A physical gel made from hyperbranched polymer gelator†

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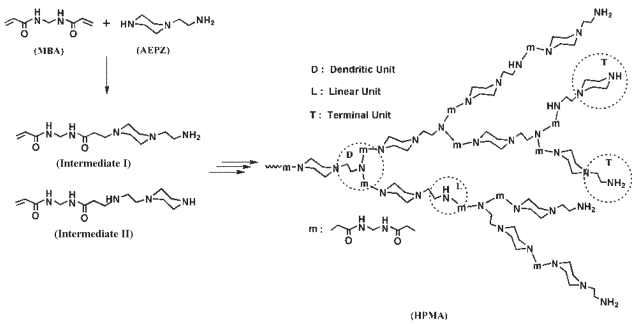
A novel hyperbranched polymer gelator has been synthesized, which can self-assemble into the thermoreversible physical gel in DMF, DMAC, pyridine, DMSO or NMP with the driving force of hydrogen bonds among amide and amine groups of the highly branched macromolecules.

Over past 10 years, there has been an explosive growth of interest in the gel-phase materials due to their potential applications in many fields, such as sensor technology, molecular recognition, extraction processes and material science, *etc*.[1] It has been known that an effective gelator should possess functional groups that interact with each other *via* temporary associative forces, including hydrogen bonds, π–π stacking, solvatophobic effect, van der Waals forces, *etc*. Until now the synthesized physical gelators were based on small molecules,[1,2] linear block copolymers,[3] dendrons or dendrimers.[4] It is known that dendrons and dendrimers are usually obtained through multi-step reactions with tedious procedures.

Here we report a hyperbranched polymer as a new type of gelator that can be prepared *via* an one-pot reaction. Hyperbranched polymers possess a three-dimensional branched structure and numerous terminal groups, which are promising building blocks for self-assembly.[5] Up to now, several impressive supramolecular aggregates from the macroscopic to microscopic scale, such as macroscopic tubes, giant vesicles, submicroscopic micelles and nanofibers, have been prepared through the molecular self-assembly of hyperbranched polymers.[6] However, no physical gels from hyperbranched polymers have been reported. In this work a novel hyperbranched poly(methylene bisacrylamide-aminoethyl piperazine) (HPMA) was synthesized, and to our surprise, HPMA could self-assemble into immobile physical gels in organic solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAC), pyridine, dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidone (NMP).

The HPMA samples were synthesized *via* the Michael addition polymerization.[7] The Michael addition of *N*,*N*′-methylene bisacrylamide (MBA) and 1-(2-aminoethyl)piperazine (AEPZ) formed AB_2 type intermediates and further gave HPMA (Scheme 1). The polymerization was monitored by one-dimensional nuclear magnetic resonance (1D NMR); the assignments of the structural units and the degree of branching (DB) were determined *via* 2D NMR (S1.2, S2, S3; ESI†). The detailed characterization of HPMAs are summarized in Table 1. It can be concluded that all the obtained samples have a highly branched structure and are noncrystalline with good thermostability.



Scheme 1 Synthesis of HPMA *via* the Michael addition polymerization of MBA with AEPZ.

Interestingly, all the HPMA samples are able to gel the solvents of DMF, DMAC, pyridine, DMSO and NMP. A typical procedure for preparing the physical gel is as follows: a mixture of 10 mg HPMA-1 and 1 mL DMF was heated at 100 °C under nitrogen until it became a transparent solution. Then the system was allowed to stand overnight at room temperature to form a translucent immobile gel. Fig. 1 shows the appearance of HPMA-1 gels in the different solvents. All the gels are stable and can be kept for at least six months at room temperature. As can be seen in Fig. 1(A) and (B), the gels in DMF and DMAC gradually change from transparent to opaque with increasing the gelator concentration from 2.5 to 100 mg mL^{-1}, while the gels in pyridine, DMSO and NMP with 100 mg mL^{-1} are nearly transparent as shown in Fig. 1(C), (D) and (E), respectively. The different appearances must be correlated to the aggregate structure of the macromolecules in the gel systems.

The gelation efficiency of HPMA was also evaluated by critical gelation concentration (CGC) measurements (S4; ESI†). In the same solvent, only some flocs are observed when the gelator concentration is below the CGC. With increasing the gelator concentration, the flocs become more apparent in the solvent. Finally the immobile gels are formed at or above the CGC and no

Table 1 Characterization of resulting hyperbranched polymers

Polymer	R^a	DB	$10^{-4}M_n$	M_w/M_n	T_g/°C	$T_d{}^b$/°C
HPMA-1	1 : 1	0.42	2.6	2.3	66	262
HPMA-2	6 : 7	0.38	1.7	2.1	51	259
HPMA-3	3 : 4	0.43	1.4	1.8	48	242
HPMA-4	3 : 5	0.39	0.9	2.0	25	239

[a] Feed molar ratio of MBA to AEPZ. [b] T_d is the temperature at which 5% weight loss occurred.

