Building ultramicropores within organic polymers based on a thermosetting cyanate ester resin†

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Ultramicropores with high surface areas (>530 m^2 g^{-1}) and narrow micropore size distribution (4–6 Å) were engineered within a new cyanate ester resin, extending the microporous concept (<20 Å) to general thermosetting resins in the area of polymer chemistry.

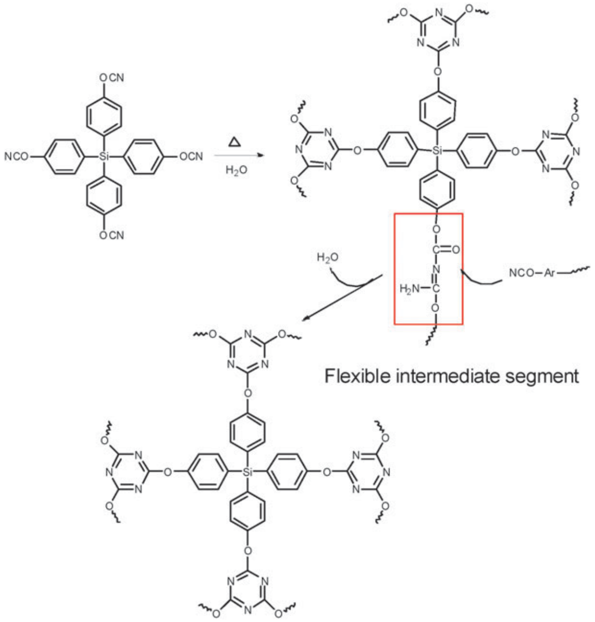
Research into microporous organic polymers, which have pore sizes smaller than 20 Å and high surface areas, is currently driven by wide potential applications in catalysis, size-selective absorbents, gas storage, *etc.*[1] Compared with conventional highly porous materials like zeolites which are usually prepared through a template strategy, micropores in organic polymers are directly engineered by their chain skeleton with the character of highly rigid, bulky, nonplanar, and contorted architectures.[2] It is also identified that the pore structure can be well defined *via* formation of rigid networks.[3] Thus, efforts to prepare these materials are mainly focused on several types of special networks including polymers of intrinsic microporosity (PIMs),[2,4] covalent organic frameworks (COFs),[5] hypercrosslinked polymers (HCPs)[6] and conjugated microporous polymers (CMPs).[7]

It is well known that thermosetting networks have provided the broadest scope for synthetic variation of both chemical functionality and structural topology. In the past decade, a number of commercial thermosetting resins, such as epoxy and cyanurate, have been successfully used to prepare macroporous polymers,[8] but reports of microporous polymers based on these resins are extremely rare. As a matter of fact, the creation of microporosity within common thermosetting resins is of fundamental significance. First, their widely accessible monomer precursors not only make the preparation of microporous polymers more convenient and cost-effective, but also they provide numerous skeletal structures which should facilitate fine control over the microporous properties. Second, the mild curing conditions provide the possibility of introducing functionalities into the porous materials. Third, good processability of these thermosets should allow them to be readily fabricated into useful forms. It is, therefore, strongly desirable to expand the concept of microporosity to the common thermosets in the area of polymer chemistry.

Moreover, micropores are classified into ultramicropores (pore widths $<$ 7 Å) and supermicropores (pore widths of 7 to 20 Å).[9] Taking advantage of high enthalpies of adsorption for H_2 and fast selective gas adsorption into account, ultramicroporous materials have attracted much attention in H_2 storage[4b,4c,10] and molecule-size separation.[11] Budd *et al.*[4c] determined that micropores in their CTC-PIMs are centered around 7 Å. Also, Germain *et al.*[6f] most recently reported hypercrosslinked polyanilines with pore sizes that range from 2.9–3.6 Å. There are numerous examples of ultramicroporous materials based on inorganic and organic–inorganic hybrid materials.[12] However, types of ultramicroporous organic polymers with high surface areas are still limited to the above examples.

In this communication, we report a new facile approach to prepare ultramicroporous polymers based on one of the most common thermosetting networks—cyanate ester resins, which are widely used in many fields such as electronics, aerospace and adhesive industries.[13] They exhibit high surface areas ($>$530 m^2 g^{-1}), a median pore diameter of 4.7 Å and narrow micropore size distribution (4–6 Å).

