Coordination polymer gels: synthesis, structure and mechanical properties of amorphous coordination polymers†

Brian S. Luisi, Kevin D. Rowland and Brian Moulton*

Received (in Cambridge, UK) 13th March 2007, Accepted 4th June 2007
First published as an Advance Article on the web 8th June 2007
DOI: 10.1039/b703768f

The synthesis and mechanical properties of a new class of coordination polymer based materials, amorphous coordination polymer sol-gels and xerogels, is presented.

The process of supramolecular self-assembly has enabled synthetic chemists to harness interactions such as non-covalent hydrogen bonds and dative metal–organic coordination bonds in the design of molecular materials and coordination polymers.[1] Crystal engineering[1b] is an approach to achieving such materials that involves the careful selection of molecular/ionic constituents which will, under the appropriate conditions, self-assemble into a pre-calculated crystalline network. Implicit in such a strategy is the requirement that each component contain the necessary geometry to encode for a desired architecture. Typically, in the synthesis of coordination polymers, metal cations or clusters that possess the prerequisite geometry are linked by rigid (*i.e.* aromatic) organic anions. Therefore, we anticipated that linking metal clusters that do not exhibit geometries predisposed to form periodic networks, and/or incorporating flexible ligands, would yield amorphous coordination polymers. Specifically, we chose to exploit a class of metallic clusters known as single molecule magnets (SMMs),[2] many of which contain multiple exohedral acetate ligands. Ligand exchange reactions aimed at affecting their quantum magnetic phenomena are known;[2a,3] indeed, a variety of mono-carboxylate ligands have been exchanged with the acetate ligands coordinated to manganese in the prototypal SMM: $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ (Fig. 1a). Herein, we describe a series of ligand exchange reactions with poly-carboxylate ligands aimed at linking the Mn_{12} SMMs, which yield amorphous coordination polymer sol-gels, and the relationship between ligand structure and mechanical properties. We also demonstrate that coordination polymer thin-films, *i.e.* xerogels, can readily be prepared.

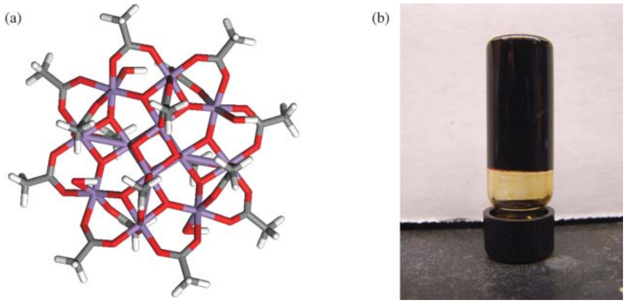

Fig. 1 (a) Structure of the $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ SMM, effective diameter *ca.* 1.7 nm. (b) Representative image of an inverted vial containing a CPG.

Low molecular weight organics which spontaneously form sol-gels, *i.e.* hydro- and organo-gelators, are well known.[4] Recently, interest in metal–organic gels, or metallogels, has increased as a result of the unique properties that can be imparted by incorporating metal ions.[5] The majority of such gels are the result of non-covalent interactions between discrete metal complexes, similar to the mechanism of gelation in organogels; however, a few gels based on dative covalent bonds, *i.e.* coordination polymer gels (CPGs), have been reported.[6] Such examples are based on poly-functional ligands bridging individual metal ions, and gel formation has been shown to be highly dependent upon the chemical nature and geometry of the bridging ligand.

Synthetically, the advantages that ligand exchange reactions with polymetallic clusters such as the SMMs have in the synthesis of CPGs are: the lack of appropriate symmetry for generating crystalline networks; the ability to undergo incomplete ligand exchange resulting in random bridging ligand positions and orientations, and numbers of connections; and the ability to exploit the ligand : cluster ratio and total concentration (*i.e.* mass loading) for affecting material properties. In a typical reaction, CPGs form when 10 equivalents of a poly-carboxylic acid are added to a sol phase of the Mn_{12}SMM in DMSO.‡ Fig. 1b shows the standard inverted vial test (note how the entire solution has gelled); Fig. 2 displays a 100X magnification optical image of a representative gel, which displays a highly branched, open architecture. In comparison to crystalline coordination polymers,

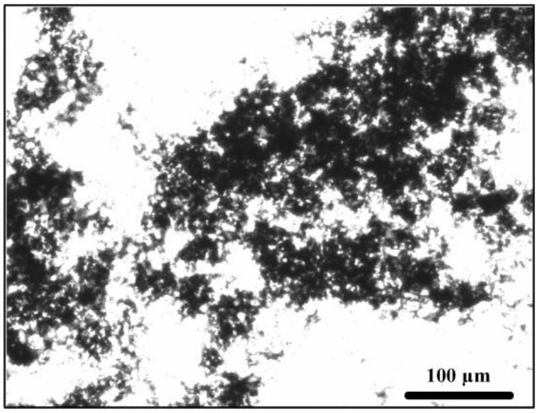

Fig. 2 100X magnification optical image of coordination polymer sol-gel microstructure, displaying the complex branched structure often associated with fractal geometry.

