

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<sup>3</sup>, 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<sup>1-4</sup> and others<sup>5,6</sup> 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.

$\omega$ -Functional and  $\alpha,\omega$ -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-(vinyl)ethyl methacrylate and diethyl 2-(vinyl)oxyethylmalonate have been successfully used<sup>7,8</sup> 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.

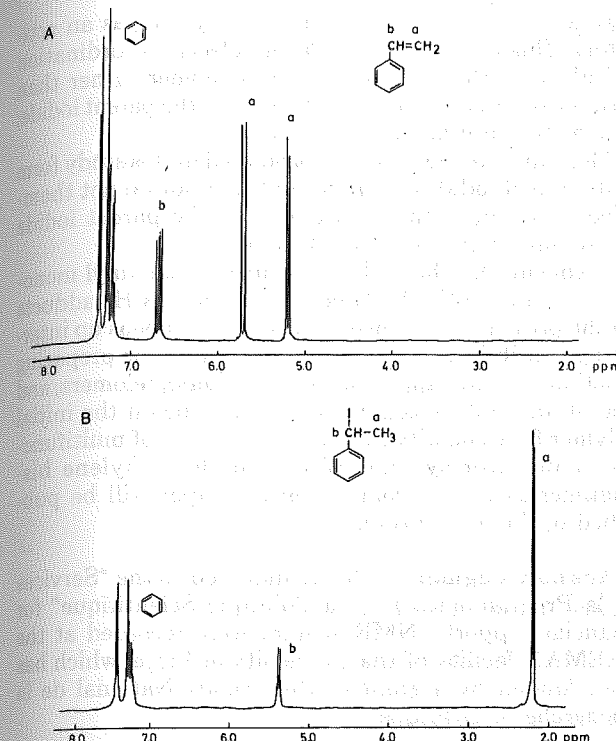
A second pathway relies upon the reaction of the living poly(vinyl ether) chains with a nucleophilic func-

tional compound as a terminating agent. Butylamine or the sodium salt of malonic esters<sup>9-11</sup> have been used effectively as terminating agents with the formation of  $\omega$ -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(vinyl)oxybutane as a bifunctional initiator followed by the termination of the living polymer by a nucleophilic functional reagent.

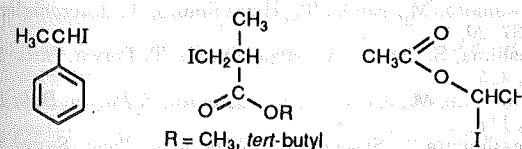
Presently, we are reporting briefly a new method of the end-functionalization of vinyl ethers by making use of the HI adducts of some conventional vinyl monomers to initiate the EVE polymerization in toluene at -40 °C. This type of end-functionalization is in sharp contrast to the reports by Nuyken and co-workers<sup>6</sup> or Higashimura and co-workers<sup>7,8</sup> 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



**Figure 1.** Addition of HI to conventional vinyl monomers at -60 °C in CH<sub>2</sub>Cl<sub>2</sub> monitored by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> at 20 °C: (A) styrene; (B) styrene + HI.

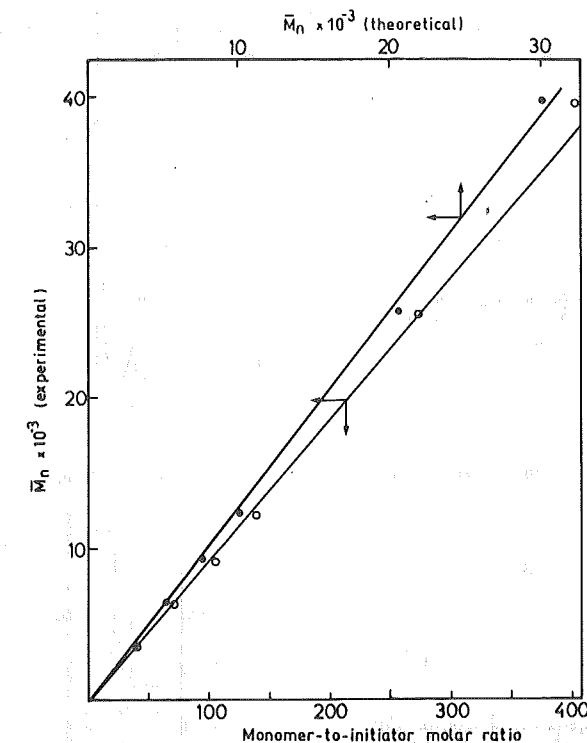
molar solution) has been investigated in methylene chloride. The <sup>1</sup>H NMR analysis of the reaction products reveals a quantitative addition of HI to the double bond. The characteristic peaks of =CH<sub>2</sub> and =CH, as seen from Figure 1 (in the example of styrene), have completely disappeared upon HI addition. The <sup>1</sup>H NMR spectra of the addition products are consistent with the expected structures; i.e.



