous materials

showed specific surface areas in the range of 1 to 3.5 m^2/g . The average pores' access diameters were 0.1 μm for the materials arising from precipitation of the porogen in the PDCPD matrix and 1 to 2 μm for the solid PDCPD consisting of agglomerated particles. The microstructure of the beaded materials showed some differences with initially similar materials produced in the bulk. Those differences were credited to the altered polymerization rates in the suspended droplets.

References

- Gawdzik, B.; Maciejewska, M. *J Polym Sci Part A Polym Chem* 2002, 40, 3079.
- Janco, M.; Xie, S.; Peterson, D. S.; Allington, R. W.; Svec, F.; Fréchet, J. M. J. *J Sep Sci* 2002, 25, 905.
- Stevenson, R. *Am Lab* 2002, May 6.
- Strancar, A.; Podgornik, A.; Barut, M.; Necina, R. *Adv Biochem Eng/Biotech* 2002, 76, 49.
- Xie, S.; Allington, R. W.; Fréchet, J. M. J.; Svec, F. *Adv Biochem Eng/Biotech* 2002, 76, 87.
- Arshady, R. *J Chromatogr* 1991, 586, 181.
- Arshady, R. *J Chromatogr* 1991, 586, 199.

TABLE III
Specific Surface Area of the Beaded Samples

Sample	M1	M2	M3	M4
Initial porogen content (vol %)	32.2	42.5	52.5	62.4
Specific surface area (m^2/g)	3.11	1.56	1.71	1.29

8. Coutinho, F. M. B.; Neves, M. A. F. S.; Dias, M. L. *Macromol Symp* 2002, 189, 27.
9. Gong, B.-L.; Ke, C.-Y.; Geng, X.-D. *Anal Bioanal Chem* 2003, 375, 769.
10. Lu, M. J. *Am Lab News* 2003, Aug, 32.
11. Shi, Y.; Sun, Y. *Chromatographia* 2003, 57, 29.
12. Xu, M. C.; Peterson, D. S.; Rohr, T.; Svec, F.; Fréchet, J. M. J. *J Anal Chem* 2003, 75, 1011.
13. Leinweber, F. C.; Tallarek, U. *J Chromatogr A* 2003, 1006, 207.
14. Leonard, M. J. *J Chromatogr B* 1997, 699, 3.
15. Wang, Q. C.; Hosoya, K.; Svec, F.; Fréchet, J. M. J. *J Anal Chem* 1992, 64, 1232.
16. Mayr, B.; Hölzl, G.; Eder, K.; Buchmeiser, M. R.; Huber, C. *J Anal Chem* 2002, 74, 6080.
17. Righetti, P. G.; Gelfi, C. *J Chromatogr B* 1996, 699, 63.
18. Della Martina, A.; Garamszegi, L.; Hilborn, J. G. *J Polym Sci Part A Polym Chem* 2003, 41, 2036.
19. Della Martina, A.; Hilborn, J. G. *J Mater Res* 2001, 16, 2045.
20. Della Martina, A.; Hilborn, J. G.; Mühlebach, A. *Macromolecules* 2000, 33, 2916.
21. Kiefer, J.; Hedrick, J. L.; Hilborn, J. G. In *Macromolecular Architectures*; Hilborn, J. G., Ed.; Springer Verlag: New York, 1999; p 161.
22. Nakanishi, K. *J Porous Mater* 1997, 4, 67.
23. Sinner, F. M.; Buchmeiser, M. R. *Angew Chem Int Ed* 2000, 39, 1433.
24. Lubbad, S.; Buchmeiser, M. R. *Macromol Rapid Commun* 2003, 24, 580.
25. A. Della Martina, L. Garamszegi and J. G. Hilborn, *React Funct Polym* 2003, 57, 49.
26. Arshady, R. *Colloid Polym Sci* 1992, 270, 717.
27. Arshady, R.; George, M. H. *Polym Eng Sci* 1993, 33, 865.
28. Dowding, P. J.; Vincent, B. *Colloids Surf A Physicochem Eng Aspect* 2000, 161, 259.
29. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: London, 1953.
30. Mühlebach, A.; van der Schaaf, P. A.; Hafner, A.; Kolly, R.; Rime, F.; Kimer, H. J. In *Ring Opening Metathesis Polymerization and Related Chemistry*; Khosravi, E.; Szymanska-Buzar, T.; Eds.; Kluwer Academic: Dordrecht, 2002; p 23.
31. Brinker, C. J.; Scherer, G. W. *Sol-Gel Science, The Science and Chemistry of Sol-Gel Processing*; Academic Press: San Diego, 1990.