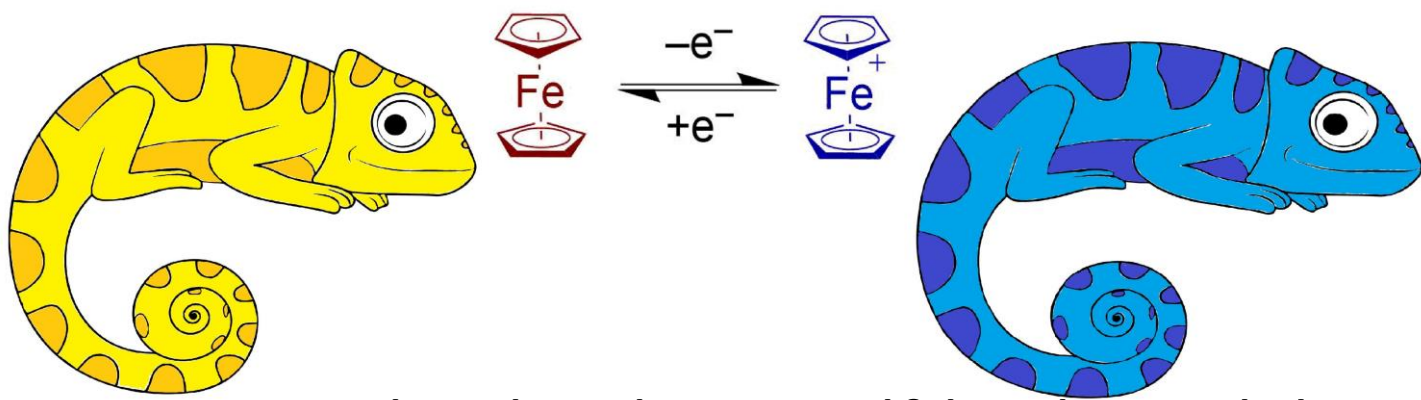


Chameleon-like self-healing flexible materials based on ferrocenyl-containing polysiloxanes

Anastasia N. Kocheva, Konstantin V. Deriabin, Regina M. Islamova
St. Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034

INTRODUCTION & AIM

Animals such as chameleons change their skin colour in case of potential threat and recover damaged tissues [1]. Some ferrocenyl-containing polymers exhibit electrochromic properties due to easy reversible one-electron redox transition of ferrocene [2].



Some polymer materials also have self-healing ability as well as chameleon skin. One of the most promising self-healing materials is silicone rubber [3]. Silicone materials that were synthesized by anionic polymerization might possess self-healing properties achieved through siloxane equilibrium. This mechanism is based on reversible interactions between “living” anionic centres and polysiloxane chains [2,3].

