Casting Platinum Jewellery Alloys

THE EFFECTS OF COMPOSITION ON MICROSTRUCTURE

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There are numerous platinum jewellery alloys available today. Two commercially available general purpose alloys that are in common use by manufacturing platinum jewellers are platinum-5% copper and platinum-5% ruthenium. In South Africa, the copper alloy is normally preferred for casting because of its lower melting point and greater fluidity, while the ruthenium alloy is preferred for hand-working and machining, although some jewellers use either alloy for all applications. In order to provide a scientific basis to the differences in finish and workability, as experienced by jewellers, we set out to compare casting characteristics of platinum-copper and platinum-ruthenium jewellery alloys and look for any substantial differences between them. We also examine factors affecting their different characteristics, and how working conditions can be manipulated to optimise the performance of each alloy in jewellery manufacture.

Many platinum jewellery alloys are available, each being marketed according to applications for which it is suitable. For instance, platinum-5 wt.% iridium has high work hardening and is suitable for making clasps, wire and the like, while softer platinum-5% palladium is used for fine casting and delicate settings (1). Two commercially available, general purpose alloys, platinum-5% copper (Pt-5%Cu) and platinum-5% ruthenium (Pt-5%Ru), are in common use by manufacturing platinum jewellers. Jewellers who work with these two alloys report some significant differences between them.

This paper will examine the differences in these alloys and reasons for their preferential use. We will look for factors affecting their different characteristics, and how working conditions can be manipulated to optimise the performance of each alloy in jewellery manufacture. Differences between these alloys, experienced during hand-working and casting, are summarised in Table I.

Physical Properties of Pt-5%Cu and Pt-5%Ru

The relevant physical properties of pure platinum, Pt-5%Cu and Pt-5%Ru are summarised in Table II. The alloys are formulated in terms of weight per cent (wt.%). Copper atoms are significantly lighter than ruthenium atoms. This means that the copper alloy contains a higher atomic per cent (number of atoms) than the ruthenium alloy.

Table I		
Comparison of Some Working Attributes of Pt-5%Cu and Pt-5%Ru		
Attribute	Pt-5%Cu	Pt-5%Ru
Hardness	Slightly softer	Slightly harder
Colour	Slightly brownish-grey	Shiny white
Melting temperature	Lower	Higher
Castability	More fluid	Less fluid
Surface finish	Susceptible to scratching	Easier to polish
Crucible corrosion	More corrosive	Less corrosive
Fuming when molten	Brown fumes	Minimal fuming

Table II			
Comparison of Relevant Physical Properties of Pure Platinum, Platinum-5 wt.% Copper and Platinum- 5 wt.% Ruthenium (1)			
Property	Platinum	Pt-5%Cu	Pt-5%Ru
Density, g cm^{-3}	21.4	20.0	20.7
Hardness, Hv (annealed)	50	125	130
Melting range, ºC	1769	1725–1745	1780–1795

There are 1.5 times more copper atoms than ruthenium atoms in an equivalent mass of 5 wt.% alloy. Both copper and ruthenium dissolve readily in platinum, and so do not decrease the density of the actual metal substantially.

In both the cast and annealed state Pt-5%Ru is slightly harder than annealed Pt-5%Cu. The addition of either of these alloying elements significantly increases the hardness of the platinum. The alloying atoms, acting like bollards on a busy pedestrian pavement, obstruct the movement of dislocations that allow planes of atoms in the metal crystals to slip past each other. This impediment makes the metal more resistant to deformation and increases the hardness. The bulk hardness is also affected by the microstructure, as will be seen later.

Pure platinum melts at 1769ºC. Alloys can melt over a range of temperatures, depending upon their composition. As copper has a lower melting point (1083ºC) than platinum, it lowers the melting range of the alloy (to 1725–1745ºC). The much higher melting point of ruthenium (2314ºC) raises the alloy melting range (to 1780–1795ºC). Figure 1 clearly shows the narrower range of solidification at higher temperatures for Pt-Ru, compared to the broader range of solidification at lower temperatures for Pt-Cu. The different compositions of these alloys lead to substantial differences in their behaviour and melting temperature ranges, and these are described and explained here.

