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Living cationic polymerization of a vinyl ether with a triester pendant

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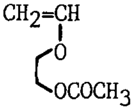
SUMMARY

Cationic polymerization of $CH_2{=}CH{-}O{-}CH_2CH_2C(COOC_2H_5)_3$, a vinyl ether with three pendent esters, initiated by the HI/I_2 system in toluene at -40 °C afforded living polymers with a controlled molecular weight ($\bar{M}_n = 10^3$–10^4) and a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.1$–$1.2$). The number-average molecular weight of the polymers was directly proportional to monomer conversion and the monomer-to-initiator (HI) feed ratio. The polymers obtained with $BF_3O(C_2H_5)_2$ had a fairly high molecular weight ($\bar{M}_w \cong 10^5$, $\bar{M}_n \cong 5 \times 10^4$) and a broad molecular weight distribution. The triester vinyl ether was similar in reactivity to alkyl counterparts and one order of magnitude more reactive than the corresponding mono- and diester vinyl ethers.

INTRODUCTION

Recently we have reported the living cationic polymerization of vinyl ethers **1** (1) and **2** (2) that possess, respectively, one and two ester functions in the pendant. When polymerized by a mixture of hydrogen iodide and iodine (HI/I_2) as the initiating system (3), **1** and **2** form well-defined living polymers, although carboxylic acid esters may induce chain transfer and termination in cationic polymerization.



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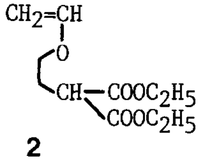

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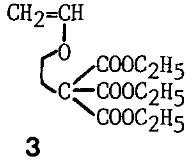

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These positive results prompted us to explore, in this study, the possibility of living cationic polymerization of vinyl ether **3** [3-tris(ethoxycarbonyl)propyl vinyl ether], the pendant of which carries three carboxylic acid esters attached to a single tertiary carbon. The triester monomer **3** is characterized by the bulkiness of its highly branched pendant and the existence of three polar ester groups therein.

The object of this study was to uncover how these structural characteristics of **3** affect its cationic polymerization in general and living polymerization in particular; no literature is available for the cationic polymerizability of this new monomer. We herein report that the HI/I_2-initiated polymerization of **3** leads to well-defined living polymers with a controlled molecular weight and a monodisperse molecular weight distribution (MWD).

RESULTS AND DISCUSSION

Cationic Polymerization of **3**

Since the cationic polymerizability of **3** was not known, **3** was polymerized in toluene at -40°C with HI/I_2, iodine, and boron trifluoride etherate (BF_3OEt_2); the first two are suitable for living polymerization of vinyl ethers (3, 4) and the last is a conventional initiator for cationic polymerization.

The polymerization by the three initiators proceeded without an induction phase to give soluble polymers of **3** in quantitative yield (see below for the polymerization reactivity of **3**). Figure 1 compares the MWDs of the polymers thus obtained. Despite the bulkiness of the triester pendant, **3** could be polymerized by BF_3OEt_2 into high polymers ($\bar{M}_w \cong 1 \times 10^5$, $\bar{M}_n \cong 5 \times 10^4$, $DP_n \cong 160$; polystyrene calibration); the MWD was rather broad ($\bar{M}_w/\bar{M}_n = 2$). HI/I_2 and iodine led to narrower MWDs and, in particular, the polymers obtained with HI/I_2 were nearly monodisperse ($\bar{M}_w/\bar{M}_n = 1.11$).

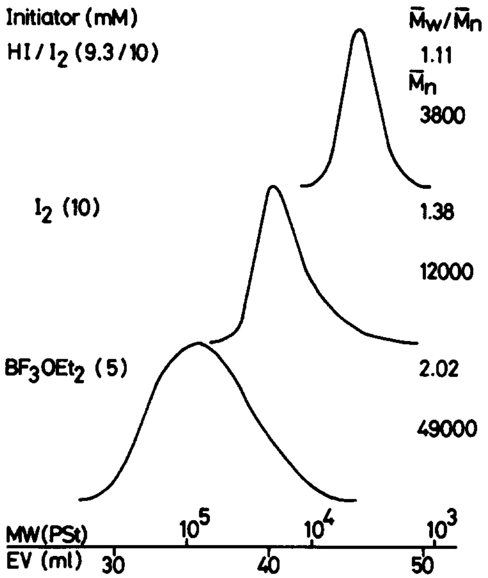

Figure 1. MWD of poly(**3**) obtained in toluene at -40°C with three initiators: $[M]_0 = 0.18$ M (5.0 vol %); conversion of **3** = 100%.