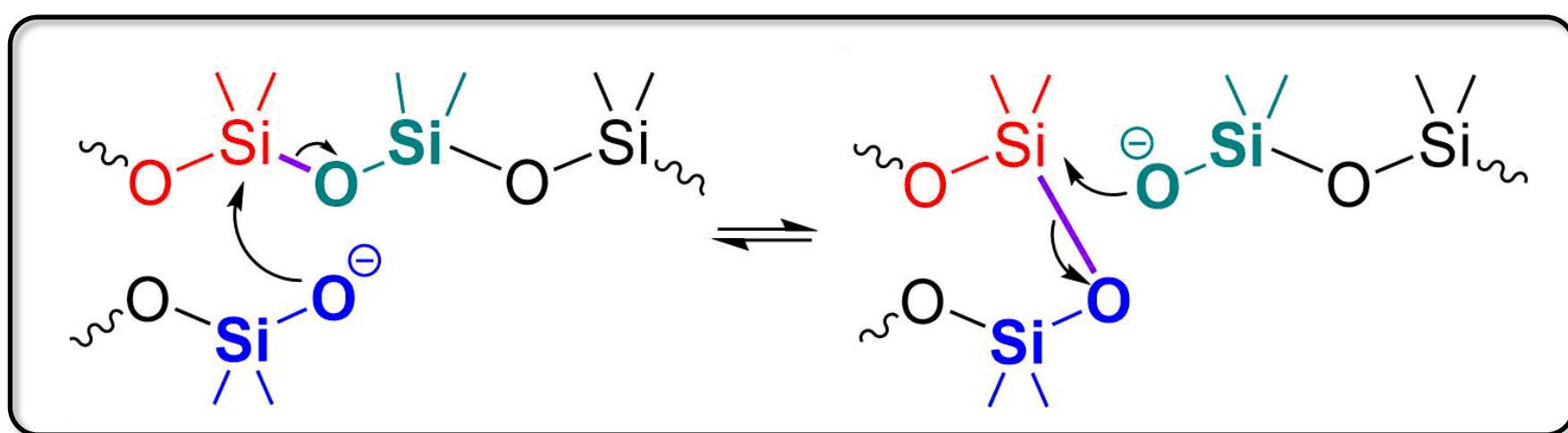


Figure 1. Scheme of siloxane equilibrium

METHOD

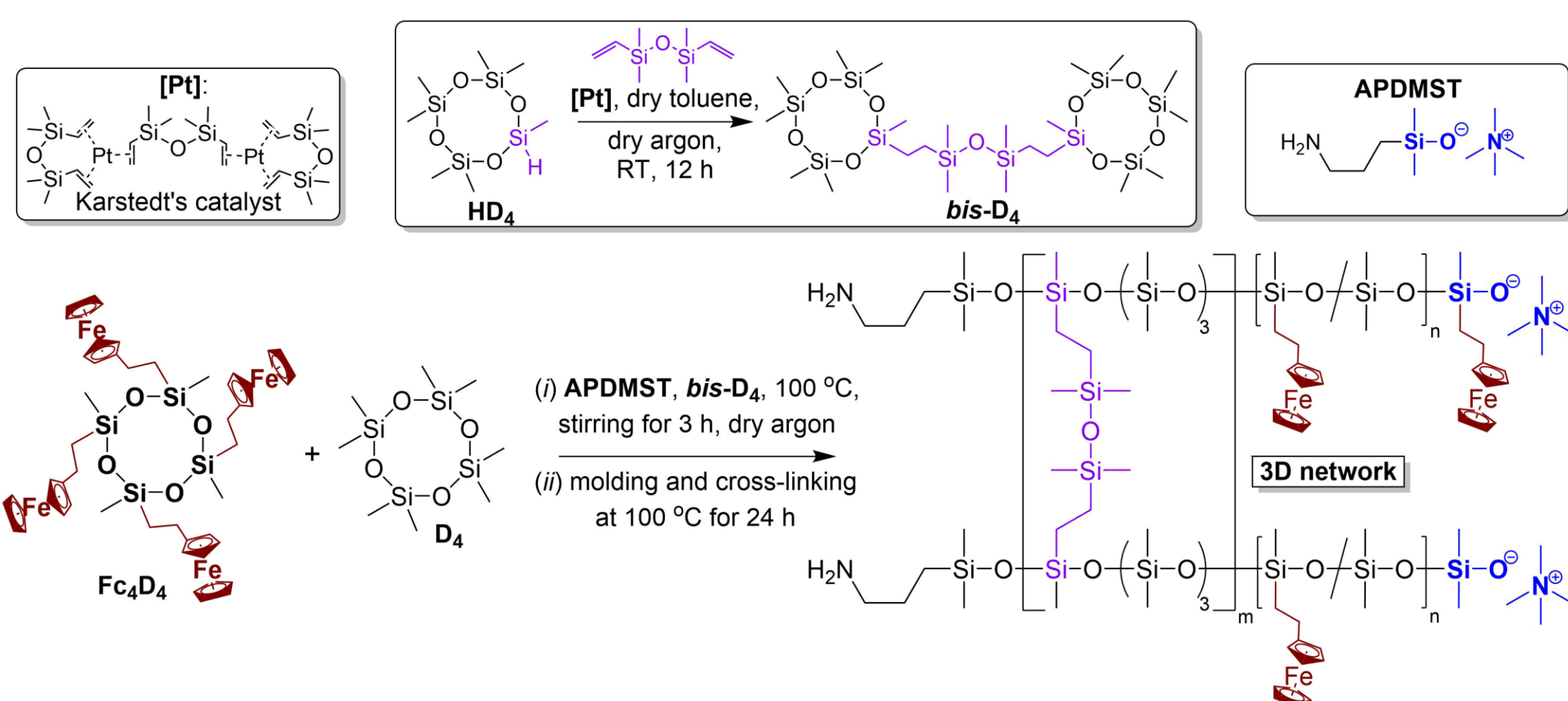


Figure 2. General synthetic scheme of FSRs

The ferrocenyl-containing silicone rubbers (FSRs) were synthesized with different ferrocenyl unit content (25 and 50 mol.%) by ring-opening anionic copolymerization of cyclic octamethylcyclotetrasiloxane (D_4), cyclic tetraferrocenyl-substituted 1,3,5,7-tetramethyltetrasiloxane (Fc_4D_4), and bicyclic oligosiloxane cross-linking agent ($bis-D_4$).