Usually cyanate esters undergo thermal polycyclotrimerization in both bulk and solution to give polycyanurates, *i.e.*, sym-triazine rings linked by aryl ether linkages, resulting in a uniformly cross-linked structure. In this work, a new tetrafunctional cyanate ester tetrakis(4-cyanatophenyl)silane (TCS) is used as the starting monomer for the highly efficient



Scheme 1 Cyclotrimerization reaction of TCS leading to the formation of a polycyanurate network.

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network-building process (Scheme 1). TCS exhibits high chemical reactivity owing to the high content of cyanate ester groups per molecule, and the cure process actually occurs just above the melting point of the monomer (ESI†, Fig. S1). To ensure a uniform three-dimensional network, we employed the following standard baking protocol designed to achieve near-full cure of TCS: 170 °C for 4 h, 190 °C for 4 h, 230 °C for 8 h, and lastly 270 °C for 20 h. Within a fully cured TCS network, every three neighboring rigid tetrahedral units are held together by a triazine ring. There is only a single oxygen-atom bridge between the two types of branch points, *i.e.*, tetrahedral branchpoints and triazine branchpoints, which produces a firm covalent crosslinked framework. Additionally, with respect to the rigid framework whose connecting struts are all identical in length, the higher density of branch points means smaller and more uniform voids can be obtained in the limited space constructed by the rigid tetraphenylsilane units.

However, it is rather difficult to obtain high conversions of the cyanate groups of TCS to the triazine rings in bulk polymerization even under a high post curing temperature and long curing time. Although the curing mechanism of the cyanate ester is not completely clear, the existence of a stable curing intermediate unit [–OCONC(NH_2)O–] in the early stage of polymerization was confirmed.[14] Fig. 1 presents the possible network-building process. Because of the branchpoint role of the monomer itself and the close packing of the reactive groups in the bulk, the time taken to reach the gel point is so short that an infinite network may have been formed before the conversion of all intermediate segments to triazine rings—new branchpoints. Then the steric and geometric constraints imposed by the branch points and crosslink points act against the approach of residual cyanate groups to intermediate segments, resulting in a final defective triazine-based network containing long flexible straight segments. In the IR spectrum (Fig. 2), besides the characteristic triazine ring bands at 1560 cm^{-1} and 1362 cm^{-1}, absorption peaks at 3482 cm^{-1} and 3392 cm^{-1} contributed by stretching of –NH_2 and at 1719 cm^{-1} by C═O stretching were also observed, indicative of the presence of [–OCONC(NH_2)O–] intermediate segments. The porosity of this cured polymer was probed by nitrogen sorption at 77 K. As expected, these defects made the triazine-based network less rigid, and the microporosity was reduced due to pore collapse caused by the remaining flexible intermediate segments. To achieve full conversion of cyanate groups to triazine rings, we then investigated the curing reaction in a thermodynamically preferred solvent, diphenylsulfone.

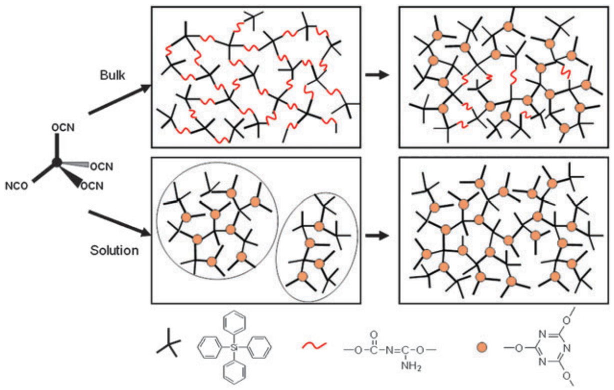

Fig. 1 Schematic representation of the possible network-building process in bulk and in solution.

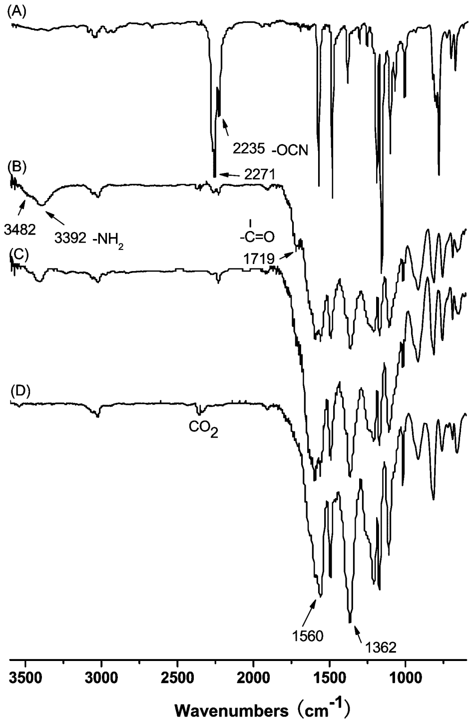

Fig. 2 FT-IR spectra (A) TCS; (B) network cured in bulk; (C) network cured in 20 wt% solution; (D) network cured in 10 wt% solution.