Casting Experiments

A large number of casting tests were carried out in a Hot Platinum integrated induction melting and casting machine. This machine melts and casts up to 250 g of platinum alloy into a shallow cylindrical flask which is rotated around a vertical axis. The invested trees consist of a central sprue with the test pieces arranged tangentially. The test

Fig. 1 Diagram showing the melting ranges for Pt-Cu and Pt-Ru alloys containing up to 10 wt.% of solute metal.
The solidification ranges for the alloys lie between the two sets of lines. There is a narrower range of solidification for Pt-Ru, compared to Pt-Cu. The range for Pt-Ru is at higher temperatures than the solidification range for Pt-Cu
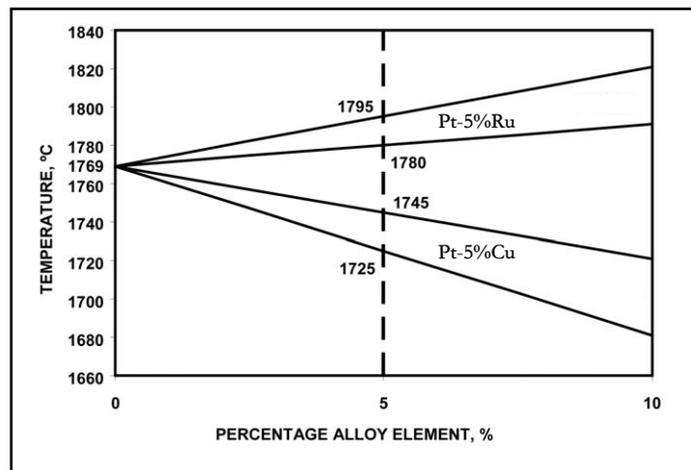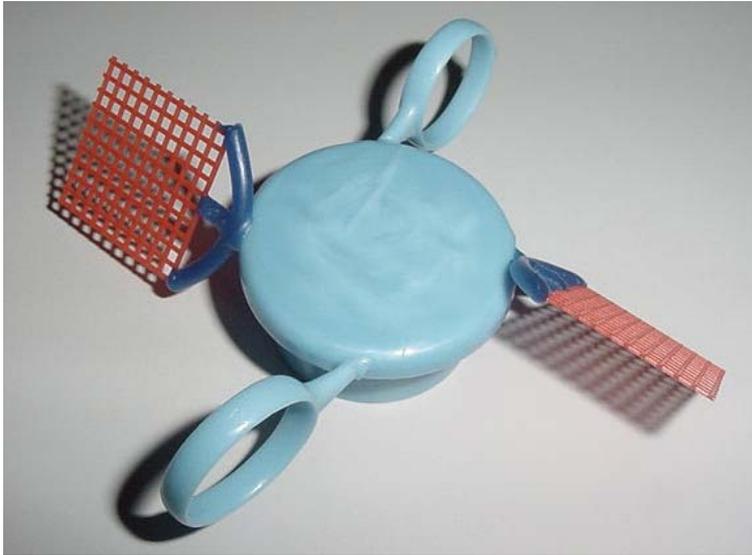
Fig. 2 Photograph of a wax test model tree with the central feeder sprue. After burn-out, when the investment is cast, it rotates about a vertical axis, throwing out the molten alloy into the two rings and the two 10 × 10 grids. The model is 110 mm across.
Samples were taken from the cross-section where the feeder sprue meets the ring shank and at the distal point through the ring shank. The grids gave a measure of fill of the casting, while inspection of the cross-sections assessed the porosity of the rings

pieces on each tree were two simple rings and two 10 × 10 grids, see Figure 2.

The testing was aimed primarily at assessing the fill and porosity that can be obtained when casting Pt-5%Cu and Pt-5%Ru in a number of different investment materials at different flask temperatures and centrifugal speeds. The investment materials used were Bego's Wirovest, Ransom and Randolph's Astro-Vest and Hoben's Platincast. Duplicate tests were conducted mainly in pairs, under nominally identical conditions. Table III shows the test schedule. Results of a comparative metallographic study of rings from twenty five of these tests are reported here. An assessment of fill and porosity will be reported in a second paper.

Most of the twenty-five rings were sampled twice, by sawing through the line joining the feeder sprue to the ring shank and also perpendicularly through the shank at the point furthest from the sprue. This produced two samples for each ring. These were mounted in resin, ground flat, diamond polished, and then electrolytically etched for examination by microscope in reflected light.