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† Electronic supplementary information (ESI) available: Polymerization details, DB determination, CGC and rheological measurements of the gel samples. See DOI: 10.1039/b701043e

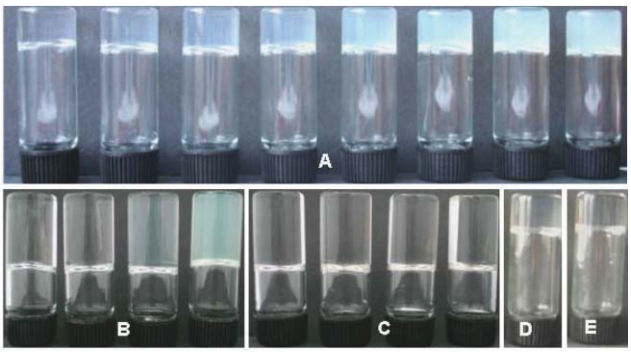


Fig. 1 HPMA-1 gels in upturned flasks at different HPMA-1 concentrations: (A) 2.5, 5.0, 7.5, 10, 25, 50, 75 and 100 mg mL^{-1} in DMF from left to right; (B) 10, 25, 50 and 100 mg mL^{-1} in DMAC from left to right; (C) 25, 50, 75 and 100 mg mL^{-1} in pyridine from left to right; (D) 100 mg mL^{-1} in NMP; (E) 100 mg mL^{-1} in DMSO.

flocs can be observed (Fig. S10; ESI†). On the other hand, the CGC of HPMA is found to be strongly dependent on the solvent. The CGC is 88 mg mL^{-1} in NMP, however, it is as low as 2.5 mg mL^{-1} in DMF, which is a very low level compared with that of reported gelators. The solvent dependence of gelation is also found in other physical gel systems, and it may be attributed to the influence of solvents on the self-aggregation of HPMA molecules and the microstructure of physical gels.[2–4]

Cryogenic-transmission electron microscopy (cryo-TEM) measurements were performed to disclose the microstructure of HPMA gels. To avoid possible artefacts, the samples were directly imaged at liquid-nitrogen temperature in the TEM after freezing-microtomy. The cryo-TEM images, which differ in the gelator concentration, directly revealed the developing process of the gel network, *i.e.*, the discontinuous aggregates of the polymer gradually develop and connect with each other to form a complete gel network (Fig. S11; ESI†). Fig. 2 displays a typical continuous open network of the polymer (the dark stripes in the image), and the solvent molecules are effectively entrapped within the network (the light gray pools in the image). The width of the dark stripes in the network varies from 50 to 300 nm. This suggests that within a

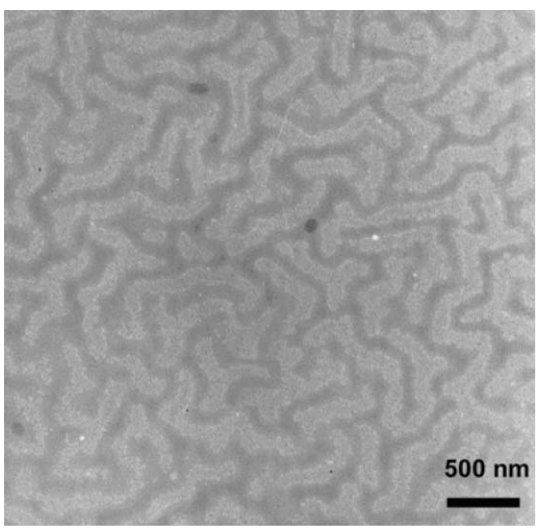


Fig. 2 Cryo-TEM image of HPMA-1 gel in DMF (10 mg mL^{-1}).

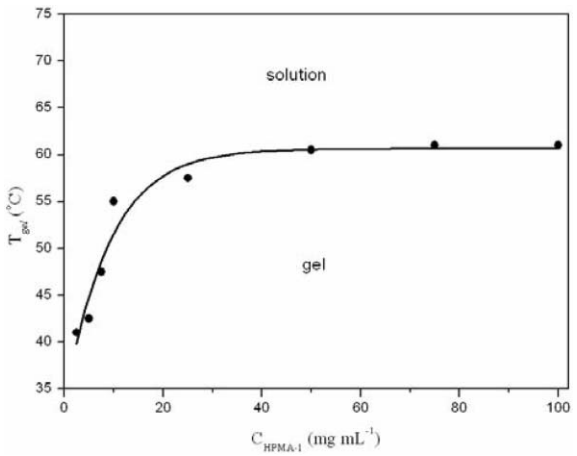
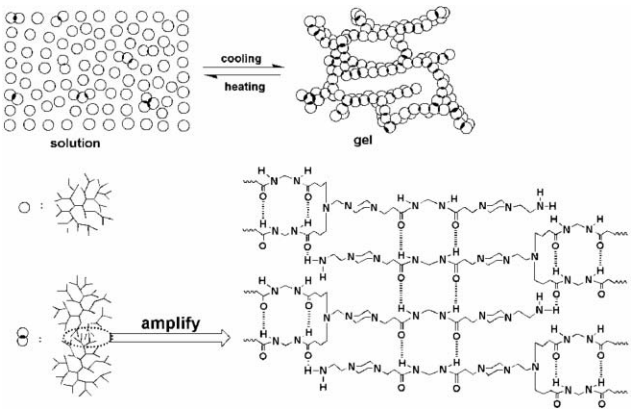