In solution, the reduced concentration of functional groups will effectively delay the time taken to reach the gel point and consequently benefit the sufficient conversion of curing intermediate segments to triazine rings. As shown in Fig. 2, with the reduction in reaction concentration, the amount of residual cyanate ester groups and intermediate segments in the cured TCS was decreased, and almost completely disappeared in a 10 wt% solution. Thermogravimetric results also demonstrate that the thermal stability of the cured products in solution are much higher than that cured in bulk due to the presence of intermediate segments in the networks (ESI†, Fig. S2). The ideal network-building process in dilute solution can be described as follows (Fig. 1): in the initial stage of reaction, nucleation of growth occurs at random through polytrimerization of the tetrahedral monomers, resulting in large numbers of pre-gel branched particles with micropores, then these branched particles meet and further connect to one another on reactable sites to form the final infinite network.

Nitrogen adsorption/desorption isotherms for cured networks obtained from various solution concentrations are given in Fig. 3a. All samples polymerized in dilution solution (below 10 wt%) show a high uptake at very low relative pressure, corresponding to gas sorption in micropores. Their isotherms also exhibit weak hysteresis, the desorption curve lies above the adsorption curve, and can be classified as Type 1B,[15]

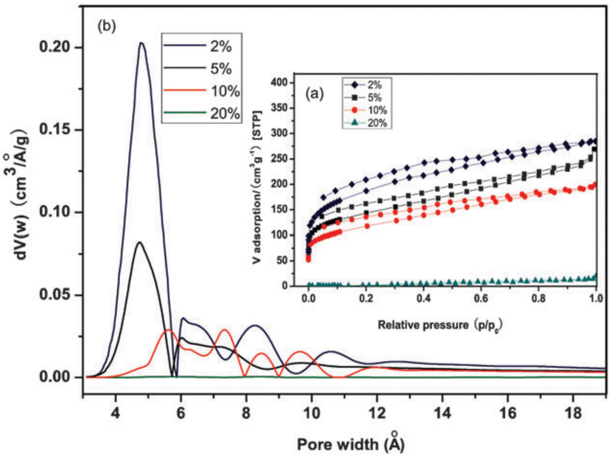

Fig. 3 (a) Nitrogen adsorption/desorption isotherms at 77 K for cured TCS obtained from different solution concentrations; (b) apparent micropore size distribution calculated by the Horvath–Kawazoe method (carbon slit-pore model) for cured TCS obtained from different solution concentrations (2%, 5%, 10%, 20%).

exhibiting the characteristics of substantially microporous materials. The BET surface area of cured TCS increases with the reduction in reaction concentration. Typically, a surface area of 538 m^2 g^{-1} can be obtained in 2 wt% solution (ESI†, Fig. S3).

Fig. 3b shows the apparent micropore size distribution for the cured TCS as calculated by the Horvath–Kawazoe method. It can be seen that the pore size distribution for the sample prepared in 2 wt% solution is mainly biased towards pores in the range 4–6 Å. Obviously, with the reduction in reaction concentration, a smaller and narrower pore distribution can be obtained. This may be ascribed to the improved development of branched particles in dilute solution, resulting in a more uniform network. It is important to note the limitations of the N_2 adsorption technique, because the N_2 molecule with a kinetic diameter of 3.64 Å finds it difficult to enter the ultramicropore ($<$5 Å).[16] So we believe that the actual surface area of cured TCS is far higher than the value reported here.

In summary, we have demonstrated a novel facile approach to introduce ultramicropores into a common thermosetting resin. In this way, it may bring about numerous microporous or mesoporous polymers through choice of initial monomers with special geometries. We are currently exploring additional polycyanurate networks to obtain larger surfaces and conducting systematic studies on their applications in hydrogen storage and size-selective molecular sieve materials.

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