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Communications to the Editor

Controlled Radical Polymerizations: The Use of Alkyl Iodides in Degenerative Transfer

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Well-defined polymers and copolymers are usually prepared in living systems in which transfer and termination reactions are absent. The first and the best example of such a reaction is the anionic polymerization of styrene leading to high molecular weight polymers with low polydispersities.[1] It has been noted, however, that well-defined polymers can also be prepared in the presence of minor chain-breaking reactions, if molecular weights are low enough and the polymerization is initiated fast enough.[2] This is especially important for radical polymerizations in which growing radicals terminate bimolecularly via coupling/disproportionation. Because termination is second order and propagation is first order in growing radicals, the proportion of termination increases with the concentration of free radicals. However, a low concentration of growing radicals provides high molecular weight polymers with no control of molecular weight and polydispersities. The solution to this apparent contradiction is provided by the reversible deactivation of growing radicals, $P^{\bullet}$, with scavanger, $S^{\bullet}$, into dormant species, P−S:

$$\mathrm{P{-}S} \underset{k_{\mathrm{deact}}}{\overset{k_{\mathrm{act}}}{\rightleftharpoons}} \mathrm{P}^{\bullet} + \mathrm{S}^{\bullet}$$

The contribution of chain-breaking reactions can be kept low by reducing the number of growing radicals and directing the synthesis toward short chains. The degree of polymerization is defined by the ratio of the concentration of the consumed monomer to that of the dormant chains, $DP_n = \Delta[M]/[P-S]_0$.

We have previously described three methods leading to controlled radical polymerization.[3] The first one is based on the reversible cleavage of covalent species into a propagating radical and a scavenging radical, which is unable to react with monomer. This is best exemplified by systems based on alkoxyamines either prepared in advance or generated *in situ*.[4−7] The second approach involves organometallic compounds which reversibly release growing radicals and has been successful for organocobalt,[8,9] organochromium,[10,11] and organoaluminum compounds.[12]

Here, we discuss the third approach based on degenerative transfer. This thermodynamically neutral reaction involves an atom or group transfer from a covalent, dormant species present in large excess to the classic initiator producing free radicals. The overall polymerization scheme consists of all typical elementary reactions, such as initiation, propagation, and termination, but is additionally supplemented by degenerative transfer. The degenerative transfer step in the radical polymerization of alkenes, $CH_2{=}CHR$, in the presence of a transfer agent, R′−X, is shown in Scheme 1: Growing radicals, $PCH_2CHR^{\bullet}$, react bimolecularly with R′−X to become dormant species by transferring a group or an atom, X. The new radical $R'^{\bullet}$ reacts with a monomer molecule to become a propagating polymer chain which then transfers group X from another dormant chain. At this stage the transfer process becomes thermodynamically neutral (degenerative), although it may not be at the first stage when R′ is different from $PCH_2CHR^{\bullet}$. If exchange is fast in comparison with propagation, all R′− moieties will become initial end groups in the polymer chains. The total number of chains in the system is equal to the sum of the chains generated by initiator and those formed from the transfer agent. Even if radicals terminate in the usual way, the maximum amount of irreversibly terminated chains cannot exceed the initiator concentration. When the transfer agent is present in a large excess over the initiator, the proportion of chains irreversibly terminated should be very low and nearly all chains will be terminated with the X group which can be activated. Examples of atom transfer and group transfer in radical processes are well-known in synthetic organic chemistry and are most efficient for alkyl iodides and corresponding organoselenium compounds.[13,14] Perfluoroalkyl iodides have been used in radical polymerization.[15]

Similar processes have been used successfully in the anionic polymerization of methacrylates in the form of group-transfer polymerization[16,17] and also in carbocationic polymerizations in the so-called inifer systems.[18,19] It has to be stressed that the pure degenerative transfer should not involve the spontaneous cleavage of dormant species but only the bimolecular reaction between growing and dormant species. It has been shown previously that in some cationic systems this was not the case.[20] It must be stressed that degenerative transfer is very different from typical telomerization in which the molecular weights do not increase with conversion, because the polymer chains are inactive after reaction with the transfer reagent.[21]