The optimal concentration of the cross-linking agent for FSRs is 5 wt.%. The FSR with a ferrocenyl-substituted siloxane unit content of 25 mol% (FSR25) is the most optimal in terms of cross-linking degree ($M_c = 60,000$), which is higher than that of FSR with a ferrocenyl-substituted siloxane unit content of 50 mol% (FSR50) ($M_c = 85,200$). The obtained FSRs exhibit self-healing ability at RT and/or elevated temperatures (100 °C) by siloxane equilibrium in the dynamic 3D polymer network.

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RESULTS & DISCUSSION

Tensile test of FSRs

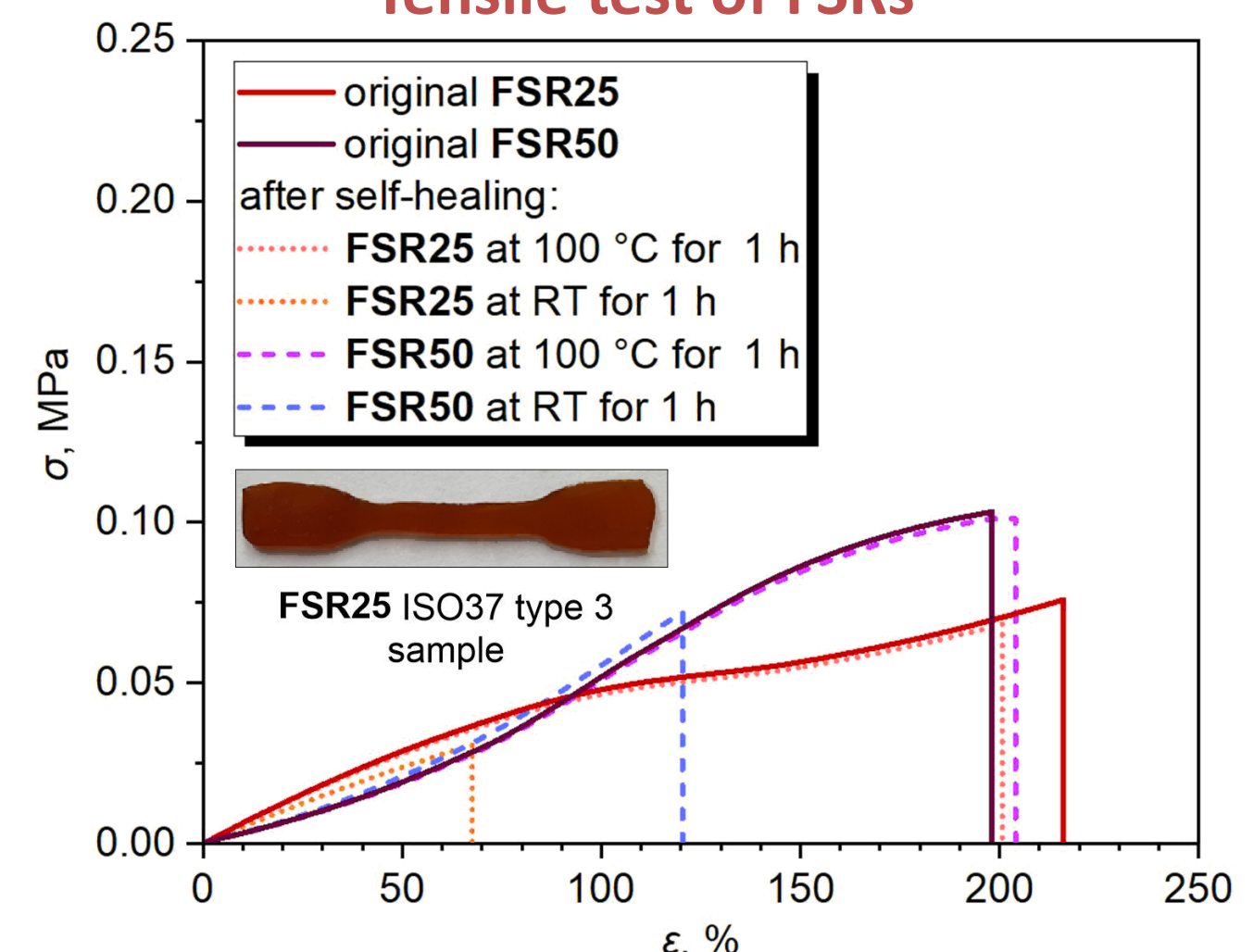


Figure 3. Stress–strain curves of the original and healed FSRs at a stretching speed of 40 mm·min⁻¹

The tensile strength of the FSRs reached 0.1 MPa, and elongation at break was 215%. After one hour recovery at 100 °C self-healing efficiency of FSR achieved 89 and 98% for FSR25 and FSR50, respectively.

