of the mass of PUI50, but since they are expected to be localized in regions of higher mass density (the ionic aggregates), they should occupy a volume fraction smaller than their weight fraction. However, to bring the numbers above into perfect agreement would require the aggregates to have a mass density of 3.6 g/cm^3, which seems rather large. This point requires further investigation, preferably using a contrast-matched sample to eliminate the subtraction method used here.

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Communications to the Editor

Novel Initiator Systems for the End-Functionalization of Poly(vinyl ethers)

The extensive investigation of the living cationic polymerization of vinyl ethers by Higashimura and co-workers[1-4] and others[5,6] has paved the way to the molecular engineering of this type of polymer. Of particular interest is the synthesis of end-functionalized and telechelic poly(vinyl ethers) (PVE) as precursors of newer materials such as multisegmented copolymers.

ω-Functional and α,ω-functional PVEs can be prepared along different reaction pathways. One of the approaches involves essentially a preliminary synthesis of the functionalized vinyl ether monomer and use of its HI adduct as an initiator for vinyl ether polymerization in the presence of a Lewis acid activator. Thus, for instance, the HI adducts of 2-(vinyloxy)ethyl methacrylate and diethyl 2-(vinyloxy)ethylmalonate have been successfully used[7,8] to initiate the polymerization of vinyl ethers. Both of these have been prepared by reaction of chloroethyl vinyl ether with sodium methacrylate and sodium malonate, respectively.

A second pathway relies upon the reaction of the living poly(vinyl ether) chains with a nucleophilic functional compound as a terminating agent. Butylamine or the sodium salt of malonic esters[9-11] have been used effectively as terminating agents with the formation of ω-functional polymers. A combination of the first and second pathways allows symmetric or asymmetric telechelic poly(vinyl ethers) to be prepared.

As an extension of the second pathway, a symmetric telechelic polymer has also been obtained by using 1,4-bis(vinyloxy)butane as a bifunctional initiator followed by the termination of the living polymer by a nucleophilic functional reagent.

Presently, we are reporting briefly a new method of the end-functionalization of vinyl ethers by making use of the HI adducts of some conventional vinyl monomers to initiate the EVE polymerization in toluene at −40 °C. This type of end-functionalization is in sharp contrast to the reports by Nuyken and co-workers[6] or Higashimura and co-workers[7,8] in that the vinyl monomers used to prepare the initiator cannot be polymerized under the conditions used for the polymerization of vinyl ethers.

I. Addition of HI to Conventional Vinyl Monomers. The addition of a stoichiometric quantity of HI (0.4 molar solution) to conventional vinyl monomers (0.04

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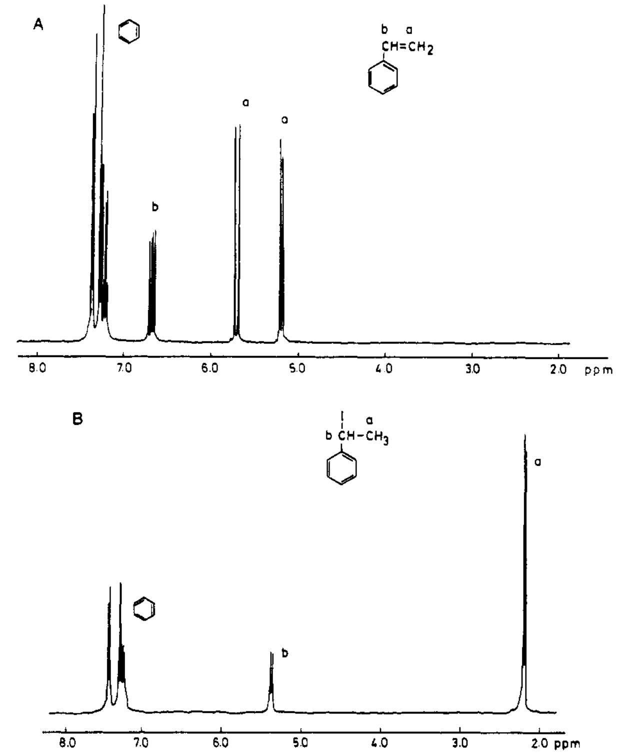
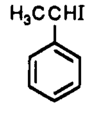
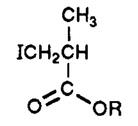


Figure 1. Addition of HI to conventional vinyl monomers at -60 °C in CH_2Cl_2 monitored by ^1H NMR spectroscopy in $CDCl_3$ at 20 °C: (A) styrene; (B) styrene + HI.