Figure 1 presents the kinetics[22] of the radical polymerizations of butyl acrylate and styrene[23] initiated by AIBN in the presence of the secondary alkyl halide, 1-phenylethyl iodide.[24] The transfer agent alone does not initiate polymerization, although cationic polymerization could be expected, especially in the presence of a Lewis acid.[25] The polymerization of butyl acrylate[26] is much faster than that of styrene under similar conditions. The acceleration observed for bulk polymerization of butyl acrylate may be due to the relative reduction of the termination rate constants in highly viscous media. The straight kinetic plot for styrene polymerization may be due to a combination of the rate reduction due to the consumption of initiator and the aforementioned rate increase.

The polymerization of styrene and butyl acrylate in the presence of AIBN or BPO alone leads to polymers with molecular weights in the range of $M_n \approx 50\,000$ to 100 000 and relatively broad polydispersities, $M_w/M_n >$

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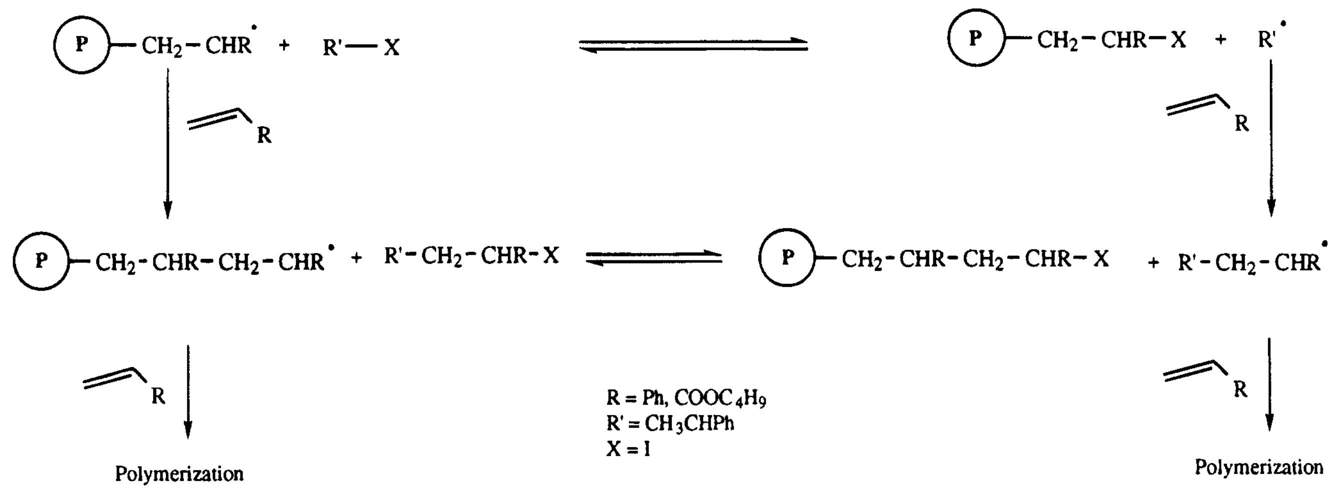
Scheme 1



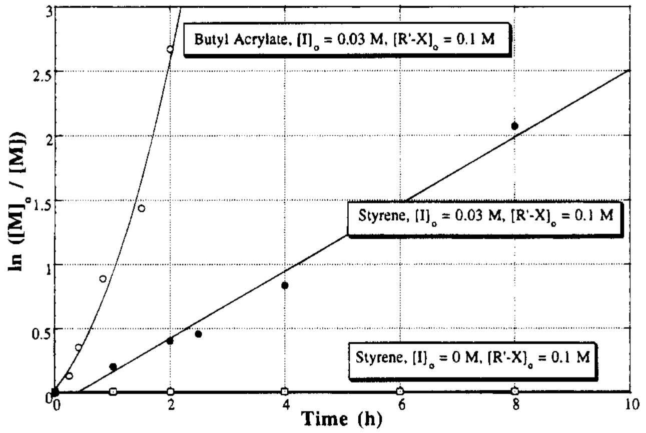


Figure 1. Kinetics of the bulk polymerization of styrene and butyl acrylate at 70 °C; [I] = AIBN, [R'−X] = 1-phenylethyl iodide.

