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### Living Polymers in Ionic and Radical Polymerizations: Recent Developments

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*ABSTRACTS*

**LIVING POLYMERS IN IONIC AND RADICAL  
POLYMERIZATIONS: RECENT DEVELOPMENTS**

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The discovery of living polymers, that is, assemblies of polymer molecules formed by anionic polymerization which may grow without chain-breaking reaction and may react subsequently with other monomers and various reagents through their end-groups, has led to great progress in the knowledge of the mechanism of anionic polymerization and to the synthesis of a large variety of well-defined block copolymers, graft copolymers, and polymers with functionalized end-groups. Since only a limited number of the current monomers are polymerizable by an anionic mechanism, many attempts have been made to obtain similar results by polymerizing other monomers by cationic, radical, and Ziegler polymerization. Systems making it possible to work at temperatures higher than those used for many anionic and most cationic polymerizations would be particularly interesting.

In this presentation, both the possibilities and some recent success in realizing living polymerizations occurring by ionic or radical mechanisms are examined, but are limited to polymerizations occurring by opening of a double bond. First, the various definitions of living polymers, “absolute” and “operational,” are discussed together with the problems of detection of possible termination and transfer reactions and of the influence of the relative rates of initiation and propagation.

Some recent results in living anionic (and related anionic group transfer) polymerizations are described, and the question of the ionic or pseudoionic nature of the active species is discussed briefly.

In carbocationic polymerization, living polymers were not generally

expected to be possible 10 years ago, in view of the well-known importance of transfer reactions and of the short lifetimes of carbocationic species, even at low temperature, but many articles asserting their existence in various polymerizing systems have been published in recent years.

The most general feature of these systems is the linear growth of the number average mol. wt. with polymer yield, with sometimes a further growth on new monomer addition. But since the distributions of mol.-wts. is often wide ( $M_w/M_n \geq 2$ ) and the mol.wts. low, there was no definite proof of the absence of termination and transfer, and it may be shown that the results might often be compatible with significant termination and with transfer constants sometimes as high as  $k_t M/k_p = 10^{-3}$ .

However, it seems that in many of the studied systems and as assumed by many authors, it is possible to have a reversible termination, growth being possible on most polymer end-groups. A second distinctive feature of these systems is that this observation of mol.wt. growth could be made only because the ratio of propagation to initiation rates  $R_p/R_i$  is not too high. If initiation is sufficiently rapid, the number of macromolecules may be equal to the initiator, as has been observed in several cases, whereas this is generally not the case in classical polymerizations.

These observations do not necessarily mean that transfer is absent and that the nature of the active sites is completely different from those in classical systems, even if some initiators might be favorable for decreasing the influence of transfer and termination. It is proposed that three main categories of polymerizations should be considered:

1. Systems that correspond to the classical criteria for living polymers: absence of transfer and termination with the consequence of further polymer growth. Polymerization of vinyl ethers by systems based on HJ or alkyl iodides associated with  $J_2$  fall in this category. The narrow distribution ( $I \leq 1,1$ ) and the high polymers obtained are further proof. These observations have been made up to 40°C, which also points to a different polymerization mechanism.
2. Systems for which the classical definitions of living polymers may also apply, but for which a different mechanism is not needed. An example is the polymerization of isobutylene with initiators of the R-Cl-Friedel Crafts acid type, again giving  $I \leq 1,1$  and high mol.-wts., but only at low temperature, the results being compatible with the transfer constants observed in usual cases.
3. The more frequent systems for which the published data are com-

patible with relatively high transfer constants and which are limited at the present time to low-mol.wt. polymers, which I prefer to call "apparently living polymers" even if in the future they may pass into the other category.

Living radical polymerization has long been expected to be still less possible in view of the strong tendency of radicals to react together to give rapid termination reactions. However, some attempts at block copolymerization have been successful with usual polymeric radicals trapped into crosslinked or other very viscous media. But the most interesting idea has been that of using systems with reversible termination. If a nonsymmetrical initiator  $R-R'$  is split into two radicals  $R\cdot$  and  $R'\cdot$ , and if the monomer is initiated only by  $R\cdot$ , the growing polymer chains  $R-M_n\cdot$  may react either with themselves (leading to termination) or with  $R'\cdot$ , giving  $R-M_n-R'$ , which may also be capable of initiation and further growth. If the crosstermination giving  $R-M_n-R'$  is favored compared to the symmetrical ones, a system more or less near a living one might be obtained. Up to now, there were only a few examples of initiators and monomers that seemed to behave in that way (particularly with styrene, methylmethacrylate, and acrylates), but secondary reactions occur and no perfect system has been described yet. However, if  $R'\cdot$  groups that do not recombine may be used, as has been proposed recently, it might be possible to obtain again systems still nearer to living polymers.

## APPLICATION OF A DIRECT COOLING METHOD IN THE CATIONIC POLYMERIZATION OF ISOBUTYLENE

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Inspired by the Leidenfrost phenomenon, a direct-cooled, general-purpose, low-temperature reactor has been developed and its applicability for polymerization was demonstrated. The Leidenfrost reactor is effi-