Synthesis of Porous Materials by 2-Nitroresorcinol/Cyanuric Chloride Thermal Polycondensation in Emulsions

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ABSTRACT: Rigid monoliths were prepared from concentrated oil in water (O/W) emulsions by a base-catalyzed polycondensation reaction of 2-nitroresorcinol with cyanuric chloride. Mercury intrusion/extrusion porosimetry confirmed that the obtained monoliths were porous with an open porosity. However, scanning electron microscopy showed that the structure of these materials was different from that of emulsion-derived materials previously described in the literature [polymerized high internal phase emulsions (polyHIPEs)]. In comparison with polystyrene/divinylbenzene-based polyHIPEs obtained by radical polymerization, these materials exhibited a higher skeletal density, and thermogravimetric analysis and differential scanning calorimetry analysis indicated that they were more thermally stable. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2808–2813, 2008

Key words: differential scanning calorimetry (DSC); macroporous polymers; polycondensation; thermogravimetric analysis (TGA)

INTRODUCTION

Highly porous systems, known in the literature for many years as polymerized high internal phase emulsions (polyHIPEs), have found an increasing number of applications, including applications as liquid absorbents,[1–3] supports for organic synthesis,[4,5] scavengers,[6] aerosol filtration,[3,7] and insulation.[8] Their preparation, developed by Unilever,[9] is based on the polymerization of the continuous phase of a high internal phase emulsion. Such an emulsion results from the dispersion of an aqueous phase into a continuous phase composed of the monomers and one (or more than one) surfactant that stabilizes the emulsion. When the volume of the dispersed phase is increased above 74%, the water droplets tend to deform into polyhedra and are surrounded by a thin film of monomer.[10,11] The polymerization of this film freezes the emulsion structure, and the resulting material presents, after removal of the water phase, a highly porous structure composed of quasispherical microcells interconnected by small pores. As the cell size of the polyHIPE corresponds to the initial water droplet size, the effective material porosity corresponds to the volume of the dispersed phase initially introduced in the emulsion.

PolyHIPEs can be obtained by radical polymerization;[12,13] ring-opening metathesis polymerization (ROMP) polymerization[14] or sol–gel chemistry[15–17] may as well be used, and hybrid[18] or interpenetrating networks[19] have also been reported, but these studies have been still very seldom. In fact, most of the work published to date has been devoted to vinyl monomers, among which styrene[12,20–22] and functionalized styrene/divinylbenzene systems[23–25] have been extensively studied. In particular, to the best of our knowledge, there has been no example of a polyHIPE prepared by the polycondensation of organic monomers.

In this article, we report our attempts to prepare direct emulsions of 2-nitroresorcinol and cyanuric chloride and to react them in a polycondensation reaction under basic conditions to obtain porous materials. We elected to study this system because (1) the feasibility of resorcinol/cyanuric chloride polycondensates was demonstrated in several articles[26,27] (nonporous materials); (2) such triazine-containing materials have found various applications,[28,29] especially as light stabilizers;[30] and (3) thanks to the presence of both a nitro functionality and a nitrogen-rich aromatic heterocycle, our target polyHIPE was expected to show a significantly enhanced backbone density compared to styrene-based materials. This

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TABLE I
Emulsion Preparation and Polycondensation Results

Sample	Toluene/water proportion (v/v)	Yield of recovered material (%)[a]
1	50 : 50	66
2	40 : 60	85
3	35 : 65	75
4	30 : 70	71
5	20 : 80	77

[a] Based on the $C_{24}H_9N_9O_{12}$ formula (quantitative reaction).

specific feature could be of interest in the field of energetic polymers.

EXPERIMENTAL

Materials

2-Nitroresorcinol (Lancaster, Alfa Aesar, Bischeim, France, purity > 98%), cyanuric chloride (Aldrich, St. Louis, MO, 99%), polyglycerol polyricinoleate (PGPR; Danisco, Copenhagen, Denmark), and sodium hydroxide (Riedel de Haën, Seelze, Germany, ≥99%) were used as received. Deionized water was used throughout the study.

Concentrated emulsion preparation and interfacial polycondensation

A series of monoliths was prepared by the polycondensation of 2-nitroresorcinol and cyanuric chloride. The final porosity of the materials was adjusted through variation of the aqueous-phase/organic-phase ratio.