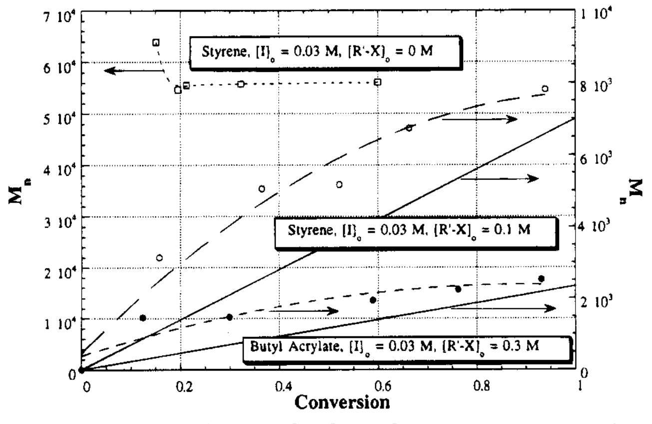


Figure 2. Molecular weight dependence versus conversion for the bulk polymerization of styrene and butyl acrylate at 70 °C: [I] = AIBN, [R'−X] = 1-phenylethyl iodide.

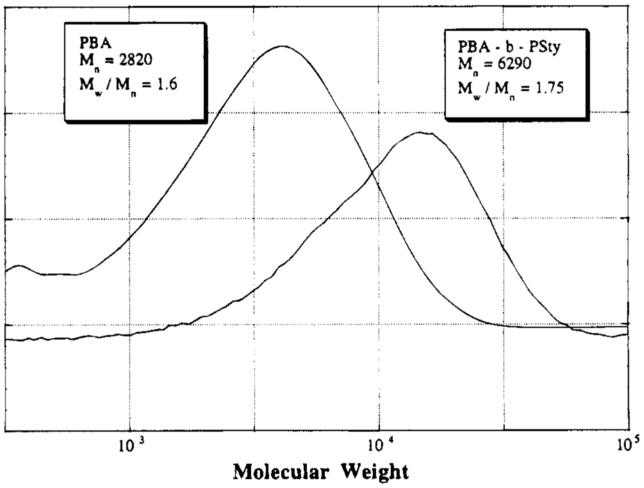


Figure 3. GPC traces for the block copolymerization of butyl acrylate and styrene. Conversion of butyl acrylate >95%; styrene ≈ 80%.

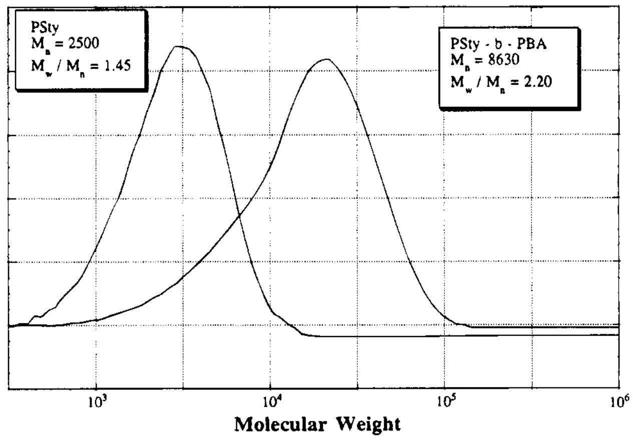


Figure 4. GPC traces for the block copolymerization of styrene and butyl acrylate. Conversion of styrene >95%; butyl acrylate ≈ 80%.

1.5.[27] However, in the presence of the degenerative transfer agent, low molecular weights, defined approximately by the ratio of the concentration of reacted monomer to the concentration of the transfer agent, were observed. The theoretical dependencies, $DP_n = \Delta[M]/([R'{-}X]_0 + [I]_0)$, are shown as solid lines in Figure 2, whereas the broken lines indicate the experimental evolution of molecular weights with conversion. The molecular weights increased monotonously with conversion, as they should in a controlled polymerization. Initially, the molecular weights were higher than predicted by ideal behavior due to an insufficient rate of the degenerative transfer in comparison to propagation.