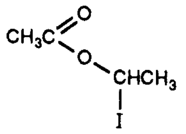
molar solution) has been investigated in methylene chloride. The ^1H NMR analysis of the reaction products reveals a quantitative addition of HI to the double bond. The characteristic peaks of $=CH_2$ and $=CH$, as seen from Figure 1 (in the example of styrene), have completely disappeared upon HI addition. The ^1H NMR spectra of the addition products are consistent with the expected structures; i.e.





$ICH_2CH(CH_3)C(=O)OR$

R = CH_3, *tert*-butyl



$CH_3C(=O)OCH(I)CH_3$

II. Ethyl Vinyl Ether (EVE) Polymerization Initiated by the HI Adduct of Conventional Vinyl Monomers. All the adducts prepared and characterized by ^1H NMR spectroscopy have been found to initiate EVE polymerization in toluene at -40 °C. The conversion is quantitative within 150 min of polymerization time, and a very narrow molecular weight distribution (<1.1) is obtained.

The living nature of the EVE polymerization has been investigated in the particular case of the HI adduct of *tert*-butyl methacrylate. This system is representative of the rest of the adducts. EVE has, thus, been polymerized at different monomer/initiator molar ratios in toluene at -40 °C. The results, plotted in Figure 2, indicate a linear dependence of the molecular mass (as determined by size-exclusion chromatography) on the monomer/initiator molar ratio at 100% conversion. This observation supports the living nature of the EVE polymerization, at least in the investigated range of molecular mass. The polydispersity of all these samples is very narrow (<1.1).

It has, however, been observed that the initiator efficiency $\bar{M}_n$(SEC)/$\bar{M}_n$(calc) in the different experiments range between 75 and 80%, on the basis of $\bar{M}_n$ values computed by the polystyrene calibration curve. This might be due to a difference in the hydrodynamic volume of polystyrene and poly(ethyl vinyl ether) and will be the subject of further investigation. It is worth noting that when the HI adduct of styrene is used as an initiator, the ^1H NMR spectrum of the polymer (Figure 3B) shows as many styrene units (PhCH at 2.23 ppm) as acetal (4.55 ppm) end groups (within the limits of experimental error). However, the calculation of molecular mass of the polymer based on a small concentration of the end groups is not precise, and the overlapping of peaks further complicates the problem. It is, therefore, proposed to synthesize a series of low molecular weight polymers of this type and then to compute their molecular mass from the end groups and compare the result with the molecular mass obtained by other techniques.

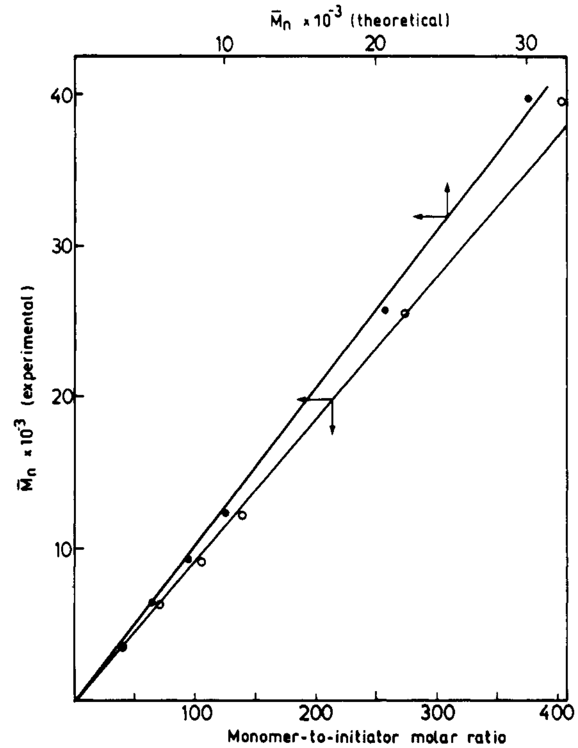


Figure 2. Plot of theoretical $\bar{M}_n$ (i.e., grams of reacted EVE per mole of HI adduct with *tert*-butyl methacrylate) vs experimental values obtained from *SEC* (polystyrene calibration), at 100% conversion. Polymerization was carried out in toluene, at -40 °C, for 120–150 min. [EVE] = 0.6 mol L^{-1}.

III. Analysis of End Groups. According to the mechanism proposed[3] for the cationic polymerization of vinyl ethers, the initiator is quantitatively attached to the growing chain. Accordingly, the substituent of each vinyl monomer involved in the initiating system has to be a chain end, the other end being the acetal resulting from the quenching of the terminal C–I bond by methanol. ^1H NMR analysis qualitatively supports this expectation as shown in Figure 3 for two representative polymers.