Department of Chemistry, Brown University, 324 Brook Street, Box H, Providence, R.I. 02912, USA. E-mail: Brian_Moulton@brown.edu

† Electronic supplementary information (ESI) available: thermal gravimetric and mechanical response data. See DOI: 10.1039/b703768f

the CPGs exhibit extraordinary porosity, containing *ca.* 95% solvent by mass, as determined by thermogravimetric analysis (TGA data are provided in the ESI).

We selected twelve bridging di-carboxylate ligands and one tri-carboxylate (Fig. 3a, abscissa axis) to demonstrate the versatility and recurrence of gel formation with this method across a range of structures and tolerance to appended chemical functionality. While gel formation is invariant with changing nature of the bridging carboxylic acid, the mechanical response of each gel is highly dependent upon it. Fig. 3a shows the effects that different poly-carboxylates have on yield stress and the elastic modulus (as calculated from the linear portion of the stress–strain curve) for each gel. Several features become immediately apparent: the yield stress of the non-aromatic "chain" linkers, which ranges from 43 Pa to 189 Pa, is much lower than those of the rigid, aromatic 1,3-substituted isophthalic acid and substituted isophthalic acid ligands which range from 832 Pa to 1101 Pa. The exception being 5-nitroisophthalic acid, which has a yield stress of 403 Pa that locates it in-between, along with the 1,4-substituted terephthalic acid and 2-bromoterephthalic acid, which have a yield stress of 318 Pa and 370 Pa, respectively.

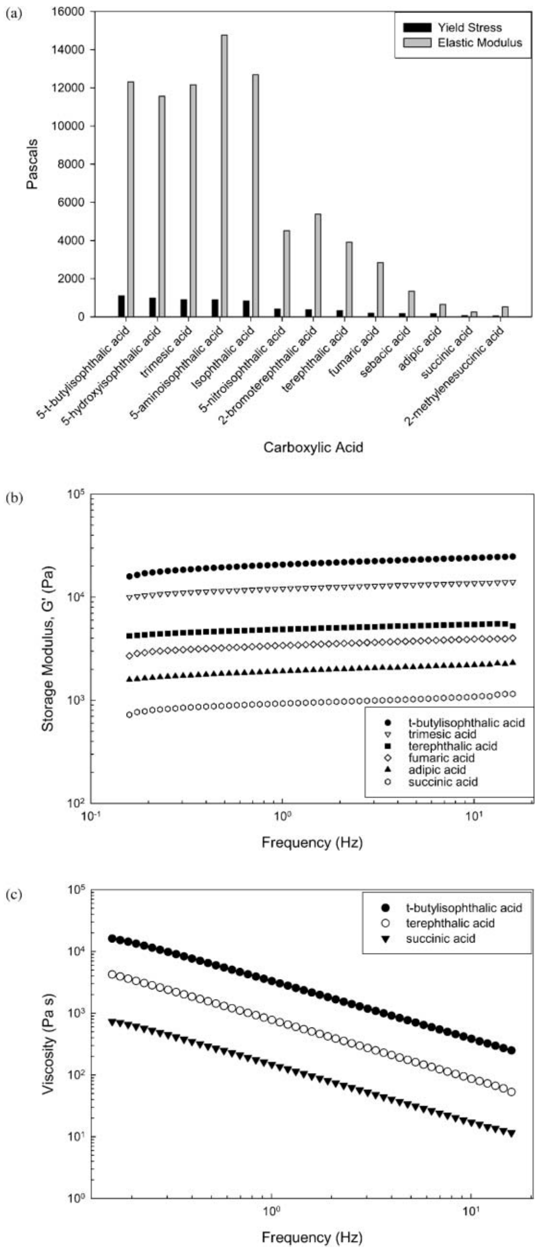

Fig. 3 (a) Yield stress and elastic modulus as a function of bridging ligand. (b) Elastic modulus as a function of frequency and bridging ligand. (c) Viscosity as a function of frequency and bridging ligand.

The elastic modulus (G′), the measure of resistance to elastic deformation or "stiffness", for each gel was determined by calculating the slope in the linear elastic portion of the stress–strain curve as well as a function of frequency as shown in Fig. 3b. Predictably, the elastic modulus shows a trend similar to that of yield stress with differences in bridging ligand. Isophthalic acid and the substituted isophthalic acids demonstrate an average stiffness more than an order of magnitude greater than the chain linkers as calculated as a function of strain. Terephthalic acid, 2-bromoterephthalic acid and 5-nitroisophthalic acid all have a stiffness intermediate to the two groups.