Results

Visual comparison of the etched metallographic sections revealed the following:

[1] Grain size varied considerably between samples, ranging from about 0.01 mm to over 1 mm, with the Pt-5%Cu tending to have larger grain size than the Pt-5%Ru under similar casting conditions. This gave rise to a measured 10% difference in the as-cast hardness.

[2] Within sample pairs for both alloys, the sprue sections always had coarser grains than the shank sections.

[3] All the etched Pt-5%Cu samples had a marked dendritic structure, while most of the etched Pt-5%Ru samples had an equiaxed grain structure without obvious dendrites, see Figure 3.

Chemical analysis of selected etched and unetched samples by energy dispersive spectroscopy (EDS) in a scanning electron microscope revealed the following:

[a] Analysis of unetched samples showed that the dendritic cores of the Pt-5%Cu were enriched in platinum, while the interdendritic areas were enriched in copper by about 1 wt.% (that is, about 20% variation relative to the bulk composition). This is evidence of strong chemical segregation.

[b] The aggressive electrolytic etching tended to dissolve the copper-rich interdendritic areas completely, producing strong visual contrast with the platinum-rich dendritic cores. The etching also leached copper from the platinum-rich cores. If the etched samples had been analysed alone, the segregation would have been visible but not detectable chemically.

Table III — Schedule of Casting Tests with Pt-5%Cu and Pt-5%Ru, in Duplicate Pairs, Except Where Indicated					
Investment	Alloy	Melt, ºC	Flask, ºC	Centrifuge, rpm	No. of tests
Wirovest	Pt-5%Cu	2050	940	600	2x
	Pt-5%Cu	2050	600	600	2x
	Pt-5%Cu	2050	300	600	2x
	Pt-5%Cu	2050	950	1200	2x
	Pt-5%Ru	1950	950	600	2x
Astro-Vest	Pt-5%Cu	1850	870	800	1x
	Pt-5%Cu	1850	870	900	2x
	Pt-5%Cu	1850	600	900	2x
	Pt-5%Cu	1850	300	900	2x
	Pt-5%Cu	1850	870	1000	2x
	Pt-5%Cu	1850	870	1200	2x
	Pt-5%Ru	2050	870	800	1x
	Pt-5%Ru	2050	870	900	2x
	Pt-5%Ru	2050	600	900	2x
	Pt-5%Ru	2050	300	900	2x
	Pt-5%Ru	2050	870	1000	2x
	Pt-5%Ru	2050	870	1200	2x
Platincast	Pt-5%Cu	1850	900	600	2x
	Pt-5%Cu	1850	600	600	2x
	Pt-5%Cu	1850	300	600	2x
	Pt-5%Cu	1850	900	800	6x
	Pt-5%Cu	1850	600	800	2x
	Pt-5%Cu	1850	300	800	2x
	Pt-5%Cu	1850	900	1000	2x
	Pt-5%Ru	2050	900	600	2x
	Pt-5%Ru	2050	600	600	2x
	Pt-5%Ru	2050	300	600	2x
	Pt-5%Ru	2050	900	800	6x
	Pt-5%Ru	2050	600	800	2x
	Pt-5%Ru	2050	300	800	2x
	Pt-5%Ru	2050	900	1000	13x
	Pt-5%Ru	1950	600	600	2x
	Pt-5%Ru	2000	900	1000	4x

[c] Neither the unetched nor etched Pt-5%Ru alloy showed visible dendritic growth, but there was some compositional inhomogeneity within individual grains. Chemical analysis of an unetched sample revealed a maximum difference of about 0.5 wt.% Ru between platinum-rich and ruthenium-rich areas within individual grains.

Discussion

These results can be explained best with reference to the compositional or phase diagrams for these two alloys. A phase diagram is a plot of alloy composition against temperature and is useful, but not infallible, in predicting the state of an alloy under given heating or cooling conditions.

First let us consider how dendrites with strong compositional segregation form in the Pt-5%Cu alloy. Figure 4 shows part of the phase diagram for a platinum-copper alloy including our 5 wt.% composition.