IV. Ability of the Conventional Vinyl Monomers To Be Polymerized by Their Parent Iodides. Since styrene is known to be polymerizable cationically, it was of interest to evaluate the polymerizability of these vinyl monomers by their parent iodides in the presence of a Lewis acid activator. The results are summarized in Table I. It is evident that styrene and vinyl acetate cannot be polymerized whatever the activator (I_2 or ZnI_2) even in a polar solvent such as methylene chloride.

On the other hand, methyl methacrylate (MMA) can be partially polymerized in methylene chloride in the presence of iodine activator. However, the conversion is lim-

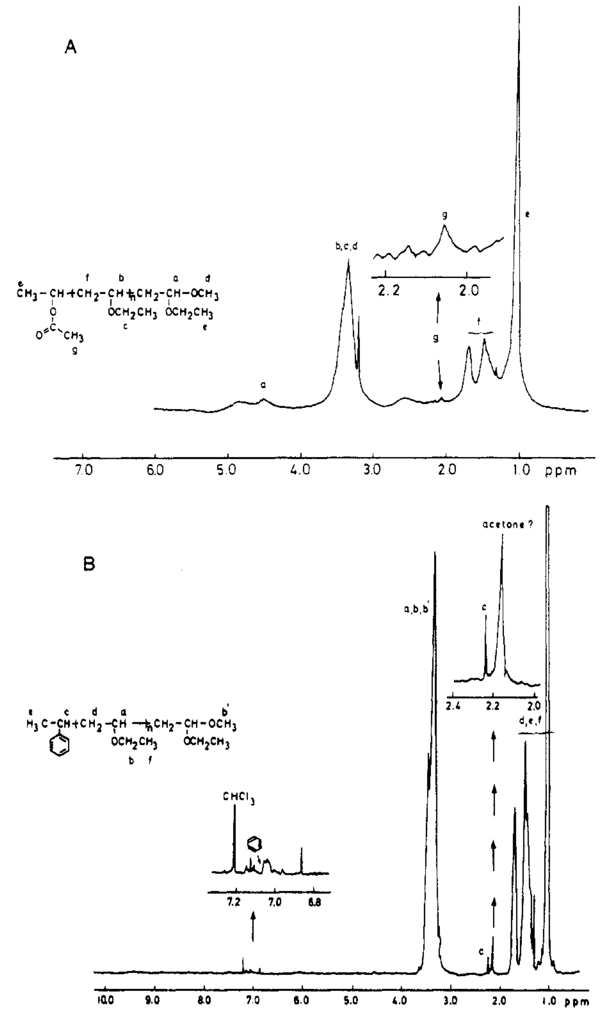


Figure 3. ^{1}H NMR spectroscopy of PEVE initiated by the HI adduct of (A) vinyl acetate and (B) styrene.

Table I
Polymerizability of Vinyl Monomers by HI/Lewis Acid Systems (at -40 °C for 150 min)

monomer	solvent	catalyst syst	polymerizability
styrene	CH_2Cl_2	HI/ZnI_2	no
	CH_2Cl_2	HI/I_2	no
vinyl acetate	CH_2Cl_2	HI/ZnI_2	no
	CH_2Cl_2	HI/I_2	no
MMA	CH_2Cl_2	HI/ZnI_2	no
	CH_2Cl_2	HI/I_2	yes[a]
	toluene	HI/I_2	no
tert-BuMeA	toluene	HI/I_2	no

[a] 25% conversion (gravimetry); bimodal distribution.

ited to 25%, and the molecular mass is at least 5 times higher than expected on the basis of monomer/initiator molar ratio. Furthermore, MMA is not polymerized in toluene. Even in methylene chloride, MMA does not even oligomerize when iodine is replaced by ZnI_2 as an activator. This is consistent with the selective coordination of ZnI_2 with the carbonyl of the monomer rather than with the terminal carbon–iodine bond of the parent iodide; i.e., the initiator is no longer activated.

Thus, the vinyl monomers considered in this study form well-defined iodides upon HI addition but do not themselves polymerize in the presence of the parent iodide under the conditions reported here.

In conclusion, the ability of conventional vinyl monomers to initiate the EVE polymerization as HI adducts (in the presence of a Lewis acid activator) opens up interesting possibilities, currently investigated for preparing functionally end-capped poly(vinyl ethers), telomers, and also di- or triblock copolymers depending on the initial polymer functionality as well as on the use of multifunctional initiator systems (for example: ethylene bis(methacrylate)). A comprehensive paper will be published in the near future.

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