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Interfacing supramolecular and macromolecular chemistry: metallo-supramolecular triple-helicates incorporated into polymer networks†

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Received (in Cambridge, UK) 14th October 2002, Accepted 1st November 2002
First published as an Advance Article on the web 15th November 2002

Metallo-supramolecular diiron(II) triple-helical cores based on pyridylimine ligands and decorated with acrylate or methacrylate units are copolymerised with methyl methacrylate (MMA) as major comonomer using AIBN.

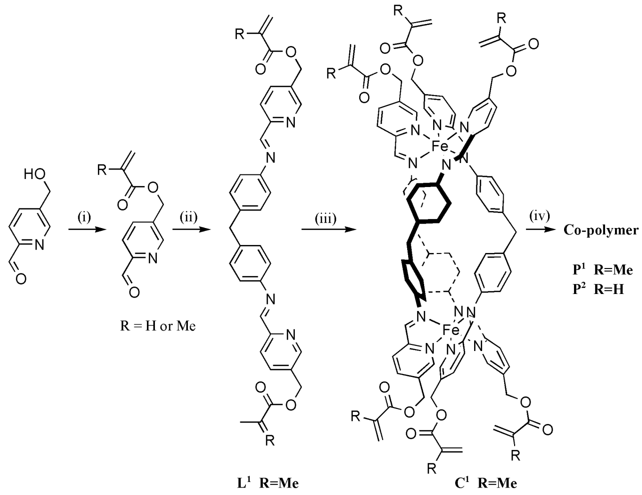
We are interested in the possibility of interfacing supramolecular synthesis with polymer synthesis. Nature frequently constructs large monodisperse macromolecules whose shape (and function) is precisely defined. By contrast, covalent synthesis constructs quite small but monodisperse molecules of controlled shape while polymer synthesis constructs large but polydisperse macromolecules. The benefits and applications of polymer chemistry in designing new materials are such that polymers are now ubiquitous in all environments, yet the approach does not afford the level of control seen in nature. Hybrid polymer–supramolecule species are potentially fascinating because the precise nano-scale architecture control afforded by supramolecular synthesis[1] might be used to control/influence the architecture of the polymer. Conversely the polymer could be used to influence the nature or properties of the supramolecular unit(s). Moreover incorporation into polymer structures is a potential route to move from discrete nano-scale supramolecular arrays to processable materials which can be manipulated and addressed.

Interfacing the two fields is complicated by the need to identify conditions which are consistent with both a supramolecular assembly process and polymerisation and to establish suitable synthetic routes. To initiate our programme we selected metal ion assembled supramolecular architectures, because of the greater strength of metal–ligand interactions compared to some other supramolecular interactions.[2] We wished to prepare a supramolecular unit which could be used as a minor comonomer in a copolymerisation process and would thus be incorporated within the network of the polymer. We have applied the imine-based approach to supramolecular architectures developed in our laboratory since this approach allows rapid construction of functional supramolecular arrays in simple mixing steps.[3] Polymers with incorporated supramolecular architectures are rare: the groups of Geerts and Sauvage,[4] and Stoddart,[5] have polymerised organo- and metallo-catenanes. Eisenbach, Newkome *et al.*[6] attached the ends of polymer chains to a bis-bipyridine ligand and propose the formation of double-helical complexes (although recent work by Constable and coworkers[7] indicates that similar ligands form a mixture of supramolecular architectures). A variety of monuclear metal complexes such as photoactive ruthenium polypyridine centres have been (co)polymerised.[8]

Six acrylate or methacrylate units were attached to the extremities of a di-iron triple-helical supramolecular core as outlined in Scheme 1. This core was selected as it is robust, monodisperse and has a well-defined architecture. Moreover it functions as a DNA major groove targetting agent and induces remarkable DNA structural effects.[9] The supramolecular complexes (which are tetracationic and isolated as their hexafluorophosphate salts) are soluble in acetonitrile, acetone or nitromethane. Analytical data are entirely consistent with the expected structures and formulations. Copolymerisation[10] was carried out with $\mathbf{C}^1$/$\mathbf{C}^2$ and MMA using AIBN initiation. In nitromethane, copolymerisation was successful while in acetonitrile and acetone, we recovered only the starting materials.