The vertical axis represents temperature in ºC and the horizontal axis represents alloy composition from 100% Pt on the left and increasing Cu towards the right. The Pt-5%Cu composition is
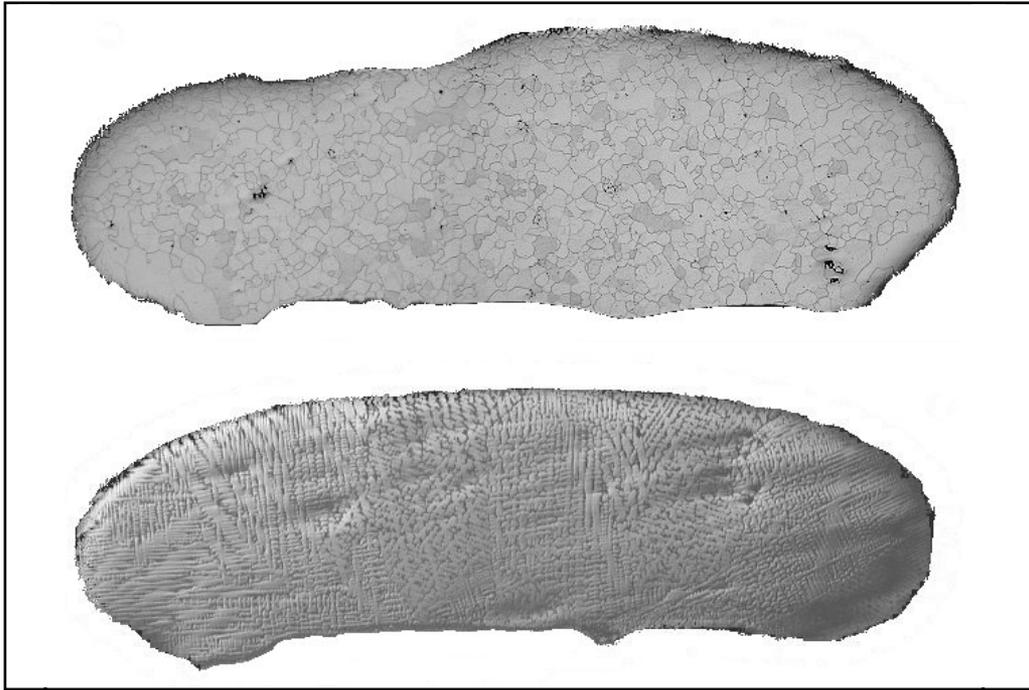
Fig. 3 Comparison of the etched microstructures of distal cross-sections of 8 mm wide shanks of cast rings (25 mm in diameter). Samples of Pt-5%Ru (above) and Pt-5%Cu (below) show the coarse dendritic segregation in Pt-5%Cu, and the finer equiaxed grain growth of Pt-5%Ru. Both casts were in Platincast investment, with a flask temperature of 900°C and rotational speed of 800 rpm. The Pt-5%Ru cast was at 2050°C and the Pt-5%Cu at 1850°C, in a Hot Platinum induction melting and casting machine

marked with a vertical dashed line. The upper line sloping down to the right is the liquidus, above which the metal should be fully molten. The lower line sloping down to the right is the solidus. Between these two lines we have a range of solidification, with solid metal coexisting with liquid. Below the solidus the material should be fully solid.

Let us consider what happens when we slowly cool a fully molten alloy with composition Pt-5%Cu through its solidification range. As the cooling liquid reaches the liquidus temperature, **a,** it does not freeze instantaneously, but solid begins to form. This solid has a composition corresponding to the solidus at this temperature, **b,** which is enriched in platinum. The liquid is thus enriched in copper. As the material cools further, more solid forms with a composition that tracks down the solidus, **bd.** The residual liquid tracks down the liquidus, **ac,** in composition. Under equilibrium conditions, that is, if the material cools slowly

enough, there is a continuous reaction between the solid forming and the liquid, so that by the time the last vestige of liquid freezes all the solid has a uniform composition.

However, in reality cooling is usually too rapid for equilibrium to occur, and as solid forms it progressively removes the element with the higher melting point, in this case platinum, enriching the melt in copper. Because of the relatively wide solidification range of the Pt-5%Cu (from 1745–1725°C) and the substantial difference in melting points of platinum and copper, there is opportunity during cooling for chemical segregation to occur. This accounts for the formation of dendritic crystals with platinum-rich cores and copper-rich margins.

Now, let us consider the cooling of a Pt-5%Ru alloy, with reference to the relevant part of the phase diagram, see Figure 5.