Preparation of samples 1–5

In a typical experiment, 2-nitroresorcinol (0.299 g, 1.93×10^{-3} mol), cyanuric chloride (0.237 g, 1.28×10^{-3} mol), PGPR (0.18 g), and toluene (1.8 mL) were placed in a test tube and stirred with a vortex (Top-Mix type, Heidolph, Schwabach, Germany). The aqueous phase was prepared separately by the dissolution of sodium hydroxide (0.154 g, 38.5×10^{-4} mol) in given volumes of distilled water (Table I). This solution was added dropwise under constant mechanical stirring to the organic solution. The obtained white emulsion was transferred in polytetrafluoro ethylene (PTFE) molds and immersed in a water bath. The polycondensation was conducted at 50°C for 1 week. The resulting monoliths were removed from the molds and extracted in a Soxhlet apparatus with water/ethanol (50 : 50 v/v) for 48 h. Then, they were dried *in vacuo* for 1 week.

Characterization of the monoliths

Elemental analyses were carried out by the Service Central d'Analyse du Centre National de la Recherche Scientifique Vernaison (France).

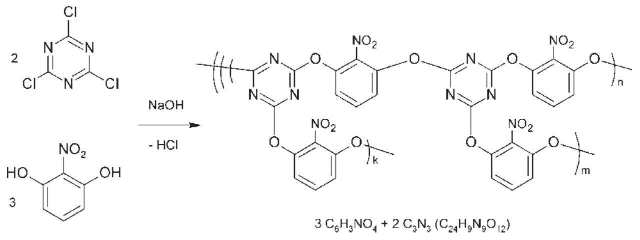

Figure 1 Expected structure of the polymer formed by interfacial polycondensation.

Scanning electron microscopy (SEM) specimens were prepared as follows: dried polymer was carefully broken into pieces, which were mounted on stubs with a fresh face uppermost in each case. It was important not to use a face that had been cut or sawed because this would have distorted and damaged the cellular structure. Samples were sputter-coated from a gold–palladium electrode, and micrographs were taken on a Jeol 840 ME scanning electron microscope (Tokyo, Japan).

To determine the specific surface area, N_2 adsorption measurements were performed on a Micromeritics ASAP 2010 V4 analyzer (Normass, GA), and the data were subjected to the Brunauer–Emmett–Teller (BET) treatment.

The pore size distribution was determined with an Autopore IV 9500 porosimeter from Micromeritics.

Skeletal density was measured with a Micromeritics AccuPyc 1330 helium pycnometer.

Thermogravimetric analysis (TGA) was performed with a PerkinElmer TGS-2 apparatus (Waltham, MA) equipped with a data station 3600 at a heating rate of 15°C/min under an argon atmosphere.

Differential scanning calorimetry (DSC) measurements were conducted at a heating rate of 5°C/min with a PerkinElmer DSC7 instrument.

RESULTS AND DISCUSSION

Emulsion preparation and polycondensation

Interfacial polycondensation is an effective technique for polymer synthesis. High reaction rates, straight-

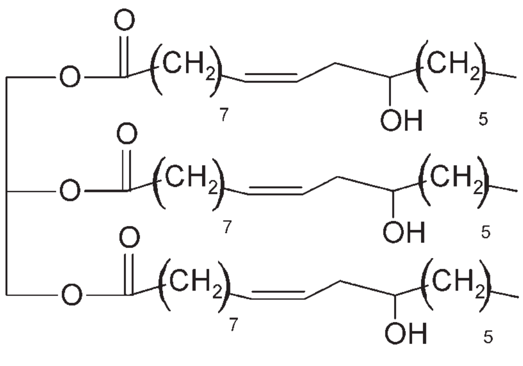

Figure 2 Simplified structure of the PGPR surfactant.

TABLE II
Experimental Elemental Analyses of Samples 1–3 Compared with the Expected Compositions

Number	Composition	C (wt %)	H (wt %)	N (wt %)	O (wt %)	Cl (wt %)	Total (wt %)	Calculated condensation degree
1	Calcd for $C_{24}H_9N_9O_{12}$	46.8	1.5	20.5	31.2	—	—	100
2	Calcd for $C_{24}H_{9.9}N_9O_{12}Cl_{0.9}$	44.5	1.5	19.5	29.6	4.9	—	85
3	Experimental (sample 1)	52.0	4.4	13.2	24.1	6.5	100	66
4	Experimental (sample 2)	51.6	4.0	14.4	28.0	0.8	98.8	97
5	Experimental (sample 3)	51.7	4.1	13.7	25.6	3.5	98.6	85
6	Average (samples 1–3)	51.8	4.2	13.8	25.9	3.6	99.3	85
7	Corrected for 28 wt % PGPR	43.9	1.5	18.9	29.5	4.9	98.7	85

forward realization, and the capability of producing insoluble polymers are among the advantages of this method. The process is based on rapid reactions of irreversible nucleophilic substitutions in heterogeneous contacting phases, one containing the reagents and the other containing the catalyst. The base-catalyzed interfacial polycondensation between cyanuric chloride and bisphenol compounds is a complex reaction:[31] the nature of the products obtained depends on the experimental conditions. In the best cases, the insolubility and the low chlorine content of the compounds leads one to conclude that condensation is quantitative and that highly crosslinked materials are formed. For the reaction of cyanuric chloride and 2-nitroresorcinol, the expected polymer structure is shown in Figure 1.