Figures 3 and 4 present the variation of molecular weights in the block copolymerization between butyl acrylate and styrene. It was possible to form both A−B and B−A block copolymers. Molecular weights increased with conversion for butyl acrylate and also after addition of the styrene when the butyl acrylate was nearly completely consumed, indicating successful block copolymerization.[28] Because the polymerization of styrene was much slower, at complete conversion nearly all initiator was consumed.[29] However, addition of more AIBN, along with butyl acrylate, resulted in the formation of block copolymers. Polydispersities of the block copolymers were relatively high, however, indicating that propagation was faster than the degenerative transfer.

We are currently studying the effects of various parameters such as the structure of the alkyl group, R′, in the transfer agents, the leaving group, X, solvent, and temperature in the polymerization of various vinyl monomers. This is being done to optimize the conditions conducive to degenerative transfer.

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(22) Conversions were obtained by measuring residual monomer using a Shimadzu GC-14A gas chromatograph. A DB-WAX capillary column from J & W Scientific was used with THF as an internal standard.

(23) *Polymerization of Styrene with 1-Phenylethyl Iodide*. Under an argon atmosphere, styrene (5 mL, 8.74 M) was added to AIBN (0.0246 g, 0.03 M). The transfer agent, 1-phenylethyl iodide (0.1160 g, 0.1 M), was then added via syringe. Samples (0.5 mL) were taken from this solution and transferred by syringe to tubes sealed with rubber septa. These samples were then immersed in an oil bath at 70 °C. At various intervals the tubes were cooled to room temperature, and 2.5 mL of THF was added to the samples to dissolve the polymer.

(24) *Synthesis of 1-Phenylethyl Iodide*. To styrene (0.1 mol) was added hexadecyltributylphosphonium bromide (0.01 mol). Hydriodic acid (0.3 mol) was then added, and the mixture was stirred at 40 °C. After 6 h, the organic layer had turned a dark red color and had moved from the top of the bilayer mixture to the bottom, and the mixture was stirred for an additional 2 h. ^{1}H NMR showed the conversion >99%. The organic layer was then separated and washed with water, followed by 3 × 50 mL of saturated solution of Na_2CO_3 and 3 × 50 mL of water. The red solution was then passed through a silica gel column with hexanes. The first, yellow, solution was collected and the hexanes removed by vacuum at room temperature in the dark. Yield 60%.

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(26) *Polymerization of Butyl Acrylate with 1-Phenylethyl Iodide*. Reaction conditions and procedures were the same as for styrene; $[\text{butyl acrylate}]_0 = 6.74$ M.

(27) Molecular weights were obtained using a Waters 712 WISP autosampler and the following Phenogel GPC columns: guard, linear, 1000 Å, and 100 Å. The molecular weights were determined using polystyrene standards measured with a Waters 410 differential refractometer. Prior to injection, the samples were passed through a column of alumina to remove any iodine from the sample.

(28) *Synthesis of Poly(butyl acrylate)-block-polystyrene*. The polymerization was carried out in a previously flamed glass reactor under an argon atmosphere. Solvent, benzene, transfer agent, and initiator were transferred into the reactor using rubber septa and syringes. After mixing the initiator, transfer agent, solvent, and monomer, the solution was degassed twice and was placed in an oil bath at 70 °C. The butyl acrylate polymerization lasted 5 h. Then, an aliquot of the reaction medium was withdrawn for analysis by SEC in order to determine the molecular weight of the first block. Styrene was then added to the reactor. The copolymerization was allowed to occur for another 36 h.

(29) *Synthesis of Polystyrene-block-poly(butyl acrylate)*. The polymerization was performed in a manner similar to the one of the synthesis of poly(butyl acrylate)-*block*-polystyrene, except that, after 24 h for the styrene polymerization, another 0.1 mol equiv of AIBN relative to 1-PEI was added together with butyl acrylate monomer. The copolymerization was continued for 6 h.

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