50 years of living polymerization

In 1956, two papers were published by Michael Szwarc that would cause a revolution in polymer science. On June 5, 1956, Szwarc, together with Moshe Levy and Ralph Milkovich published an article entitled *Polymerization initiated by electron transfer to monomer. A new method of formation of block copolymers*. In this article the term “living polymer” appeared for the first time. However, it is Szwarc’s article in *Nature*, simply named ‘Living’ polymers, which appeared on November 24, 1956, that is widely regarded as the birth of a number of techniques that have enabled synthetic polymer chemists to prepare a realm of new structures permitting generations of polymer physicists to create and test new theories. In this and the following two issues of *Progress in Polymer Science* we want to commemorate the 50th anniversary of this important milestone in polymer science.

The discovery of living anionic polymerization (defined as a reaction without chain-breaking reactions) and subsequently other controlled/living systems (in which chain-breaking reactions do occur but allow formation of well-defined (co)polymers) had tremendous impact on polymer and material science. It facilitated major developments in synthetic polymer chemistry but also in polymer physics as it opened an avenue to the preparation of well-defined polymers with precisely designed molecular architectures and nano-structured morphologies. As an example, block copolymers described by Szwarc et al. [1] 50 years ago and later commercialized under the trade name Kraton® are landmark materials made by living anionic polymerization. These thermoplastic elastomers were originally designed to be used in tire industry, but first applications came in footwear and later in other compounding applications, including automotive, wire and cable, medical, soft touch overmolding, cushions, as well as thermoplastic vulcanizates, lubricants, gels, coatings, or in flexographic printing and road marking. It is anticipated that materials made by other controlled/living processes will lead to more applications with even larger market impact.

Although, preparation of novel materials is an important result of Szwarc’s discovery, the most important is the intellectual impact. Polymer synthetic chemists started to search for conditions in variety of systems in which termination and transfer could be eliminated or suppressed. Many efforts were made in other polymerization methodologies to achieve a level of control attainable in living carbanionic polymerization. Ring-opening living polymerizations in both anionic and cationic mechanisms were already based on the earlier work of Flory and Meerwein. However, it took nearly 30 years until group transfer polymerization (GTP; a process close to anionic polymerization) was reported in 1983 and the living carboxationic polymerization of vinyl ethers and isobutylene in 1984. Subsequently, living ring opening metathesis polymerization (ROMP) was reported in 1986 and various controlled/living radical polymerization mechanisms (SFRP, ATRP and various degenerative transfer techniques) were reported in the 1990s (preceded by the less controlled “iniferter” mechanism in 1982). It is intriguing that nearly all controlled/ living mechanisms have one common feature, i.e. the co-existence of active and inactive (“dormant”) species, which are in a dynamic equilibrium, either via reversible activation/deactivation processes or via degenerative transfer. The kinetics and thermodynamics of such equilibria were described for cationic ring opening polymerization of tetrahydrofuran in 1974, but the concept of “dormant” species was introduced by Szwarc already in 1962 [3].
In the present issue, three former collaborators of Michael Szwarc, Thieo Hogen-Esch, Johannes Smid and Marcel Van Beylen describe the discovery of living polymerization and some of the mechanistic studies that led to an understanding of the mechanism of carbanionic polymerization. Nikos Hadjichristidis, Hermis Iatrou, Marinos Pitsikalis, and Jimmy Mays highlight how living polymerization can be used to tailor a multitude of polymer architectures. Yusuf Yagci and Attila Tasdelen show how new structures are obtained by transforming the mechanisms of polymerization.

In the first issue of 2007, Christopher Bielawski and Robert Grubbs will review ROMP, Gregory Domski, Jeffrey Rose, Geoffrey Coates, Andrew Bolig and Maurice Brookhart will show how coordinative polymerization of olefins was made living and Wade Braunecker and Krzysztof Matyjaszewski will highlight the status and prospects of controlled/living radical polymerization. Finally, Tsutomu Yokozawa and Akihiro Yokoyama demonstrate that even polycondensation can be living.

In the second issue of 2007, Durairaj Baskaran and Axel Müller will present the status and outlook for anionic vinyl polymerization (including GTP), Eric Goethals and Filip du Prez will describe the history and prospects of living cationic polymerization and finally, Stanislaw Penczek, Andrzej Duda, Przemyslaw Kubisa, and Stanislaw Slomkowski will review ionic ring-opening polymerization.

We are confident that papers presented in these special issues provide an excellent overview of various controlled/living polymerization techniques, will stimulate new discoveries and will facilitate developments of new polymeric materials for many exciting applications.

References


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