Reverse-stable concentrated emulsions were obtained by the emulsification of a saturated toluene solution of 2-nitroresorcinol (1.5 equiv) and cyanuric chloride (1 equiv) by various volumes of a sodium hydroxide aqueous solution with the hydrophobic nonionic PGPR as the surfactant (28 wt % of the total amount of monomers; Fig. 2). (The concentration of organic compounds in toluene was limited to 33–37 wt % because of the low solubility of cyanuric chloride and PGPR; attempts to improve this situation by the use of more polar solvents such as nitrobenzene or chlorobenzene were unsuccessful.)

The composition of the different emulsions prepared and the yields of recovered dried material are reported in Table I.

After washing and drying, the obtained yellow monoliths were reasonably mechanically strong when manipulated; however, a substantial volume shrinkage (ca 30–50%) of the final monoliths was visually observed. This contraction occurred partly during the polymerization step but mostly during the drying step, probably because of the expulsion of toluene.

Experimental elemental analyses of the synthesized samples revealed the presence of residual chlorine. Furthermore, for all of the materials, nitrogen and oxygen contents were always lower than expected, whereas hydrogen and carbon contents were always higher than the calculated values. Starting from the average molecular formula of the expected material (Table II, no. 1), the average experimental elemental analyses values for samples 1–3 (Table II, no. 6) were consistent with calculated values corresponding to a polycondensation degree of only 85% (Table II, no. 2), conjugated with the hypothesis that PGPR remained trapped into the polymer, presumably because of esterification reactions

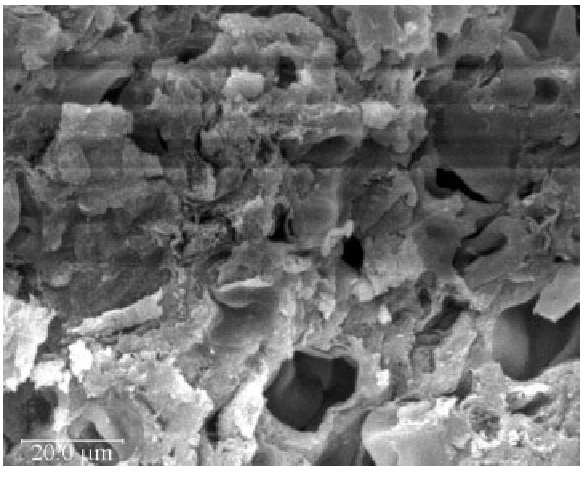

Figure 3 SEM micrograph of sample 1 (magnification = 1000×).

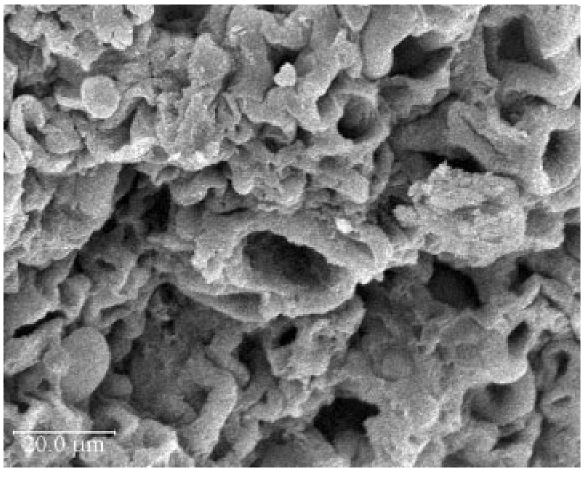

Figure 4 SEM micrograph of sample 2 (magnification = 1000×).

TABLE III
Mercury Intrusion Porosimetry and N_2 Adsorption Results

Sample	ϕ_{total} (%)	ϕ_{water} (%)	$\phi_{measured}$ (%)	Surface area (m^2/g)[a]
1	83.1	50.0	50.8	23
2	84.4	60.0	60.7	0.3
3	87.6	65.0	66.5	2.2
4	89.2	70.0	71.0	0.3
5	92.6	80.0	81.1	3.2

[a] From the BET treatment of the N_2 adsorption data.

between some alcoholic groups present on the surfactant and cyanuric chloride (Table II, no. 7).

