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Radical Polymerization: Reversing the Irreversible?**

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NMR spectroscopy · photochemistry · polymerization · radical reactions · reversibility

Free radical polymerization is arguably the most frequently employed method to generate polymeric materials with a wide variety of properties. Over the last 15 years, the field has experienced significant attention owing to the advent of polymerization protocols that can impart living characteristics onto the polymerization process and allow an exact tailoring of the polymer topology and molecular weight.[1] Concomitantly, the study of the mechanism and kinetics of radical polymerization processes has experienced increased interest, as a thorough understanding of the underpinning polymerization processes, including accurate knowledge of the rate coefficients governing the elemental reactions that constitute the polymerization, is required for the design of well-defined polymers. A particular area of interest is the detailed study of the initiation processes of radical polymerizations.[2]

The reasons for obtaining a detailed image of photochemical and of thermal initiation are manifold: First, it is important to establish at what rates primary radicals are released from the initiation source (that is, when initiating molecules are employed) under a certain set of reaction conditions, as the initiator has to be tailored to the monomer and the specific polymerization conditions. Second, it is paramount to elucidate which reactions occur immediately after the birth of the primary radicals before the reaction with monomer units. Such so-called in-cage processes can include the recombination or disproportionation of two radicals, intramolecular rearrangements, or transfer reactions. Knowledge of in-cage processes allows the design of initiating entities that display as few side reactions as possible. Third, and correlated to the second point: it is desirable to know the number of radicals that are available to initiate macromolecular growth, which is typically rationalized by the initiator efficiency f (the fraction of radicals that initiate the polymerization process). In any given radical polymerization, f should ideally approach unity. Finally, it must be established with which rate the individual initiating radicals react with the vinyl function of the monomer and at which end of the vinyl function the reaction occurs. In many cases, more than one radical type is provided by the initiation source, and thus the importance of the reactivity of each individual radical towards the monomer needs to be assessed. The importance of understanding the initiation step not only lies in the optimization of synthetic procedures in (living) radical polymerization processes, where the initiator (co)-determines the end group (and thus the properties) of the generated material, but also in the determination of kinetic rate coefficients, which are frequently assessed by the use of photoinitiated pulsed laser techniques.[3]

At present, our understanding of the processes governing initiation in radical polymerization is reasonably advanced;[4] even so, significant knowledge is still lacking in certain areas, and specifically in the realm of determining initiator efficiencies (also as a function of monomer to polymer conversion) and the proportions and rate with which individual radicals react with the variable monomers. One key assumption that is employed in the kinetic modeling of polymerization reactions and in almost all discussions regarding the initiation process is the irreversibility of the addition of an initiator derived radical to the monomer.

Chemically induced dynamic nuclear polarization NMR spectroscopy (^{1}H-CIDNP),[6] which is a technique that is often employed to study transient free radicals and their reaction mechanisms, was used by Gescheidt and colleagues[5] to provide evidence that the addition of an initiator-derived radical may indeed be a reaction with significant reversibility. These authors studied the photoinitiated polymerization of *tert*-butylmethacrylate (*t*BAM) and *n*-butyl acrylate (*n*BA) by employing bisacylphosphinoxide as a photolabile radical source. The analysis of the CIDNP NMR experiments revealed that the generated primary radicals add onto the monomer as expected; surprisingly however, it was found that monomer is regenerated after the primary addition step has taken place (see Scheme 1 for a general overview of the process).

Such a result was initially thought to be caused by the congested steric nature of the employed *t*BAM monomer, which, in analogy to monomers such as dimethylitaconate, could possibly feature a tendency to undergo depropagation (that is, display a low ceiling temperature).[7] However, a further experiment using *n*BA (for which steric reasons for a reverse reaction can certainly be excluded) revealed a similar result. Further experiments suggest that the reversibility is not limited to primary radicals derived from the employed photo-