Living Polymerization of **3** *by HI/I_2*

Encouraged by the high polymerizability of **3** and by the narrow MWD of its polymers obtained by HI/I_2, we studied the possibility of living cationic polymerization of the triester monomer using this initiating system. Thus, **3** was polymerized by HI/I_2 in toluene at -40°C, and the number-average molecular weight ($\bar{M}_n$) and MWD ($\bar{M}_w/\bar{M}_n$ ratio) of the polymers were followed as a function of monomer conversion and the feed ratio of monomer to initiator ($[M]_0/[HI]_0$). Figure 2 gives the pertinent data.

The $\bar{M}_n$ increased in proportion to monomer conversion up to 100 %, and a very narrow MWD ($\bar{M}_w/\bar{M}_n = 1.1$-$1.2$) was maintained throughout the polymerization (Fig. 2A). The polymer molecular weight was also proportional to the $[M]_0/[HI]_0$ ratio, over the whole range of which the polymers exhibited a narrow MWD (Fig. 2B). These facts demonstrate that the HI/I_2-initiated polymerization of the triester vinyl ether **3** leads to monodisperse living polymers with controlled molecular weight, although the monomer has three pendent ester functions that might cause chain transfer and termination.

Structure of the Polymers

Figure 3 illustrates a typical ^{13}C NMR spectrum of poly(**3**) obtained with HI/I_2 in toluene at -40°C. The spectrum is fully consistent with the expected structure of poly(**3**), exhibiting all absorptions of the pendant group of the monomer such as the ester carbonyls (peak f) and the ethyl groups (peaks g and h). The vinyl signals of the monomer were completely absent (their peak positions are indicated by the arrows), and the polymer main-chain carbons are in turn seen as peaks a and b. Thus, the triester pendant of **3** stays intact during the polymerization.

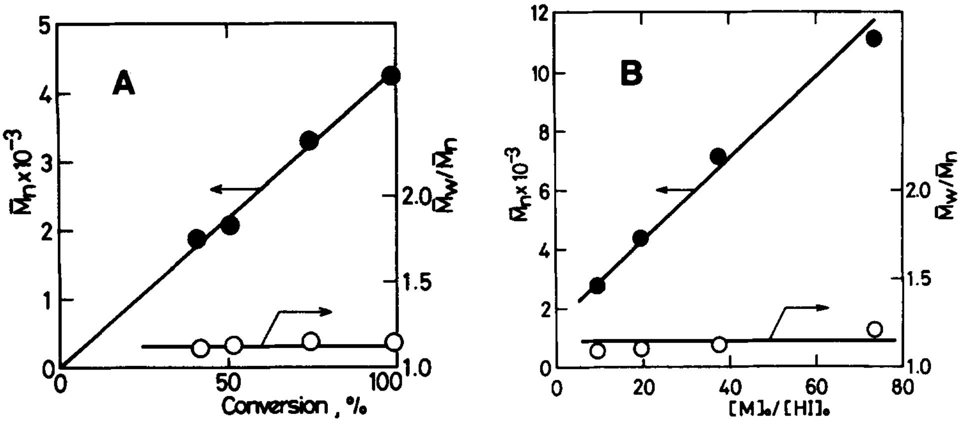

Figure 2. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values for poly(**3**) obtained with HI/I_2 in toluene at -40°C as a function of (A) monomer conversion or (B) the monomer-to-initiator feed ratio: $[M]_0 = 0.18$ M (5.0 vol %). (A) $[HI]_0 = 8.9$ mM, $[I_2]_0 =$ 10 mM; (B) $[HI]_0 = 2.5$-18.8 mM, $[I_2]_0 = 2.5$ mM, conversion of **3** ≅ 100 %.

