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Iridium(III)-catalysed cross-linking of polysiloxanes leading to the thermally resistant luminescent silicone rubbers

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Cyclometallated iridium(III) complexes with 2-phenylpyridine [Ir(ppy)2(CNR)Cl] (ppy = (2-phenylpyridinato-C2,*N*), R = Xyl, Mes), [Ir(ppy)2(CNR)2](OTf) (R = Xyl, Mes), and *fac*-[Ir(ppy)3] catalyse cross-linking of polysiloxanes exclusively at temperatures above 100 °C leading to luminescent rubbers.

In the last decades, silicone-based technology has evolved from specialty, high-performance applications into broad industrial usage.1 Cured silicone coatings possess substantial thermal, weather corrosion, biofouling, and abrasion resistance.2 These coatings are accounted for almost three quarters of contemporary paper and film coating production;3 they are also used for metal3b and glass protection,4 and as substrates for pressure-sensitive adhesives.5

Conventional preparation of silicone coating involves metal-catalysed hydrosilylative cross-linking (curing) of vinyl- and hydrogen-functional poly(dimethylsiloxanes).2c, 3a, 6 Ideally, coating composition should not gel at RT but to cure rapidly at temperature above 100 °C allowing the coated substrate to be further processed without cooling down.3a Although these requirements can be addressed by application of a suitable catalyst, commonly used Karstedt’s catalyst [platinum(0) complex with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, Figure 1a) shows limited chemical and thermal stability, and excessive activity. Use of inhibitors is required to prevent immediate cross-linking even at RT, therefore, its application at higher temperatures is not upfront.7 Marciniec et al.7 first reported iridium(I)-based siloxide catalysts (Figure 1b) that cure siloxanes at *ca*. 200 °C, however, the properties of the thus prepared rubbers were not rationalized.

Figure 1. (a) Karstedt’s platinum-disiloxane and (b) and Marciniec’s iridium-siloxide catalysts for hydrosilylative silicone curing.

In the current study, we scrutinised a series of alternative iridium(III) complexes **1**–**6** (Scheme 1) as catalysts for cross-linking of ɑ,ω–di(vinyldimethylsiloxy)poly(dimethylsiloxane) (PDMS) with trimethylsilyl-terminated poly(dimethylsiloxane-*co*-ethylhydrosiloxane) (EHDMS). We established the temperature-curing profile for these complexes and evaluated the properties of the silicone compositions obtained. In addition, we measured luminescence emission profiles for **2**–**6** and for the corresponding rubbers prepared, and developed a procedure for immediate measurement of the coating thickness based upon optical detection.

*Synthesis and characterization of catalysts*. Iridium(III) complexes [Ir(ppy)2(CNR)Cl] (ppy = (2-phenylpyridinato-C2,*N*), R = Xyl **2**, Mes **3**), and [Ir(ppy)2(CNR)2](OTf) (R = Xyl **4**, Mes **5**; OTf = CF3SO3–) were prepared from chloro-bridged dimer [Ir(ppy)2(-Cl)]2 (**1**, Scheme 1). Thus, reaction of **1** with two equivs of isocyanide CNR (R = Xyl, R = Mes) in CH2Cl2 at RT afforded **2** or **3** in 82–85 % isolated yield. Further reaction of 1 equiv of **2** or **3** with 1 equiv of CNAr in the presence of 1 equiv of AgOTf in CH2Cl2 at RT gave **4** or **5** in 74–85% yield. Complex *fac*-[Ir(ppy)3] (**6**) was prepared via the known procedure starting from **1** and ppy.8 Complexes **2**–**5** were obtained as pale yellow (**2** and **3**) or colourless (**4** and **5**) air- and moisture-stable solids. Detailed characterization of new species **2**­, **3**, and **5** using elemental analyses (C, H, N), HR-ESI+-MS, FT-IR, 1D (1H, 13C{1H}) and 2D (1H,1H-COSY, 1H,13C-HMQC/1H,13C-HSQC, 1H,13C-HMBC) NMR spectroscopy are provided in the Supplementary Information (SI). Spectral data for the known species **1**, **4** and **6** (1H and 13C{1H} NMR) were in agreement with the data reported.8-9

Scheme 1. Preparation of catalysts **2**–**6**.