Structural analysis of the monoliths

SEM allowed the visualization of the structure of the obtained materials with a resolution of about 20 nm. SEM analysis of samples 1 (Fig. 3) and 2 (Fig. 4) showed that their visual aspect was very different from that of a typical styrene/divinylbenzene-based polyHIPE.[12,20,21] Because of this specific structure, this analytical technique, by itself, was not sufficient to help us determine if the materials studied possessed an open porosity.

Specific surface area measurements and porosity characteristics

It was possible to define different porosities for the obtained materials. ϕ_{total} is defined as the porosity produced by all the nonpolymerizable constituents of the emulsion (water, toluene, and surfactant), whereas ϕ_{water} corresponds to the porosity coming solely from water. $\phi_{measured}$ is the experimental porosity calculated from mercury intrusion data. The data for these different porosities are reported in Table III for all of the samples studied, together with the corresponding BET[32] specific surface area.

A low specific surface area was obtained for all of the compounds examined. This result was somewhat surprising because, according to Sherrington et al.,[12] the introduction of a porogen such as toluene in a polyHIPE formulation generally increases the specific surface area of the material considerably by generating mesoporous porosity by phase separation. This phenomenon did not seem to occur in this case. (A possible explanation for the low specific surface compared with other polyHIPEs from free-radical polymerization was put forward by one of the referees: contrary to radical polymerization, in this case, no further polymerization occurred within the swollen polymer nuclei and within the voids of the agglomerates of nuclei that appeared during chain growing; therefore, macropores and mesopores were not changed secondarily into micropores, and thus, there was no increase in the specific surface.)

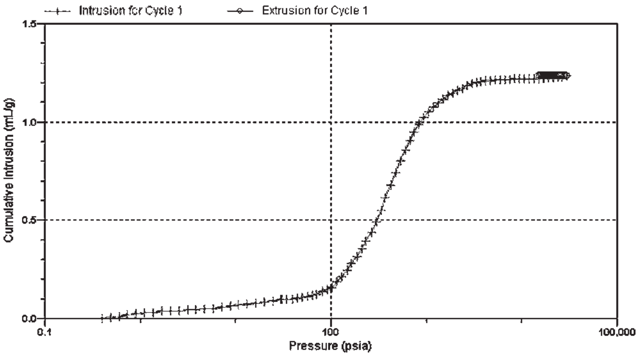

Figure 5 Mercury intrusion/extrusion porosimetry data for sample 2.

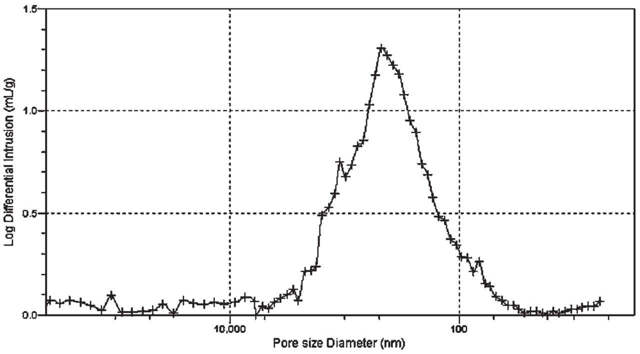

Figure 6 Pore size distribution from mercury intrusion porosimetry for sample 2.

The measure of the total porosity by mercury intrusion/extrusion porosimetry showed that the actual pore volume fractions were very close to ϕ_{water} for all of the samples (Table III). Thus, again, toluene did not seem to generate a secondary porosity. An example of a mercury intrusion/extrusion volume versus pressure plot is shown in Figure 5. One can observe that the extrusion curve was superimposed with the intrusion curve, which indicated that the material did not collapse under the mercury pressure. These two observations also confirmed that the materials possessed an open porosity.

The pore size distribution of the different samples as estimated by mercury intrusion was found to be very broad. A typical experimental curve is pre-

TABLE IV
Pore Sizes as Estimated by Mercury Intrusion Porosimetry

	Pore diameter (nm)	
Sample	Peak maximum	Range
1	260	10–300
2	490	80–2,000
3	2,250	200–5,000
4	2,200	330–4,600
5	1,250	150–10,000