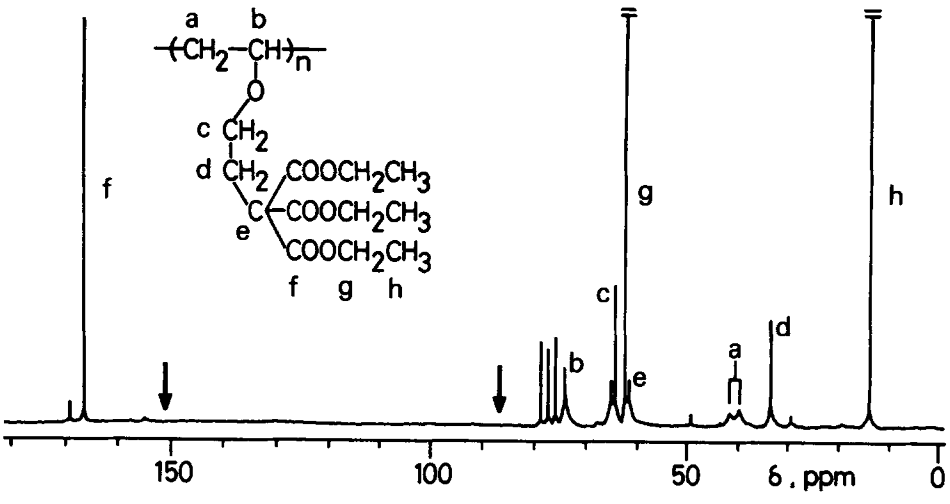

Figure 3. ^{13}C NMR spectrum of poly(**3**) obtained with HI/I_2 in toluene at -40°C: $\bar{M}_n = 4400$, $\bar{M}_w/\bar{M}_n = 1.10$. The thick arrows indicate the signal positions of the vinyl carbons of **3**. The minor non-assigned resonances are due to the repeat units arising from **2** (6 mol % in the initial feed of **3**).

The main-chain methylene signal (peak a) is split into two peaks, according to the dyad steric structure of the backbone. Similar splitting was observed for the polymers prepared with iodine and BF_3OEt_2. The dyad isotacticity (meso content) of these polymers, based on the integration of peak a (5), was almost independent of the initiators (HI/I_2, 60 %; iodine, 63 %; BF_3OEt_2, 63 %), and close to the value (~ 65 %) for poly(ethyl vinyl ether) and poly(**1**) obtained under the same conditions (6). Rather surprisingly, therefore, the bulky pendant of **3** exerts no specific effects on the stereochemistry of its polymerization.

Table 1

Polymerization Rates[a] and ^{13}C NMR Chemical Shifts (^{13}C δ) of Vinyl Ethers $^{\beta}CH_2{=}^{\alpha}CH\text{-}OCH_2CH_2\text{-}X$

Monomer Code	Substituent X	t(100%),[b] min	^{13}C δ[c] $^{\beta}CH_2$	^{13}C δ[c] $^{\alpha}CH$	Ref
1	$OCOCH_3$	420	86.5	151.1	(6)
2	$CH(COOC_2H_5)_2$	216	86.5	151.2	(2)
3	$C(COOC_2H_5)_3$	13	86.7	151.2	this work
4	OC_2H_5	5	86.3	151.5	(6)
5	H	30	86.0	151.6	(6)

a) By HI/I_2 in toluene at -40°C; $[M]_0$ = 5.0 vol % (0.18-0.38 M); $[HI]_0 = [I_2]_0$ = 10 mM.

b) Time to reach 100 % conversion, determined by extrapolating a time-conversion curve.

c) In $CDCl_3$ at room temperature.

Polymerization Reactivity of **3**

Monomers **1** - **3** are similar in structure but differ in the number of the pendent ester groups. To investigate the effect of ester functions on the reactivities of these vinyl ethers and their propagating species, we compared, in Table 1, the time to reach 100 % conversion [t(100%)] for **1** - **3** and related vinyl ethers **4** and **5** in the HI/I_2-initiated living polymerizations; t(100%) was determined by extrapolating a time-conversion curve to 100 % conversion.

As we reported recently (6), the polymerization of the monoester derivative **1** is one order of magnitude slower than that of its alkyl counterpart **5** (ethyl vinyl ether); namely, introduction of one ester function into the pendant greatly retards polymerization. In contrast, the di- and triester monomers (**2** and **3**, respectively) polymerize more rapidly than **1**. Among **1** - **3**, the polymerization rate increases with increasing number of pendent ester groups (**1** < **2** < **3**). Note that the rate for **3** is comparable to or higher than that for the alkyl monomer (**5**) and even close to the rate for **4**, one of the most reactive vinyl ethers that carry a poly(oxyethylene) chain in the pendant (6).

Despite the clear differences in polymerization rate, the vinyl carbons of monomers **1** - **5** have nearly the same ^{13}C NMR chemical shifts (Table 1), indicating that their pendants hardly affect the electron density of the vinyl ether double bond (6). The final explanation for the high polymerization rate of **3** must await more detailed investigations of the kinetics, but the bulkiness of the triester pendant apparently plays an important role to activate either the monomer or its growing end or both.

Poly(**3**) consists of a flexible poly(vinyl ether) main-chain and three ester functions in each repeat unit. In view of this unique structure, it would prove useful for the synthesis of new multifunctional polymers by, for example, "cascade"-type (7) modification (multiplication) of the triester pendants. Studies along these lines are now in progress (8).