A sample taken after 18 h and analysed by ^{1}H NMR (300 MHz) in DMSO-d_6 after removing the solvent under vacuum, showed that the copolymerisation has taken place. A broad singlet at δ 3.57 represents the protons of the polymeric methoxy groups. A broad singlet at δ 1.84 was assigned as the CH_2 groups of the polymer. The broad multiplet at δ 0.85 (poly-CH_3) appears to exhibit a broad doublet pattern. This is due to different proton environments resulting form the differing arrangements of substituents on the polymer backbone, which is here atactic. The integration of small signals at δ 6.03, 5.67 corresponding to MMA compared to the poly-CH_2 signal revealed that the conversion has reached approximately 94%. A further 18 h of reaction allows complete conversion (disappearance of the signal corresponding to the vinylic protons). The peaks corresponding to the supramolecular comonomer are in too low concentration to be detected *via* NMR, being swamped by PMMA peaks. After 36 h, we precipitated in hexane a purple viscous solid. The purple colouration confirms the integrity of the supramolecular unit. The solid is soluble in THF which facilitated the analysis by size exclusion chromatography (SEC) (Fig. 1).

DRi detection revealed a quite high PDI ($\mathbf{P}^1$ 2.3; $\mathbf{P}^2$ 2.2) not unusual for free radical polymerisation where recombination and chain-transfer side reactions occur, and a relatively low M_n ($\mathbf{P}^1$ 7800; $\mathbf{P}^2$ 8300). In these copolymerisations the quantity of



Scheme 1 *Reagents and conditions*: (i) (meth)acryloyl chloride, THF, NEt_3, 0 °C; (ii) 4,4′-methylenedianiline, EtOH, rt; (iii) $FeCl_2$, MeOH reflux; (iv) MMA, AIBN, $MeNO_2$, 75 °C, 36 h[10]

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† Electronic supplementary information (ESI) available: synthetic details for the compounds described and the polymerisation experiments. See http://www.rsc.org/suppdata/cc/b2/b210019c/

DOI: 10.1039/b210019c

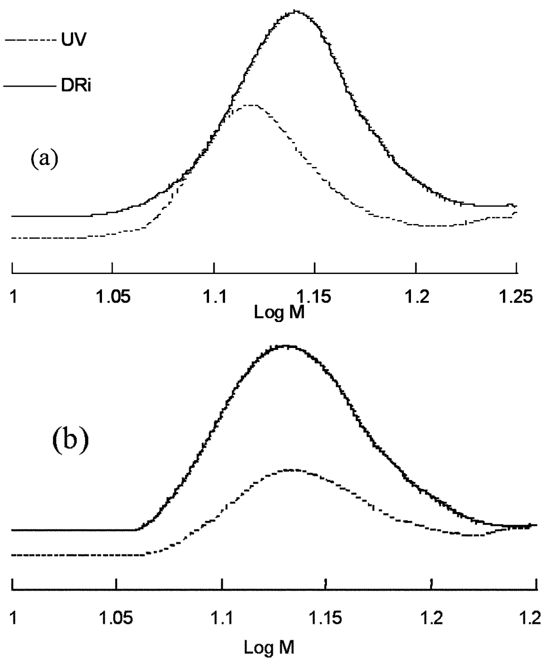

Fig. 1 SEC overlay of DRi and UV (280 nm): (a) copolymer $\mathbf{P}^1$, PDI = 2.3, M_n = 7800, M_w = 18000; (b) $\mathbf{P}^2$, PDI = 2.2, M_n = 8300, M_w = 19000 in PMMA backbone (eluent THF, toluene flow rate marker, 1 ml min^{-1}).[11]