Ruthenium has a higher melting point than platinum, so on cooling a liquid Pt-5%Ru alloy the first

Fig. 4 Part of the platinum-copper phase diagram (after Savitskii et al. (2)).
*Hot alloy cools from the high casting temperature, through its solidification range. At the liquidus temperature, **a**, solid begins to form of composition, **b**, enriched in Pt, leaving the liquid copper rich. As material cools further, more solid forms, tracking down, **bd**. At the same time residual liquid tracks down, **ac***
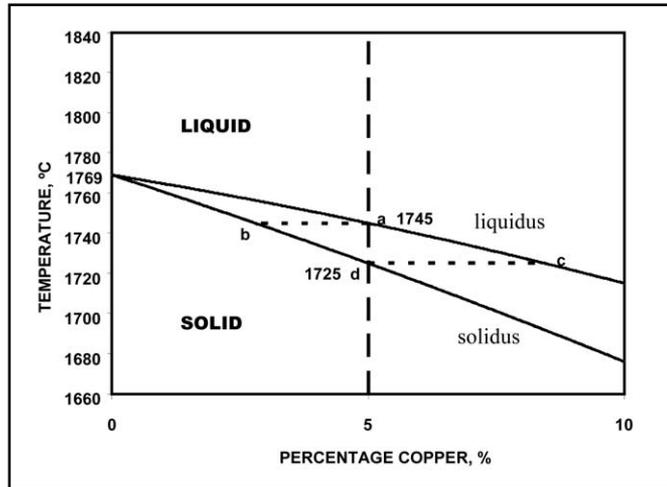
crystals to form at 1795°C should be ruthenium-rich, **b**, and the liquid will be enriched in platinum, **a**. On further cooling the solid composition should track down the solidus towards a more platinum-rich composition, **bd**. This explains the existence of ruthenium-rich cores to the crystals. The solidification range of Pt-5%Ru is narrower (1795–1780°C) in comparison with Pt-5%Cu, see Figure 1, and the cooling rate faster because of the greater difference between the temperature of the molten metal and the much cooler investment material. This means there is little opportunity for substantial segregation and cored dendritic growth to take place. The rapid solidification also explains why the equiaxed crystals in the Pt-5%Ru rings

were much smaller than the large dendritic grains in the Pt-5%Cu.

In both cases, as the liquid freezes the first crystals to form are enriched in the higher melting point element. This enriches the liquid in the lower melting temperature element. Thus, for a short distance away from the freezing interface, the freezing point of the liquid is lowered below the actual temperature of the melt because of this compositional segregation. This constitutional undercooling is the mechanism that allows dendrites to grow from a freezing surface into a hotter liquid.

One way to suppress the dendritic growth, and produce a finer grained and more uniform

Fig. 5 Part of the phase diagram for platinum-ruthenium (after Hutchinson (3))
*On cooling hot alloy the first crystals to form will be Ru rich, at **b**, leaving the liquid Pt rich. Then, on further cooling, more solid forms, tracking down the solidus, **bd**. The Pt-rich liquid tracks down **ac**. As the solidification range is narrow (compared to Pt-5%Cu) and the cooling rate is faster, due to the larger temperature difference between alloy and investment, there is less opportunity for segregation or dendritic growth to occur*
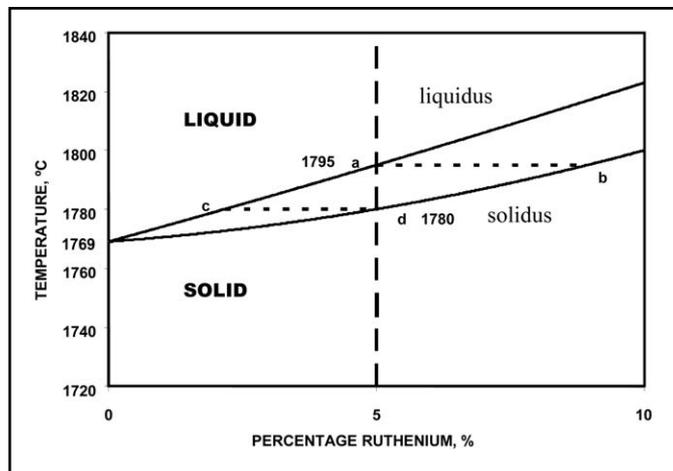
microstructure is to increase the thermal gradient or temperature difference between the freezing surface and the still molten metal (4). This can be achieved by selecting an alloy with a narrow solidification range, or by casting into a mould which is cool relative to the alloy's melting temperature.