EXPERIMENTAL

Synthesis of **3**

Vinyl ether **3** was prepared by the reaction of 2-chloroethyl vinyl ether with triethyl sodiomethanetricarboxylate (**7**) (eq 1). In a 300-mL,

$$\underset{\mathbf{6}}{HC(COOC_2H_5)_3} \xrightarrow[\text{benzene/DMF, room temp.}]{NaH} \underset{\mathbf{7}}{Na^{\oplus\ominus}C(COOC_2H_5)_3} \xrightarrow[100^{\circ}C,\ 10\ hr]{CH_2{=}CH{-}O{-}CH_2CH_2{-}Cl} \underset{\mathbf{3}}{CH_2{=}CH{-}O{-}CH_2CH_2{-}C(COOC_2H_5)_3} \tag{1}$$

three-necked, round-bottom flask equipped with a paddle stirrer, a reflux condenser, a dropping funnel, and a nitrogen inlet was placed sodium hydride dispersion (60 wt % in mineral oil, 12.1 g, 0.302 mol) in 100 mL of a benzene-DMF (1:1 v/v) mixture. The set-up was flushed with dry nitrogen, and a solution of triethyl methanetricarboxylate (**6**) (50.0 g, 0.316 mol) in the same solvent mixture (50 mL) was added dropwise with stirring at room temperature, while the evolving hydrogen was purged with continuous nitrogen flow. 2-Chloroethyl vinyl ether (70 mL, 0.69 mol) was then added dropwise with stirring. After the addition was completed, the mixture was gradually heated to 100°C in an oil bath, stirred at this temperature for an additional 10 hr, cooled to room temperature, diluted with benzene (100 mL), and poured into water (250 mL). The organic layer was separated, washed with three 100-mL portions of water, dried overnight with anhydrous sodium sulfate, and condensed by evaporating off the benzene and unreacted 2-chloroethyl vinyl ether under reduced pressure. The oily condensate consisted of two layers; the lower brown phase (ca. 13 mL) was the crude product (a mixture of **2**, **3**, and the unreacted **6**) and the upper phase was the mineral oil coming from the sodium hydride dispersion. The lower layer was separated by a syringe and purified by preparative column chromatography (Merck LiChroprep Si 60) in chloroform to give vinyl ether **3** [colorless oil; purity ca. 94 mol % by gas chromatography; containing **2** (6 mol %)]. The purified monomer was freeze-dried four times and sealed in brown ampules under dry nitrogen. ^1H NMR ($CDCl_3$, 90 MHz) δ 6.38 ($OCH{=}$), 4.26 (CH_2COO), 4.19 ($C\underline{H}{=}CHO$, anti), 3.99 ($C\underline{H}{=}CHO$, syn), 3.96 ($C\underline{H_2}OCH{=}$), 2.53 ($C\underline{CH_2}CH_2O$), 1.28 ($\underline{CH_3}$); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 166.3 ($C{=}O$), 151.2 ($OCH{=}$), 86.7 ($CH_2{=}$), 64.1 ($\underline{C}H_2OCH{=}$), 62.0 ($\underline{C}H_2COO$), 61.2 ($\underline{C}(COOC_2H_5)_3$), 32.1 ($C\underline{C}H_2CH_2O$), 13.7 ($CH_3$).

Other Materials

Anhydrous hydrogen iodide (as an *n*-hexane solution), iodine, and BF_3-OEt_2 were obtained as reported previously (3). Toluene (polymerization solvent) and tetrahydronaphthalene (internal standard for gas chromatography) were purified by the usual methods (3) and distilled twice over calcium hydride before use.

Procedures

Polymerization was carried out at -40°C under dry nitrogen in a baked glass tube equipped with a three-way stopcock, and quenched with prechilled ammoniacal methanol. The conversion of **3** was followed by gas chromatography [column: Silicon DC 11 (20 %), supported on Celite 545 U (60-80 mesh), 2 m x 5 mm i.d., 230°C; carrier gas: hydrogen] with tetrahydronaphthalene as internal standard. The quenched reaction mixtures with HI/I_2 or iodine were washed sequentially with 10 % aqueous sodium thiosulfate solution and with water, evaporated to dryness, and vacuum dried to give the product polymers. The polymer solutions with BF_3OEt_2 were worked up in the same manner except for omitting the treatment with sodium thiosulfate.

The MWD and $\bar{M}_n$ of the polymers were determined by size-exclusion chromatography on the basis of a polystyrene calibration (3). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at room temperature on a Jeol FT-90Q spectrometer.

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