Fig. 3 Relationship between T_{gel} and the HPMA-1 concentration in DMF.

cross section of a stripe, there are several tens of HPMA molecules which aggregate together. The network in the HPMA physical gel exhibits numerous Y-junctions and possesses a rather irregular morphology. Such an irregular morphology has not been observed in other gel systems from small molecules, linear block copolymers or dendrimers.[1–4] It may be attributed to the ill-defined hyperbranched structure and the high polydispersity index of HPMA molecules. In addition, no crystallization domains have been found in this physical gel according to X-ray diffraction (XRD) measurements (Fig. S12; ESI†).

All of the HPMA physical gels are thermoreversible. They can form gels at room temperature and transform into solutions on heating. The effect of concentration on the sol–gel phase transition temperature (T_{gel}) was monitored by the tube inversion technique (Fig. 3).[4d,4f] The T_{gel} increases at first with increasing the concentration of HPMA-1 in DMF, and then reaches a plateau value of *ca.* 61 °C when the polymer concentration is over *ca.* 50 mg mL^{-1}. The result indicates that the gel network becomes more developed with increasing the polymer concentration. However, when the polymer concentration is above a certain value, the developing network reaches a equilibrium structure. Hence, the thermostability of the gel can not be improved any more by further increasing the polymer concentration. A rheological method was also used to evaluate the HPMA gels (S5; ESI†). The results show that HPMA gels exhibit the typical dynamic mechanical behavior of physical gels. Besides, the T_{gel} values obtained by this approach are consistent with those from the tube inversion technique. We have also attempted to investigate the thermal behavior of the gels by DSC. Unfortunately, the DSC endotherms were rather broad and the reproducibility was poor. This problem was also reported in previous work on the thermodynamics of small-molecule organogelators and dendrimer gelators.[3f,8]

The driving force for the gelation of HPMA can be ascribed to the hydrogen bonds among the amide and amine groups in the hyperbranched gelators. The FTIR spectrum of the HPMA-1 solution (25 mg mL^{-1} in DMF) displays the absorption bands of amide I, amide and NH-stretching at 1670, 1506 and 3482 cm^{-1}, respectively. However, these bands shift to 1654, 1540 and 3282 cm^{-1}, respectively, in the gel state (Fig. S7; ESI†). This



Scheme 2 Schematic plots of the sol–gel phase transition and the aggregation of hyperbranched gelators through hydrogen bonds.

indicates that strong hydrogen bonds among the amide and amine groups in HPMA-1 (C=O···H–N) are formed. Furthermore, the terminal amine groups are found to be very important for the gelation. The abundance of terminal amine groups can provide many hydrogen bonding sites to facilitate the formation of strong intermolecular hydrogen bonds. When the terminal amine groups were changed to vinyl groups or acidified by hydrochloric acid, the intermolecular interactions were sharply weakened and no gelation occurred. For example, HPMA with terminal vinyl groups (HPMA-vinyl) and HPMA hydrochlorate (S1.2, Fig. S8; ESI†) could not self-aggregate into physical gels but exhibited a good solubility in DMF, DMAC, NMP, pyridine and DMSO.

To further verify the contribution of the hydrogen bonds in the gelation, LiBr was used as a competitive hydrogen-bonding agent. The HPMA-1 solution in DMF (10 mg mL^{-1}) could no longer form the gel by adding as little as 1 wt% LiBr. FTIR data show that the hydrogen bonds among amide and amine groups have been weakened after adding LiBr, which is clearly reflected by the absorption band shifts (Fig. S8; ESI†). In other words, the HPMA physical gel would be broken down with the destruction of the hydrogen bonds.

Taking into account the microstructure of the HPMA gel and the driving force for the gelation, we propose the gelation mechanism as shown in Scheme 2. In the hot solution, the hydrogen-bond interaction among HPMA molecules is weak due to the strong thermal motion, leaving the HPMA molecules well dispersed in the solvent. On cooling, more intermolecular hydrogen bonds among HPMA molecules are formed, and the HPMA molecules begin to aggregate and insert with one another to form a continuous gel network. As illustrated in the amplified part in Scheme 2, both of the amine groups and amide groups in HPMA molecules are involved in the formation of hydrogen bonds.

In conclusion, this work has described a novel hyperbranched gelator HPMA, which can form a thermoreversible physical gel in DMF, DMAC, DMSO, NMP and pyridine. The TEM images reveal an irregular network morphology of the gel. The hydrogen bonds among the amide and amine groups of the gelator molecules are disclosed to be the driving force for the gelation. These results may be helpful to develop some novel gelators and extend the applications of hyperbranched polymers. Furthermore, the HPMA gel can emit blue fluorescence, which will be investigated in detail elsewhere.

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