the supramolecular comonomers are so small that the figures obtained from SEC may be considered accurate.[11] The relatively low molecular weight of the copolymers is attributed to the relatively large quantity of initiator, compared to MMA, used. To confirm the incorporation of the supramolecular units $\mathbf{C}^1$ and $\mathbf{C}^2$ in the PMMA matrix, SEC experiments were run with additional UV-Vis detection. Detection at 573 nm was firstly chosen. This wavelength corresponds to an MLCT transition in the metal complex. The SEC traces were relatively weak but coincident with the DRi trace. Detection at 280 nm proved more useful because the UV-Vis spectrum of the complex shows an intense absorbance in this region (ligand-based transition). The SEC using this method showed a more intense band in the same molecular weight range as the trace shown in DRi detection. Overlap of the two SEC traces shows that they run in similar molecular weight ranges. The results suggest that while the incorporation of the iron(II) complex can be considered successful, not all PMMA polymer chains contain the complex.

To establish co-polymer formation a number of control experiments were undertaken: Pure samples of $\mathbf{C}^1$ and $\mathbf{C}^2$ were not soluble in the THF–toluene mixture used to prepare the sample of copolymer for SEC; this in itself may be taken as an indication of the incorporation of the complex. Free radical polymerisation of pure MMA was undertaken under the same conditions to achieve the same molecular mass; no signals were observed in the SEC traces with UV detection at 573 or 280 nm. The sample of pure PMMA was taken with a small quantity of $\mathbf{C}^1$ or $\mathbf{C}^2$ and mixed thoroughly in nitromethane. A SEC trace using DRi and UV detection at 280 nm showed that the peak for the complex did not overlap with the curve corresponding to PMMA chains. This proves that the complex in the copolymer is truly incorporated into the polymer backbone and that the UV trace is not merely a result of the encapsulation of the complex by the solvent swollen PMMA chains. To further confirm this, we attempted to encapsulate the analogous unsubstituted dinuclear triple helicate,[3] during the polymerisation process. We recovered an off-white (not purple) solid of PMMA, and SEC with UV detection showed no absorbance.

The reactivity of $\mathbf{C}^1$ and $\mathbf{C}^2$ is expected to be different and this is reflected in the extent of incorporation in the growing polymer chain. For the copolymer of $\mathbf{C}^1$ with MMA ($\mathbf{P}^1$) the UV trace is greater in intensity at higher molecular weight compared to the DRi trace. For copolymer $\mathbf{P}^2$ the SEC overlay of the DRi and UV distribution traces fits better. The copolymer $\mathbf{P}^2$ gives a homogeneous composition whereas the copolymer $\mathbf{P}^1$ exhibits compositional heterogeneity with more of $\mathbf{C}^1$ copolymerised relative to MMA at higher mass. This is ascribed to a combination of the effects of changes in reactivity ratio and propagation rate constants.

The iron(II) can be extracted from the polymers by treatment with EDTA, a loss of colour indicating the successful extraction. The SEC UV trace (280 nm) of the resulting polymer shows a weaker absorbance which is consistent with the continued incorporation of the ligand in the polymer. No significant change in the number average molecular mass M_n is observed, confirming that we achieved a truly cross-linked network between the polymer chains, with a cage formed by the pre-organised helicates inside this network. On reintroducing iron(II) chloride into a solution of $\mathbf{P}^2$ in DCM and sonicating, the purple colour is recovered confirming that the iron can be returned to its binding site.

We are currently studying the selectivity of these cages towards different metal ions and investigating the application of controlled radical polymerisation techniques (*e.g.* ATRP and RAFT).

This work was supported by an EU Marie Curie Fellowship (A. L.) and the University of Warwick (J. H.).

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11 These values were obtained using the Mark–Houwink parameters ($K = 10.4 \times 10^{-5}$ and $\alpha = 0.697$). The molecular weight data obtained using these values are usually taken to accurate to within ±5% for 100% MMA as monomer with errors increasing up to ±50–60% for completely different monomers. PDIs are generally considered accurate regardless of K and α.