The fact that crystal size is influenced by the cooling rate, or thermal gradient, also explains why in all the paired ring samples studied the distal shank sections had finer grain size than the proximal sprue sections. The distal shank is surrounded by relatively cool investment material and freezes more rapidly than the sprue connection, which is in contact with the hot metal 'reservoir' of the sprue itself. Even if a lower metal casting temperature is used, there will be a difference in cooling rate of thicker and thinner sections, which is reflected in the eventual grain size.

Conclusions

The use of relevant phase diagrams coupled with metallurgical analysis of the microstructure can provide useful insight into the physical characteristics of jewellery alloys. However, using phase diagrams alone has limitations. They allow one to predict the compositions of phases present at equilibrium for different bulk alloy compositions and temperatures. To some extent they also enable the prediction of disequilibrium phase compositions, suggesting the possibilities for significant segregation on cooling, as observed for the Pt-5%Cu alloy, for instance. However, they do not allow prediction of the grain size, or the geometric relationships of grains to each other or to the margins of a casting. In order to evaluate the effects of grain size or grain orientation, microstructural analysis must be used, usually coupled with direct hardness measurements.

In practical terms, the finer and more uniform as-cast grain structure of Pt-5%Ru gives rise to about 10% greater indentation hardness. This in turn should contribute to easier polishing and enhanced scratch resistance, compared to the Pt-5%Cu alloy. We noticed no discernable difference in as-cast surface texture between the two alloys. It has been reported that Pt-Ru has a rougher as-cast finish (5, 6), but this may be dependent on the

investment used. The main ingredient of most investments is silica, which melts at 1723ºC. The higher melting temperatures required for Pt-Ru alloys could result in more reaction and pitting of the investment surface.

The wide solidification range of the Pt-5%Cu alloy gives rise to significant compositional segregation, with a 20% enrichment of copper to the interdendritic areas. This not only contributes to undesirable shrinkage porosity, but also imparts a brownish colour to the cast alloy because of the copper-rich areas.

From a microstructural point of view, it appears that if the higher melting temperature of the Pt-5%Ru alloy can be met, by induction melting for instance, then it is a superior alloy for casting. The greater uniformity in crystal size, shape and composition enhances both the colour and the hardness. The advantage of the greater fluidity and lower melting point of Pt-5%Cu is compromised by chemical segregation, leading to large dendritic crystals with compositional inhomogeneity, poor colour, and reduced hardness.

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Reversible Gelation of Palladium-Based Fluid by Sound

Aggregating materials of low molecular weight by stimuli, electrochemically or with light, has been studied in gels, micelles, etc., to find ways to control fluidity, optical transmission, elasticity, and so on. Sound transmission increases molecular movement in liquids, but has not been considered suitable for molecular switching as it usually only breaks weak noncovalent interactions between molecules. Now, scientists in Japan (1) have developed the first molecule that is assembled by brief irradiation with ultrasound (sonication).

A dinuclear Pd complex, **1**, stabilised by an intramolecular π-stacking, but inert to forming associations, can instantly become jelly-like in various organic solvents upon exposure to sound. A clear, homogeneous solution of **1** was prepared by the reaction of $Pd(OAc)_2$ with N,N'-bis(salicylidene)-1,5-alkanediamines in boiling benzene (2). When placed in various solvents and irradiated with sound (0.45 W cm^{-2}, 40 kHz) for a few seconds, the stable sol state was completely converted to gel. For instance, a 1.2×10^{-2} M solution of **1** in acetone irradiated for 3 seconds at 293 K gave a totally opaque gel. Other organic solvents, such as CCl$_4$, 1,4-dioxane and ethyl acetate with **1** also gelled completely and instantly upon presonication for 10 seconds. However, without sonication these solutions remained stable at ambient temperature.

The resulting gels are readily converted back to the original solution by heating at above T_{gel}, followed by cooling to room temperature. The controllable switching can be repeated indefinitely as the gel transition is due only to a simple conformation change of the complex. The aggregation rate can be controlled between 'no gelation' and 'instant gelation' by tuning the sonication time.

Conventional self-assembly depends on static reaction parameters, such as temperature, concentration, solvents and additives, but sonication gives dynamic control to the aggregation rate, so is a useful addition to chemistry – and possibly industry.

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