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COMMUNICATIONS

Published on Web 04/12/2002

Aqueous Room Temperature Metal-Catalyzed Living Radical Polymerization of Vinyl Chloride

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Received January 15, 2002

Metal-catalyzed living radical polymerization (LRP) initiated with alkyl[1] and sulfonyl halides[2] has been accomplished both in organic[1,2] and in aqueous[3] media only for activated monomers, such as styrene,[1,2a] methacrylates,[2b] acrylates,[1−4] and acrylonitrile.[5] This polymerization proceeds via a metal-mediated redox process in which a low oxidation state metal complex acts as catalyst to facilitate a fast exchange between an extremely small amount of radicals and their dormant alkyl halide species.[2b] The equilibrium between active and dormant species is shifted toward the dormant species via an excess of the higher oxidation state of the catalyst that is generated by a small extent of radical dimerization during the initial steps of the polymerization (*internal suppression of fast reactions* or *persistent radical effect*,[6] PRE). The PRE is not only responsible for the control of the metal-catalyzed LRP[2b,6] and other LRPs,[7] but also for the development of chemoselective organic radical reactions.[6]

In a previous publication we have reported the first steps toward the elaboration of the metal-catalyzed LRP of the nonactivated olefin vinyl chloride (VC).[8] At 130 °C in *o*-dichlorobenzene the polymerization of VC initiated by alkyl iodides such as CHI_3 is catalyzed only by metals in their zero-valent oxidation state. Low oxidation state metal complexes are not catalysts for the polymerization of VC although they mediate the initiation step. Radical polymerization of VC is dominated by chain transfer to monomer rather than by bimolecular termination.[9] Therefore, in the case of VC, even if low oxidation state metal complexes would act as catalysts for the polymerization of VC, no mechanism is available for the generation of the classic PRE.[6] As a consequence, zero valence metals (i.e., Cu(0)) catalyze the radical polymerization of VC only up to 20% conversion via a combination of metal-catalyzed initiation and degenerative transfer processes[8] that are maintained also in the new process described below.

Here we report the discovery of a method for the Cu/tren or PEI (tren, tris(2-aminoethyl)amine; PEI, poly(ethylenimine) as ligands and emulsifiers) catalyzed LRP of VC at room temperature in a two-phase system containing H_2O and THF. The main steps of this polymerization are presented in Scheme 1. *Both the extremely reactive Cu(0) and Cu(II)X_2(ligand) required for this polymerization are generated by the disproportionation of the Cu(I) species in H_2O* (eq 1 in Scheme 1).[10] This disproportionation is favored by ligands that form stronger complexes with Cu(II) than with Cu(I) species. Therefore, the disproportionation generates via a self-regulated mechanism, in situ, the Cu(II) species that in the case of VC are not accessible via a PRE mechanism (vide supra). *By this means the inactive Cu(I) species are spontaneously consumed and the catalytically active Cu(0) species are continuously produced.* The formation of Cu(0) and Cu(II) species is visible when mixing all reagents except the initiator and VC (Supporting Information). Furthermore, the presence of Cu(II) was also detected by UV−vis spectroscopy (Supporting Information).[11] If alkyl iodide initiators (CH_nI_{4-n}, $n = 0-2$) are used in the presence of tren and Cu(I) compounds (Cu_2O, Cu_2Te, CuCl, CuI) in H_2O/THF the thus formed Cu(tren)I_2 is persistent, while the Cu(0) generated undergoes the same cycle of transformations as described previously. In two experiments we have compared Cu_2Te vs Cu(0) catalysts in the presence of tren and both rate constants were identical (Supporting Information). This is proof that the active Cu(0) species were formed in situ from Cu_2Te, and this mechanism should apply for Cu_2O as well. The small difference between the rates of Cu_2O and Cu_2Te is most probably due to powders of different sizes that visibly affect their rate of disproportionation.

Scheme 1. Simplified Mechanism of LRP of VC

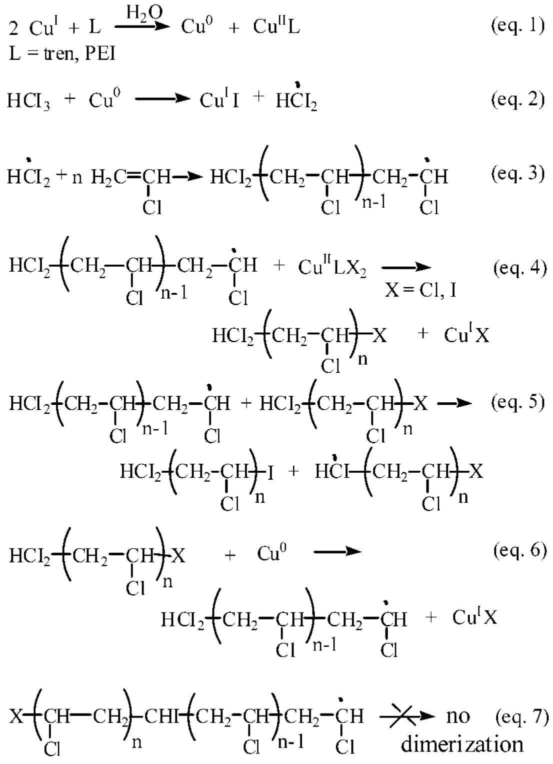

Figure 1 shows typical kinetic experiments for the radical polymerization of VC initiated with CHI_3 and catalyzed by Cu_2O/tren (△) and Cu_2O/PEI (○). In both cases, the ln($[M]_0/[M]$) exhibit two linear dependencies on reaction time. The first linear dependence (up to 28% conversion with a $k_p = 0.34$ h^{-1} for tren, and

