

Editorial

Introduction

Polysilane chemistry has been attracting much attention due to its potential applications in the electronic and photonic fields. This special volume of the *Journal of Organometallic Chemistry*, entitled “A Half Century of Polysilane Chemistry”, has been edited to celebrate the 50th anniversary of polysilane chemistry in 2003, since Makoto Kumada, Emeritus Professor of Kyoto University, and his coworkers published the first paper of a series of studies on polysilane chemistry in 1953. More than 30 leading scientists in the field have contributed to this volume, to whom we are very grateful. It is our great pleasure to have an essay by Prof. Kumada as the opening paper of this volume [1].

His essay describes some exciting stories of early history of polysilane chemistry which include the discovery of hexamethyldisilane in quantity from the “still-pot residue” of the “Rochow Direct Process”, the halogen cleavage of the Si–Si bond, the halodemethylation method, and the disilane-to-disilmethylene thermal rearrangement; pertinent references are listed in his essay. Several additional milestone findings were pub-

lished from his group by the end of 1970s, in addition to the first exhaustive review article on polysilane chemistry [2]; e.g., the preparation of a series of well-defined permethylated oligosilanes up to dodecasilane [3], UV absorption spectral data of phenyldisilanes [4], AlCl_3 -catalyzed skeletal rearrangement of polysilanes [5], photochemical formation of silylene species from polysilanes [6], photochemical rearrangement of phenyldisilanes [7], and Pt-catalyzed [8], Ni-catalyzed [9], and Pd-catalyzed cleavage of the Si–Si bond [10].

Some important later developments in polysilane chemistry included the synthesis of cyclic silanes $(\text{SiCl}_2)_n$ and $(\text{SiH}_2)_n$ [11], the extensive chemistry of $(t\text{-Bu}_2\text{Si})_3$ [12], and the study of cyclic dialkylpolysilanes [13]. The latter compounds were found to undergo reduction to anion radicals, $[(\text{R}_2\text{Si})_n]^{-\bullet}$, in which the unpaired electron is delocalized over the ring as in aromatic anion radicals [14]. In an epoch-making discovery, the first stable disilene, $\text{Mes}_2\text{Si}=\text{SiMes}_2$, was synthesized by photolysis of a trisilane [15,16]. This finding led to the downfall of the “double bond rule” and to the rapidly

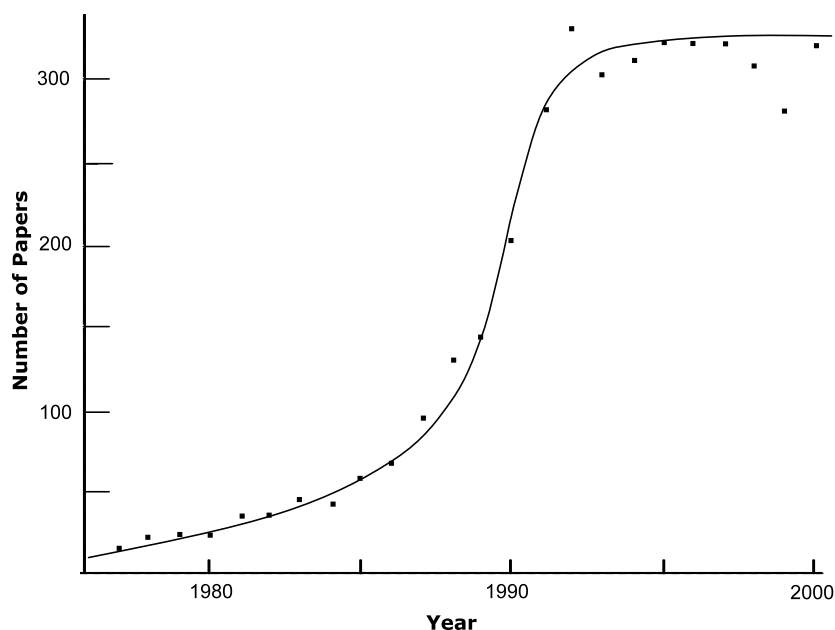


Fig. 1. A plot of the total number of publications and patents on polysilanes, per year, as a function of time.

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developing field of multiply bonded heavier elements [17].

Interest in polysilanes was greatly stimulated by the discovery of soluble polysilane polymers and their remarkable electronic properties, resulting from delocalization of the sigma electrons in the cumulated Si–Si bonds [18]. These polysilanes are chromotropic [19], strongly fluorescent and electroluminescent [20], can be patterned lithographically, and are excellent hole conductors [21]. Polysilane polymers are generally made from dichlorosilanes by Wurtz condensation, a complex reaction which is only now becoming understood [22]. Newer methods of synthesis include dehydrogenative coupling of dihydrosilanes [23] and anionic polymerization of “masked disilenes” [24]. Polysilanes in solution show fascinating helicity and chiral properties [25]. Quite recently, studies of the conformations and thermochromism of polysilanes have led to a thorough revision of the theory of rotational isomeric states [26], broadly applicable to linear oligomers and polymers [27].

Fig. 1 shows the total number of publications and patents on polysilanes, per year, as a function of time. Note how the field has grown in popularity, with the number of publications rising from only a few in the early 1980s to about 300 papers per year in 2000. Although research on polysilane polymers has been intense, it has not yet led to large-scale industrial applications, but these may be expected in the future.

References

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