Structure of **2**, **3** and **5** were additionally elucidated by single-crystal X-ray diffraction (see Tables S1, S2, and Figures S1, S2). In all complexes, the iridium(III) centre has a distorted octahedral coordination environment, and the two nitrogen atoms of the phenylpyridine ligands are placed in *trans*-position to each other. Bond distances and angles in **2**, **3**, and **5** are comparable to those in the known iridium isocyanide complexes (see SI for details).9a, 10

*Iridium(III)-catalysed cross-linking*. Iridium-catalysed hydrosilylative cross-linking was studied on model PDMS/EHDMS mixtures with catalysts **1**−**6** pre-dissolved in those (10–3−10–5 M, Scheme 2). A course of cross-linking was monitored by the DSC through measurement of the heat effect of the process. At the temperatures below 80 °C, **1**–**6** did not demonstrate any visible catalytic activity. In addition, we found that solutions of **1**–**6** in the siloxane mixture could be stored at RT for at least one year without decomposition.

Curing properties of **1**–**6** were evaluated in 80‒180 °C temperature range allowing to identify the curing time (τcuring) and the enthalpy of cross-linking process (ΔH). Representative data (catalyst concentration 1.0×10−4M) are included in Table 1, while full data are provided in Table S3 of SI). Catalyst **1**−**6** started to work at *ca*. 125 °C, while the optimal temperature range was found to be 150−180 °C. Complexes **2**, **3** and **6** were the most efficient giving the shortest τcuring of 5–50 min with 1.0×10−4M catalysts concentration; catalysts **1**, **4** and **5** were substantially less active at 150−180 °C. Longer curing times were observed with lower catalyst concentration (1.0×10−5M). Although we found that an increase of the concentration to 1.0×10−3M shortens further the curing times, it greatly increases the catalyst consumption (Table S3).

According to DSC, the average peak temperature (Figure S3) for representative catalysts **2** and **3** (1.0×10−4 M) was 155 °C, the average onset peak temperature was 140 °C and the endset peak temperatures were 205 (for **2**) and 190 °C (for **3**), respectively. The values of enthalpy of cross-linking were –0.8 J/g for both **2** and **3**.

Scheme 2.Iridium-catalysed cross-linking of PDMS and EHDMS.

**Table 1.** Parameters of the catalytic cross-linking of PDMS and EHDMS.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst*a* | τcuring, min at a selected temperature (°С)*b* | | | | | ΔH,  *J* g–1 |
| 80 | 100 | 125 | 150 | 180 |
| **1** | –*c* | –*c* | 300 | 100 | 45 | –1.3 |
| **2** | –*c* | 360 | 70 | 50 | 15 | –0.8 |
| **3** | –*c* | 300 | 70 | 45 | 15 | –0.8 |
| **4** | –*c* | –*c* | 300 | 107 | 20 | –1.8 |
| **5** | –*c* | –*c* | 630 | 147 | 30 | –1.9 |
| **6** | –*c* | –*c* | 390 | 45 | 5 | –1.7 |

*a*Catalyst concentration used 1.0×10−4M; *b*PDMS 100 poise; *c*no curing observed after 24h

*Properties of silicone compositions formed*. Silicone formulations obtained with catalysts **1**−**6** incorporate no structural defects, *i.e.* no bubbles and the surface of silicone rubbers is uniform. All iridium catalysts **1**–**6** increased thermal stability of obtained rubbers (Table S4). At air, the temperature of the initial weight loss of the silicone rubber obtained with **1**–**6** is higher by 80–120 °C when compared to those obtained with Karstedt’s catalyst used as benchmark. Under argon, temperature of the initial weight loss of the silicone rubber obtained with **1** and **2** is higher by 35–45 °C when compared to a reference, while **3**–**6** showed no effect on this temperature or reduced it.

 Figure 2. Phosphorescence spectra for (*a*, left) solutions of **2**, **3**, and **5** in CH2Cl2 (1.0×10–4 M), and (*b*, middle) rubbers obtained with catalysts **2**, **3**, and **5** (initial catalyst concentration 1.0×10–4 M). (*c*, right) Plot of emission at 408 nm as a function of film thickness for a silicone composition obtained with **3**; linear fitting (correlation coefficient was 0.99457).