Cyclic voltammetry of FSR25

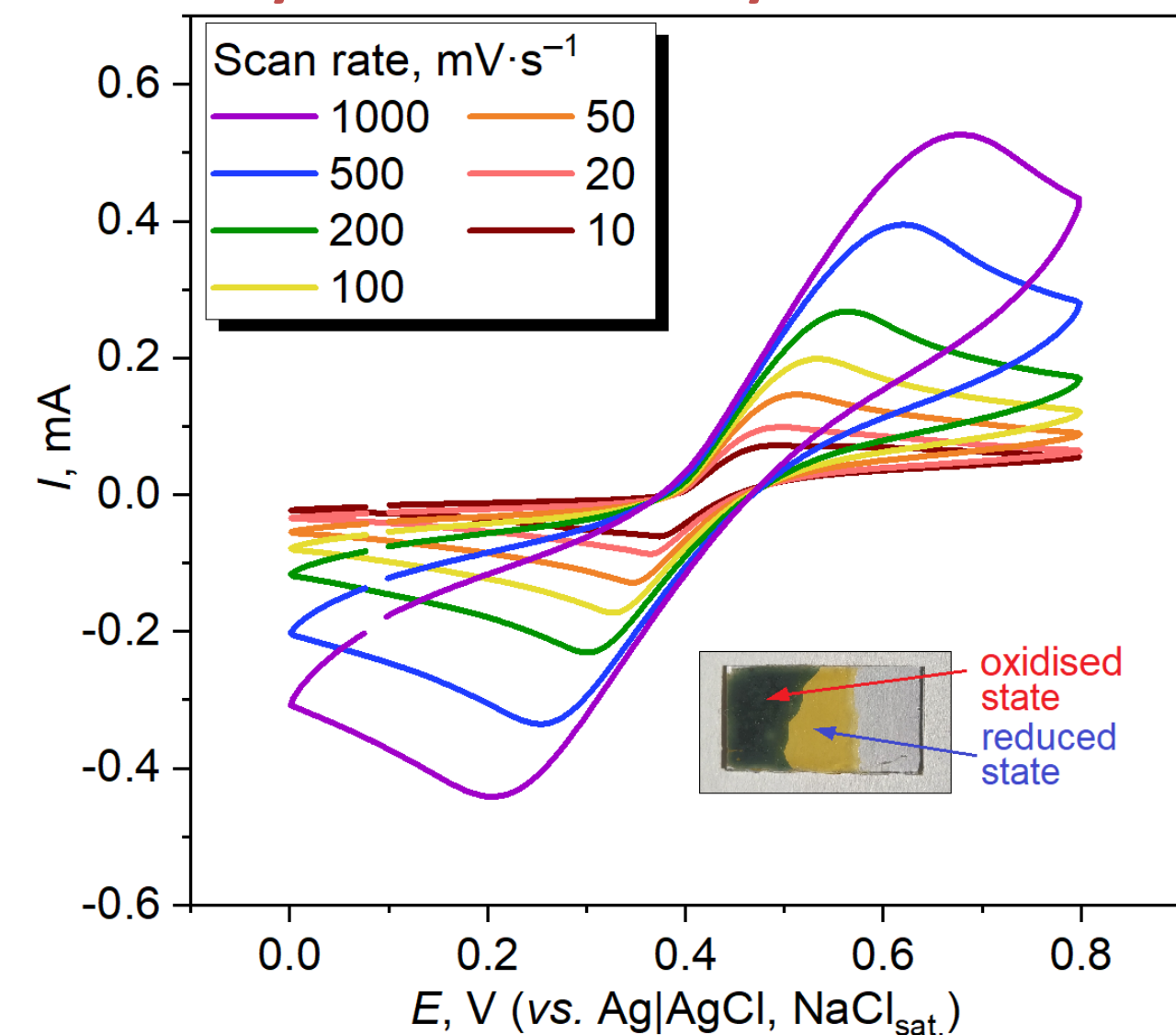


Figure 4. CV curves of FSR25 film deposited on glassy carbon electrode

The FSRs also possess redox activity due to Fc/Fc^+ transformations at $E^0 = 0.43$ V and electrical conductivity at the level of antistatic materials (approximately 10^{-10} S·cm⁻¹). The FSR films change their colour from yellow (reduced state) to blue (oxidized state).

CONCLUSION

Chameleon-inspired simultaneously redox-active and self-healing silicone materials based on ferrocenyl-containing polysiloxanes were obtained. Self-healing was achieved through siloxane equilibrium. Our materials could find potential application as redox-active and flexible electrochromic coatings.

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