The elastic modulus for representative gels from each section is shown in Fig. 3b in the linear region as a function of oscillation frequency. The slight increase in G′ with frequency indicates a more elastic response of the network with increasing frequency. Overall the gels show a highly elastic response indicated by the large difference between the storage and loss modulus (G′ and G″; see ESI†). Gels built from t-butylisophthalic acid and trimesic acid have a G′ an order of magnitude higher than those gels built from adipic acid and succinic acid. At frequencies greater than 200 Hz, network collapse begins to occur with the onset of inelastic deformation.

The geometry of the aromatic ligand, the nature of appended functionalities, as well as chain structure and length afford some degree of control over the mechanical properties of the resultant gel. The 1,3-substituted angular aromatic linkers yield gels that have more than double the physical strength of the gels formed from the linear aromatic linkers. Isophthalic acid with appended functionalities that are capable of acting as both hydrogen bond donors and acceptors shows an increase in the yield stress and elastic modulus over unsubstituted isophthalic acid. Although, this is in sharp contrast to 5-nitroisophthalic, which is a strong electron withdrawing group, that shows a yield stress and elastic modulus less than half that of isophthalic acid. t-Butylisophthalic acid, which exhibits the highest yield stress, cannot undergo hydrogen bonding but the bulky t-butyl group may help to prevent flow and rearrangement of the gel, leading to a higher strength.

Of the chain linkers, the conjugated fumaric acid has the highest yield stress and elastic modulus. Mechanical strength decreases with decreasing chain length where the 10-carbon chain linker, sebacic acid, shows the highest yield stress and elastic modulus and the 4-carbon chain linkers, succinic acid and 2-methylenesuccinic acid, have the lowest. The importance of a rigid linker is illustrated by the difference between fumaric acid and 2-methylenesuccinic acid. Both ligands possess 4-carbon backbones, but the yield stress of 2-methylenesuccinic acid is less than one quarter that of fumaric acid.

The results of the viscosity tests are in agreement with the frequency oscillation tests. Fig. 3c shows representative examples of the change in viscosity as a function of frequency. t-Butylisophthalic acid and those gels in the high yield stress

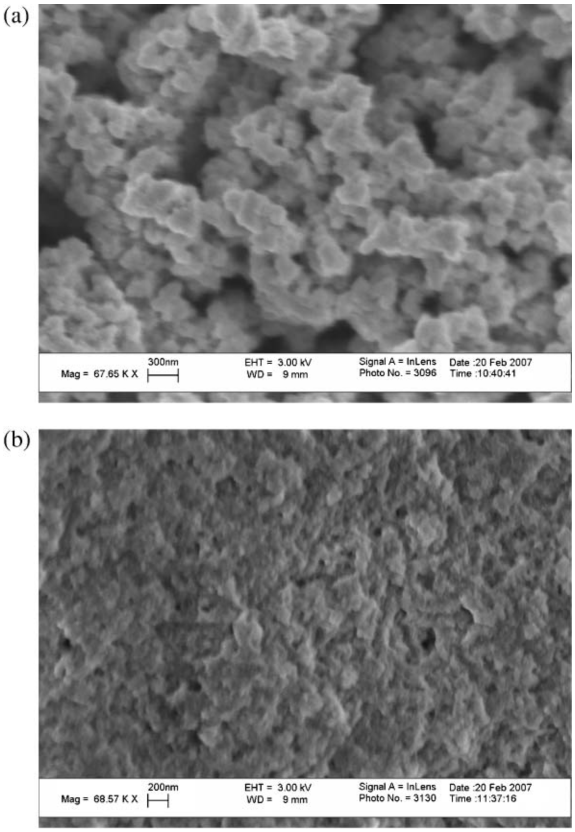

Fig. 4 SEM images of xerogels made from (a) trimesic acid and (b) fumaric acid.

region exhibit a viscosity an order of magnitude higher than succinic acid and those gels in the low yield stress region. Thixotropic loop tests were attempted in order to check for possible hysteresis effects; reformation of the gel state did not occur in a reasonable experimental time-frame, precluding the possibility of obtaining the return curve.

In an attempt to correlate the microstructure of the coordination polymers with the physical measurements of the gels, thin films of the CPG's were prepared on glass slides. Over a period of 3 days solvent expulsion was accompanied by network shrinkage to produce a dried xerogel. Figs. 4a and 4b show SEM images obtained from xerogels made from trimesic acid and fumaric acid, respectively. Xerogels constructed from fumaric acid show a dense material with a near uniform surface roughness and some scattered macropores 50–100 nm in diameter. In contrast, xerogels made from trimesic acid show a more open, macroporous structure with agglomerates on the order of 300 nm that are threaded through the structure. The differences in density and surface porosity are attributed to the degree of flexibility each CPG is capable of during drying: trimesic acid CPG's, which are mechanically stronger, experience less shrinkage upon drying, leading to a more open microstructure.