Final residues of all rubbers (upon heating for up to 800 °C) were *ca.* 3–7% and 51–54% in argon and in air, respectively. Different results obtained in air and argon are expected and can be partially rationalized by the mechanism of thermal degradation proposed earlier.11 In our previous study,6e, 6f [PtCl2(NCCH2Ph)2] used as catalyst increased the temperature of the initial weight loss by 30–40 or 80–90 °C against Karstedt’s catalyst in air or argon, respectively. Hence, iridium complexes **1**–**6** produce silicone formulations far more thermally stable in air than Karstedt’s catalyst or [PtCl2(NCCH2Ph)2]. Thermal stability of silicone rubber depended also on the temperature during cross-linking and concentration of catalyst (Figure S4 and S5, Tables S4–S6). Rubbers prepared at higher temperatures and with the greater catalyst loading showed higher temperature of the initial weight loss and larger final residue due to plausible increase of degree of crosslinking in this case.11-12

Swelling measurements provided information about soluble fraction (wsol) and polymer volume fraction (υ). Silicone compositions obtained with 100 poise PDMS using representative catalysts 2 and 3 (1.0 × 10–5 M) had wsol of 13.3% (for **2**) and 10.7 (for **3**), and υ of 0.2 (for both). Soluble fractions were larger that in case of rubbers obtained with both Karstedt’s catalyst (1.0×10–5 M, wsol 5.1%, υ 0.22), and with [PtCl2(PhCH2CN)2] (1.0×10–5 M, wsol5.8%, υ 0.21).6e, 6f Interestingly, silicone compositions obtained with the less active catalyst **5**, possess wsol 2.7% and υ 0.2 indicative of a higher degree of cross-linking in those. Tensile tests for elastic properties suggested that silicone rubbers prepared have similar elongation at break (L) and tensile strength (σ) when compared to the rubbers obtained with Karstedt’s catalyst.6e, 6f

*Photophysical studies*. As the next step, we evaluated the luminescent properties for new complexes **2**, **3**, and **5** (as 1.0×10–4 M solutions in CH2Cl2) and for those of the silicone compositions prepared using these catalysts (Figures 2, S8–S11, Tables S5, S6). Photophysical properties of **4** and **6** were previously reported.8-9

Among new species **2**, **3**, and **5**, the strongest phosphorescence was observed for complexes **2** and **3** followed by **5** with two maxima for each (469, 496 nm for **2**, 453, 484 nm for **3**, and 472, 502 nm for **5**, Figure 2a). This agrees well with the data reported for complexes **4** and **6**, where maxima were observed at 454 and 486 nm (for **4**) and at 510 nm (for **6**).8-9 Maximum phosphorescence quantum yields (Φ) CH2Cl2 were achieved with **2** (43%), and **3** (41), they are twice larger when compared to **5** (23%) and the known complex **4** (24%), and are akin to **6** (40%). Lifetimes (τ) were in the range 1.5–1.9 μs. Complex **1** does not exhibit luminescence under conditions of this study.

Prepared silicone compositions showed different luminescence profile (Figure 2b). Herein, a strong shortwave shift is evident, and for all samples, only one broad emission wavelength is observed (e.g. at 417 nm for rubbers prepared with **3**). Overall emission intensity for crosslinked silicone rubbers have also substantially decreased when compared to that of **2**–**6** in solution. Quantum yield cannot be carefully estimated for cured rubbers because of complexity of calculations and polymer self-absorption.

One of the major problems in polymer industry concerns the immediate measurement of coating thickness, that is typically achieved using mechanical tools, while application of methods based on the reading of optical density of intensity of luminescence, are limited.13 In the course of this study, we prepared a series of thin films (0.1–1.0 mm) using representative catalyst **3**, and measured their luminesce at 408 nm in reflectance mode. Plot of the luminescence intensity as a function film thickness is given on Figure 2c. A linear fit was applied for all the points between 0.15–0.80 mm, where good correlations coefficient (Pearson correlation coefficient 0.99457) was achieved. For samples thinner than 0.15 mm and thicker than 1.0 mm, the values of intensity reading do not follow the linear dependence. Our measurements clearly indicate that the thickness of the polymer coating prepared with catalysts **2**–**6** can easily be monitored using optical detection on basis of Beer–Lambert–Bouguer law, and that this approach might be further explored towards industrial applications.

To conclude, we showed that cyclometallated iridium(III) complexes with 2-phenylpyridine **1**–**6** show temperature-curing profile in the cross-linking of PDMS and EHDMS. Maximum efficiency is achieved in the 150–180 °C temperature range, where curing is completed within 5–50 min. Complexes **1**–**6** demonstrated dissimilar activity with [Ir(ppy)2(CNR)Cl] (**2**, **3**) and *fac*-[Ir(ppy)3] (**6**) being more active than the others. Silicone compositions prepared with **1**–**6** showed thermal stability in air superior to those achieved with benchmark Karstedt’s catalyst and comparable mechanical properties. Complexes **2**–**6** and silicone rubbers prepared using those exhibit luminescent properties enabling the measurement of the thickness of the coating using optical detection. Further studies on design of new metal catalysts for siloxane cross-linking and identification of mechanism of their action are currently underway in our group.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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