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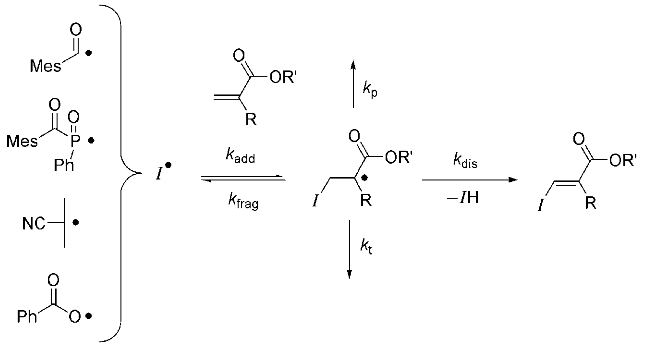

Scheme 1. Reversible addition of photolytically generated primary radicals to vinyl bonds in the initial stage of free-radical polymerization, as established by ^{1}H-CIDNP experiments. As a follow-on reaction, the adduct radicals may disproportionate and the resulting product may add a radical. Mes = 2,4,6-trimethylphenyl, I = initiator; k_p: propogation rate coefficient, k_t: termination rate coefficient.

initiator, but extends to benzoyl peroxide and also the frequently employed initiator azobisisobutyronitrile.

Assuming that no unforeseen artifacts arise during the experiments and the results are genuine, the consequences of the finding could be highly consequential, as our current perception of the addition of primary radicals would have to be altered to allow for a significant reversibility of the reaction. If the current findings are further substantiated and quantified (see below), the kinetic scheme of radical polymerization has to be rewritten. Given the fact that the reversibility already occurs at ambient temperatures, the rate of the fragmentation reaction would be expected to increase significantly at elevated temperatures. To what extent the regeneration of monomer is influenced by an elevation of the reaction temperature depends on the magnitude of the activation energies of the forward and the reverse processes. If an activation energy of around 20–30 kJ mol^{-1} is anticipated for the forward process, which is similar to the activation energy of typical propagation reactions, and a substantially higher activation energy is assumed for the fragmentation process, the value of the equilibrium constant may be strongly influenced by the temperature. The proposed fragmentation process is of fundamental importance in judging the stability of radical monomer adducts; furthermore, it seems to be a matter of importance to assess what the consequences of the potential reversibility for the kinetics are by utilizing kinetic modeling of free radical polymerization processes.

Whilst the current findings of Gescheidt and co-workers are highly fascinating, they can only constitute the first step in a series of investigations. The key questions that need to be addressed in forthcoming work are as follows:

1) What is the extent of the reversibility (i.e., the size of the equilibrium constant) as a function of the attacking primary radical and of the monomer? As steric factors do not seem to play a very pronounced role, it seems a matter of priority to establish structure–reactivity correlations between the radical and the monomer. If possible, it would highly desirable to access unimolecular rate coefficients that govern the reverse reaction as a function of temperature. Photochemical systems seem predestined for such investigations as the number of generated radicals is independent of the system temperature.
2) Are the observations made in the contribution from Gescheidt et al. only valid for photochemically generated radicals, or are these observations equally applicable in thermally initiated polymerizations? Based on the available data, it seems plausible that similar observations hold true for thermally generated cyanoisopropyl radicals, as those generated photolytically are postulated to undergo reversible addition.
3) What is the concentration of the adduct radicals during the polymerization? Their concentration will be governed by the rates of propagation of the adduct and its fragmentation along with additional side reactions that the adduct radicals may undergo (see below).
4) Finally, and most importantly, what is the driving force for the reaction? The reversibility of the reaction is indeed surprising, and especially at the ambient reaction temperature that is employed (24 °C). It would be recommendable to perform high-level ab-initio quantum mechanical calculations on the radical adducts that are generated, as such an exercise will allow for a determination of the equilibrium constant and also provide an estimate for the fragmentation rate coefficient.

Whilst the reversibility of the primary radical addition is a significant finding, it should also be noted that Gescheidt and co-workers have identified a follow-on reaction of the adduct radicals besides propagation (see Scheme 1); that is, consumption of the radicals in hydrogen transfer reactions to the primary radicals leading to unsaturated entities that can themselves participate in polymerization processes. The presence of such entities should be identifiable with relative ease, for example by a mass spectrometric analysis of the generated polymeric material.

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