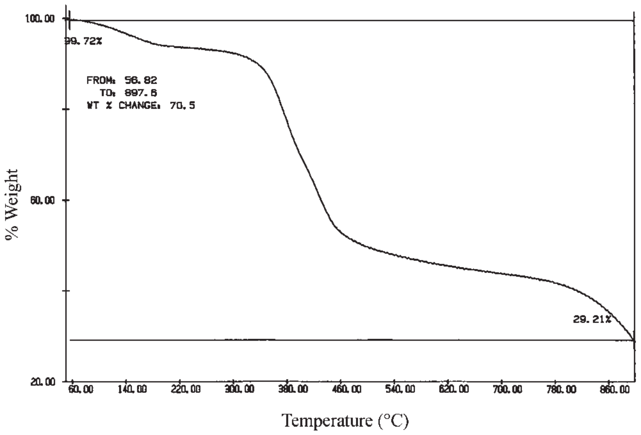

Figure 7 TGA trace of sample 5.

sented in Figure 6. Because it was difficult to evaluate an average pore size characteristic for each material obtained, Table IV lists the range of the pore sizes and the maximum peak values. The pore size seemed to increase with the total porosity.

Density

The absolute density of the samples was determined with a helium pycnometer. The obtained values, in the range 1.4–1.6 g/mL, were significantly higher than that of a styrene/divinylbenzene polyHIPE (~ 1 g/mL). This clearly shows that the introduction of nitrogen heterocycles and nitro functionalities positively affected this parameter, which is crucial for application as energetic materials.

Thermal stability

The thermal behavior of some of the synthesized samples was investigated. The TGA trace of sample 5 heated under argon (Fig. 7) showed two weight losses at 180 and 450°C. The main weight loss was 42% at 450°C, and the final residue was about 30% at 900°C. By contrast, a styrene/divinylbenzene polyHIPE exhibited a single weight loss near 400°C and almost no residual char at 900°C.

The DSC analysis displayed comparable traces for all compounds. An exotherm was observed near 280°C (Table V), with an enthalpy of transition (ΔH) between −1200 and −1400 J/g. This peak was probably due to the decomposition of the polymer, as it disappeared in a second heating run (Fig. 8). A new, large endothermic peak appeared in the range 80–90°C with a ΔH comprised between 26 and 47 J/g.

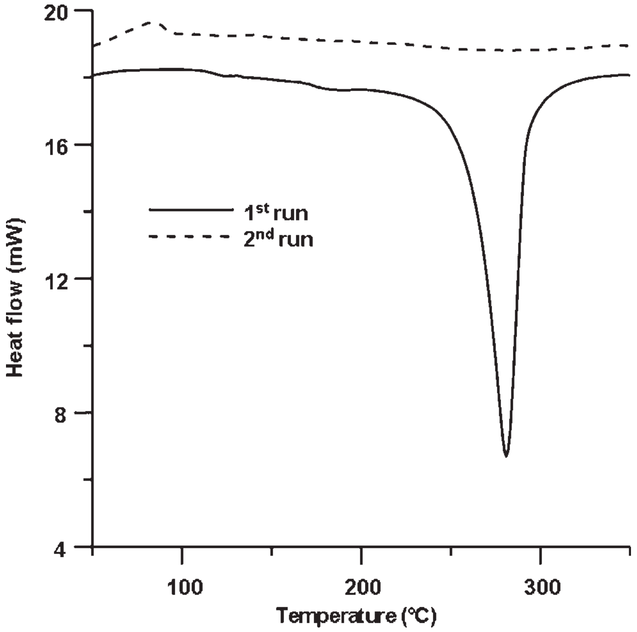

Figure 8 DSC trace of sample 1.

TABLE V
Decomposition Temperatures and ΔH Obtained by DSC

Sample	ΔH (J/g)	$T_{\text{decomposition}}$ (°C)
1	−1370	281
2	−1063	274
3	−1203	278
4	−1397	281
5	−925	272

$T_{\text{decomposition}}$, the onset of the exothermic peak.

CONCLUSIONS

The polycondensation of 2-nitroresorcinol with cyanuric chloride was successfully performed in toluene/water emulsions. It enabled us to prepare rigid, polymeric monoliths. Porosimetry analysis indicated that the porosity created in the material was only due to the volume of water introduced as the internal phase in the starting concentrated emulsion. The solvent of the external phase (toluene) did not generate any secondary porosity: its expulsion from the material provoked a strong volume shrinkage, partly during the polymerization but mostly during the drying step. Therefore, the expected polyHIPE-type morphology was not obtained: the SEM characterizations of the materials did not display any typical interconnected cellular structure, although mercury intrusion porosimetry data confirmed the presence of an open porosity. The thermal properties of the prepared material were examined by TGA and DSC. When compared to conventional styrene/divinylbenzene polyHIPE materials, these new porous polymers were more thermally stable and possessed a higher skeletal density.

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