**II. Ethyl Vinyl Ether (EVE) Polymerization Initiated by the HI Adduct of Conventional Vinyl Monomers.** All the adducts prepared and characterized by <sup>1</sup>H 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  $\bar{M}_n(\text{SEC})/\bar{M}_n(\text{calc})$  in the different experiments range between 75 and 80%, on the basis of  $\bar{M}_n$  values



**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<sup>-1</sup>.

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 <sup>1</sup>H 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.

**III. Analysis of End Groups.** According to the mechanism proposed<sup>3</sup> 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. <sup>1</sup>H 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<sub>2</sub> or ZnI<sub>2</sub>) 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-

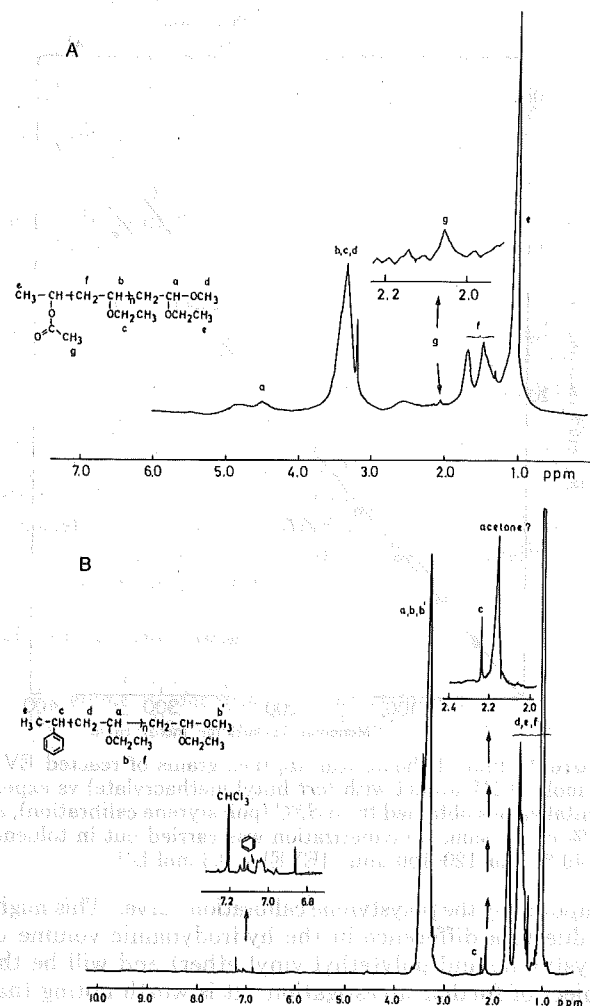


Figure 3.  $^1\text{H}$  NMR spectroscopy of PEVE initiated by the HI adduct of (A) vinyl acetate and (B) styrene.

Table I  
Polymerizability of Vinyl Monomers by HI/Lewis Acid Systems (at  $-40^\circ\text{C}$  for 150 min)

monomer	solvent	catalyst syst	polymerizability
styrene	$\text{CH}_2\text{Cl}_2$	$\text{HI}/\text{ZnI}_2$	no
	$\text{CH}_2\text{Cl}_2$	$\text{HI}/\text{I}_2$	no
vinyl acetate	$\text{CH}_2\text{Cl}_2$	$\text{HI}/\text{ZnI}_2$	no
	$\text{CH}_2\text{Cl}_2$	$\text{HI}/\text{I}_2$	no
MMA	$\text{CH}_2\text{Cl}_2$	$\text{HI}/\text{ZnI}_2$	no
	$\text{CH}_2\text{Cl}_2$	$\text{HI}/\text{I}_2$	yes <sup>a</sup>
	toluene	$\text{HI}/\text{I}_2$	no
tert-BuMeA	toluene	$\text{HI}/\text{I}_2$	no