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10.1021/ja0256055 CCC: $22.00 © 2002 American Chemical Society

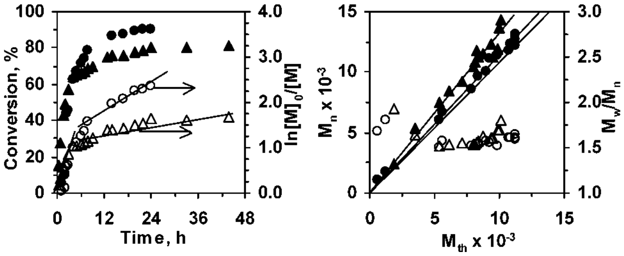

Figure 1. LRP of VC initiated with CHI_3 and catalyzed by Cu_2O in the presence of tren (△) and PEI (○) ([VC]/[I]/[Cat]/[L] = 200/1/2/4).

52% conversion with a $k_p = 0.21$ h^{-1} for PEI) corresponds to a liquid−liquid emulsion polymerization while the second linear dependence corresponds to a solid−liquid dispersion polymerization process. As expected, the dispersion process proceeds with a lower k_p (0.05 h^{-1} for tren and 0.06 h^{-1} for PEI) than that of the emulsion process. The change in slope of the ln([M]$_0$/[M]) vs time corresponds to the reaction time when the PVC separates as an agglomerate from the reaction mixture, as observed visually. Both linear dependencies of ln([M]$_0$/[M]) demonstrate a first-order rate of polymerization in [VC] and a constant radical concentration throughout the polymerization process.[1,2] For both ligands, the experimental M_n agrees with the M_{th}, as seen in Figure 1b. This demonstrates that a quantitative initiation takes place. However, the M_w/M_n values decrease with increasing conversion to values of only about 1.5. There are at least five possible explanations for this behavior: (i) a slower initiation than propagation;[2b] (ii) the heterogeneity of the reaction medium; (iii) two mechanisms involved in the formation of the dormant species (a degradative chain transfer and a chain transfer to CuX_2(ligand)); (iv) a slow rate of exchange between radicals and dormant species; and (v) the presence of more than one kind of dormant species, i.e., $-CHClI$, $-CHI_2$, and $-CHCl_2$ (vide infra). A combination of any of these five phenomena is most probable.

To provide additional evidence for a living polymerization taking place for VC, a re-initiation experiment from a purified PVC sample separated at 15% conversion was conducted. Under identical conditions, at 90% conversion, an increase of M_n from 3800 to 14800 was found (see Supporting Information). The low polymerization temperature for this process is the result of the single electron transfer (SET) mechanism of activation of the $-CHClI$ dormant chains by the electron donor Cu(0) (Scheme 1, eq 6). There is previous literature evidence that polyhalocarbons facilitate SET processes catalyzed by good electron donors.[12] Reversible deactivation is also a SET process and, therefore, proceeds in heterophase.

At low conversion, ^{1}H NMR analysis of the resulting PVC revealed signals at 5.27, 5.92, and 6.03 ppm, corresponding to the CHI_2[13a] starting polymeric chain, and, respectively, the $CHClI$[13a] and $CHCl_2$[13b] dormant species as chain ends. Growth in two directions is seen at high conversion. A signal at 3.76 ppm and a small signal found at 1.26 ppm belong to CH_2Cl[9] and CH_3 dead chain ends. This is corroborated by the fact that treatment of this polymer with Cu(0)/tren in water/THF at 50 °C for 17 h leads to a complete disappearance of the other end-group signals and an increase of the signals at 3.76 and 1.26 ppm. The dihalogenated end groups were simply reduced under these conditions via a possible LCu−C transient complex.[14] Control experiments showed that this process is negligibly slow at room temperature. A thus modified polymer no longer functioned as initiator for further polymerization when subjected to the reaction (re-initiation) conditions outlined above.

In conclusion, we have reported the first metal-catalyzed room-temperature living radical polymerization of VC in aqueous media. This new, unprecedented type of LRP creates both the active Cu(0) catalyst and the Cu(II) species required for the reversible termination step in situ via a self-regulated disproportionation of the Cu(I) species. The disproportionation of Cu(I) species that is crucial for this process is controlled, as mentioned above, by the nature of the ligand. In this polymerization, the classic PRE[6] is therefore no longer operative. This novel LRP process will facilitate for the first time access to the elaboration of preparative methods for the design and synthesis of complex architectures[15] based on VC and other halogenated monomers. Attempts to generate LRP methods for other classes of nonactivated olefins continue to represent one of the most important challenges of the field of LRP.[16] The new process reported in this publication provides a solution for the LRP of VC and of other halogenated monomers. The mechanism of this polymerization with the current and with other SET catalytic systems is under investigation.

Acknowledgment. Financial support from EPIC, NSF, and ARO-MURI is gratefully acknowledged.

Supporting Information Available: Experimental procedure, kinetic plots, NMR and UV spectra, and GPC traces for re-initiation experiment (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0256055