In conclusion, we have developed a universal sol-gel approach toward the formation of amorphous coordination polymers. Metal clusters that militate against periodic network propagation can be used as nodes in the construction of coordination polymer gels with a broad range of bridging ligand structures, functionalities and electronic characteristics, which can be used to control the physical properties and microstructure of the gels. Moreover, these materials have the advantage of processability (*i.e.* they adopt the form of the vessel, or mold, that they are made in) and we have also demonstrated that they can be easily processed into thin-film xerogels. Current studies are aimed toward additional characterization of xerogel porosity (*i.e.* bimodal porosity) and toward solvent removal processes for the generation of coordination polymer aerogels.

Notes and references

‡ $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ was prepared by the method originally outlined by Lis.[7] In a typical reaction, gels were formed when 8.35×10^{-5} moles of $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ (0.172 grams) were mixed with 8.35×10^{-4} moles of a poly-carboxylic acid in 5 ml of DMSO. Thin films were prepared by coating a glass slide with a solution of SMM in DMSO followed by dropping a solution of carboxylic acid in DMSO onto the surface with a pipette. Rheometric measurements were performed on a Rheometrics Dynamic Stress Rheometer with parallel plate geometry (gap = 0.5 mm) at a temperature of 298 K (the authors thank Arkwright Incorporated of Coventry, R.I. for use of their rheometer). Frequency oscillation tests were performed at a constant strain of 2%; yield stress measurements were done at a constant frequency of 1 Hz while increasing the elastic stress logarithmically and monitoring the strain. Thermal gravimetric analysis (TGA) was performed with a TA instruments Q500 instrument in air from ambient temperature to 650 °C. Optical microscopy was performed with a Nikon epifluorescence microscope (Eclipse E800; Nikon Inc.)

1 J. M. Lehn, *Science*, 2002, **295**, 2400; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
2 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141–143; R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804; A. R. Schake, H.-L. Tsai, R. J. Webb, K. Folting, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1994, **33**, 6020; D. Foguet-Albiol, T. A. O'Brien, W. Wernsdorfer, B. Moulton, M. J. Zaworotko, K. A. Abboud and G. Christou, *Angew. Chem., Int. Ed.*, 2005, **44**, 897; A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud and G. Christou, *Angew. Chem., Int. Ed.*, 2004, **43**, 2117; M. Soler, W. Wernsdorfer, K. Folting, M. Pink and G. Christou, *J. Am. Chem. Soc.*, 2004, **126**, 2156–2165.
3 H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1995, **117**, 301; T. Kuroda-Sowa, T. Nogami, H. Konaka, M. Maekawa, M. Munakata, H. Miyasaka and M. Yamashita, *Polyhedron*, 2003, **22**, 1795.
4 L. A. Estroff and A. D. Hamilton, *Chem. Rev.*, 2004, **104**, 1201; P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133.
5 F. Fages, *Angew. Chem., Int. Ed.*, 2006, **45**, 1680.
6 J. B. Beck and S. J. Rowan, *J. Am. Chem. Soc.*, 2003, **125**, 13922; Y. Zhao, J. B. Beck, S. J. Rowan and A. M. Jamieson, *Macromolecules*, 2004, **37**, 3529; S. J. Rowan and J. B. Beck, *Faraday Discuss.*, 2005, **128**, 43; W. Weng, J. B. Beck, A. M. Jamieson and S. J. Rowan, *J. Am. Chem. Soc.*, 2006, **128**, 11663; Q. Wei and S. L. James, *Chem. Commun.*, 2005, 1555; J. Zhang, X. Xu and S. L. James, *Chem. Commun.*, 2006, 4218; B. Xing, M.-F. Choi and B. Xu, *Chem. Commun.*, 2002, 362; B. Xing, M.-F. Choi, Z. Zhou and B. Xu, *Langmuir*, 2002, **18**, 9654; L. Applegarth, N. Clark, A. C. Richardson, A. D. M. Parker, I. Radosavljevic-Evans, A. E. Goeta, J. A. K. Howard and J. W. Steed, *Chem. Commun.*, 2005, 5423; H.-J. Kim, W.-C. Zin and M. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 7009; K. Kuroiwa, T. Shibata, A. Takada, N. Nemoto and N. Kimizuka, *J. Am. Chem. Soc.*, 2004, **126**, 2016; J. M. J. Paulusse, D. J. M. van Beek and R. P. Sijbesma, *J. Am. Chem. Soc.*, 2007, **129**, 2392.
7 T. Lis, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **36**, 2042.