<sup>a</sup> 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  $\text{ZnI}_2$  as an activator. This is consistent with the selective coordination of  $\text{ZnI}_2$  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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## Cyclopolymerization of Diethyl Dipropargylmalonate by Transition-Metal Catalysts

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**ABSTRACT:** Diethyl dipropargylmalonate was polymerized by  $\text{MoCl}_5$ - and  $\text{WCl}_6$ -based catalysts to give a new, high molecular weight polymer. A  $\text{MoCl}_5$ -based catalyst was found to be a particularly effective catalyst for cyclopolymerization of diethyl dipropargylmalonate. The number average molecular weight of the resulting polymer was in the range of 76000–127000. The effects of catalysts and solvents on polymerization were also studied. The IR, NMR, and UV-visible spectra of poly(diethyl dipropargylmalonate) supported the idea that the resulting polymer possesses polyene structure having a cyclic recurring unit in the polymer backbone. Poly(diethyl dipropargylmalonate) is a black, soluble, and thermally stable solid.

#### Introduction

Cyclopolymerization of nonconjugated diynes has been investigated in order to prepare a polymer that contains conjugated double bonds along the polymer backbone and a cyclic recurring unit.<sup>1,2</sup>

Recently, we reported that  $\text{MoCl}_5$ - and  $\text{WCl}_6$ -based catalyst systems were very effective for the cyclopolymerization of dipropargyl compounds.<sup>3-7</sup> However, there has been no report on the cyclopolymerization of a dipropargyl compound containing an ester group.

In the present paper, we deal with the cyclopolymerization of diethyl dipropargylmalonate (DEDPM) containing ester groups using  $\text{MoCl}_5$ - and  $\text{WCl}_6$ -based catalysts.

#### Experimental Section

**Preparation of DEDPM.**<sup>8</sup> Diethyl malonate (27 g) was added to dry ethanol (150 mL) containing sodium ethoxide (from sodium, 7.8 g). After 5 min, propargyl bromide (42 g) was slowly added to the stirred suspension, and the mixture heated under reflux for 30 min. After removal of the alcohol in a vacuum, the residue was diluted with water, and the neutral fraction was isolated and dissolved in hexane. DEDPM (33 g) slowly separated in octahedra: yield 79%; mp  $45.5^\circ\text{C}$  (lit.<sup>8</sup> mp  $45.5^\circ\text{C}$ ).

**Other Materials.** Tungsten(VI) and molybdenum(V) chloride (Aldrich Chemicals, resublimed, 99+%) were used without further purification. Tetra-*n*-butyltin (Aldrich Chemicals, 99%) and ethyl aluminum dichloride (Aldrich Chemicals, 25%

solution in hexane) were used as received. All solvents were purified in the usual manner.

**Polymerization.** Catalyst preparation and polymerization were carried out under the dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved to make 0.2 M solution in each solvent before use. A typical polymerization procedure is as follows; solvent, catalyst solution, and cocatalyst solution (in case of need) are injected into a 20-mL ampule equipped with a rubber septum in the order given. When a cocatalyst was used, these catalyst systems were aged at  $30^\circ\text{C}$  for 15 min. Finally, monomer in each solvent was injected into the polymerization ampule. After the mixture stood at  $60^\circ\text{C}$  for 24 h, the polymerization was terminated by adding a small amount of methanol. The resulting polymer was dissolved in chloroform followed by precipitation with a large excess of methanol. The polymer was filtered from the solution and dried to a constant weight under vacuum at  $40^\circ\text{C}$  for 24 h. The polymer yield was calculated by gravimetry.

**Instruments for Characterization.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Varian FT-80A spectrometer and a Bruker AM-200 spectrometer, respectively. An infrared spectrum was taken on a Perkin-Elmer 283B spectrometer with a potassium bromide pellet. UV-visible spectra were obtained with a Beckman DU-6 spectrometer. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{min}$  with a Du Pont 951 TGA. Thermal transitions were measured with a Du Pont 910 differential scanning calorimeter under nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{min}$ . Number average molecular weights ( $M_n$ ) were determined in THF solution by Waters GPC-150C with a calibration curve for polystyrene standards. Tensile tests were carried out at  $20^\circ\text{C}$  at a strain rate of 86%/min by using Instron 1122; the specimen size was  $35 \times 10 \times 0.2$  mm. Electrical con-

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