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Living Cationic Polymerization of Vinyl Ethers with a Functional Group

4. Synthesis of Poly(Vinyl Ether) Macromers with a Methacrylate Head

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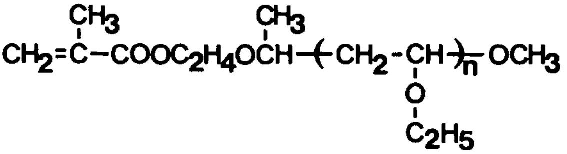
SUMMARY

A new poly(vinyl ether) macromer (1) having a methacrylate group has been prepared. The adduct [CH_2=$C(CH_3)$-$COOCH_2CH_2$-CHI-CH_3] obtained by the reaction of 2-vinyloxyethyl methacrylate with hydrogen iodide was employed as an initiator to induce living polymerization of ethyl vinyl ether in the presence of a small amount of iodine. According to ^1H and ^{13}C NMR analysis, the products were poly(ethyl vinyl ether) macromers 1 with a narrow molecular weight distribution having one methacrylate group at the chain end per molecule. The molecular weight of macromer 1 could be controlled by regulating the feed ratio of monomer to initiator.



$$CH_2{=}\overset{CH_3}{\overset{|}{C}}-COOC_2H_4O\overset{CH_3}{\overset{|}{C}H}-\!\left(CH_2-\underset{\underset{C_2H_5}{|}}{\underset{O}{\underset{|}{C}H}}\right)_{\!n}-OCH_3 \qquad (1)$$

INTRODUCTION

Recently, we have found that not only alkyl vinyl ethers (1) but vinyl ethers with a functional pendant (2) can be polymerized into living polymers by the HI/I_2 initiator under suitable conditions. Among a number of synthetic advantages offered by "living" polymerization, the elaborate control of polymer molecular weight distribution (MWD) and end functionality is of particular importance. Our previous investigations on the HI/I_2-initiated living polymerization have concerned primarily the extension of the scope of the process and the control of polymer molecular weight and MWD (synthesis of monodisperse polymers). In this paper, we now turn our attention to the control of the end functionality of poly(vinyl ethers), focusing in particular on the synthesis of macromolecular monomers (or "macromers") that have a radically polymerizable end-group attached to a monodisperse poly(vinyl ether) chain.

Principle of the Macromer Synthesis

The HI/I_2-initiated living polymerization of alkyl vinyl ethers proceeds as eq. 1 (4): (i) addition of HI to vinyl ether monomer to form adduct 2; (ii) activation of the C-I bond of 2 by added iodine; (iii) insertion of a monomer molecule (propagation); (iv) repetition of reactions (ii) and (iii) to give living polymer. Importantly, vinyl ether-HI adduct 2 has been found to initiate, in the presence of a small amount of iodine, a living polymerization that is essentially identical with that by the HI/I_2 initiator (5).

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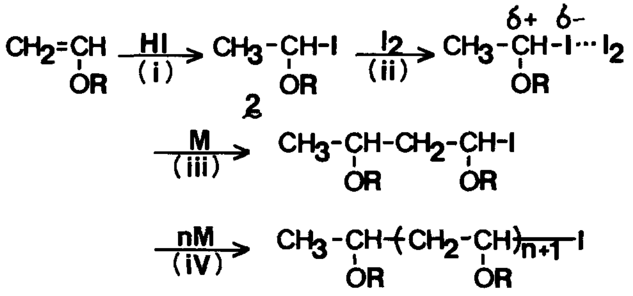
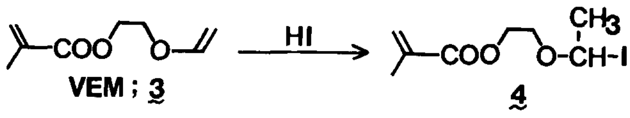


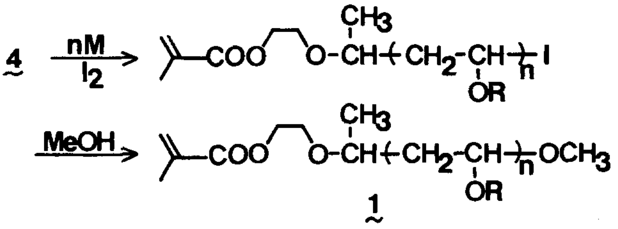
$$\mathrm{CH_2{=}CH(OR)} \xrightarrow[\text{(i)}]{\mathrm{HI}} \underset{\mathbf{2}}{\mathrm{CH_3\text{-}CH(OR)\text{-}I}} \xrightarrow[\text{(ii)}]{\mathrm{I_2}} \mathrm{CH_3\text{-}\overset{\delta+}{C}H(OR)\text{-}I\cdots \overset{\delta-}{I_2}} \xrightarrow[\text{(iii)}]{\mathrm{M}} \mathrm{CH_3\text{-}CH(OR)\text{-}CH_2\text{-}CH(OR)\text{-}I} \xrightarrow[\text{(iv)}]{\mathrm{nM}} \mathrm{CH_3\text{-}CH(OR)\text{-}(CH_2\text{-}CH(OR))_{n+1}\text{-}I}$$

[Eq.1]

In usual homopolymerizations, adduct **2** comes from the monomer itself, so that the head group [CH_3-CH(OR)] and the main chain of the polymer have the same pendant group OR. The proposed mechanism (eq. 1), however, implies that adduct **2** can polymerize vinyl ethers having an alkoxyl pendant OR' different from that (OR) in it. If HI adduct **4** (eq. 2) can be selectively prepared from vinyloxyethyl methacrylate (VEM) (**3**) and utilized as a "functionalized" initiator for living polymerization of vinyl ethers other than **3** (eq. 3), then the resulting polymers (**1**) will have a methacrylate head group attached to a poly(vinyl ether) chain with a monodisperse MWD. Thus, eqs. 2 and 3 provide a new simple method for preparing macromers via our living polymerization by the HI/I_2 initiator.



[Eq.2]



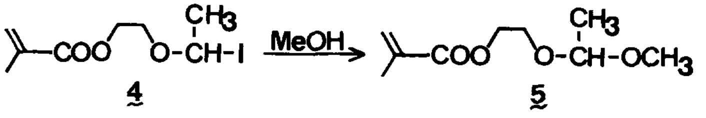
[Eq.3]

The present paper describes preliminary results of the synthesis of a methacrylate macromer (**1**) having a poly(ethyl vinyl ether) pendant, based on the strategy shown above. Initiator **4** is potentially able to polymerize any vinyl ethers, but in this study we employed ethyl vinyl ether, one of the simplest alkyl vinyl ethers, because of the easy structural characterization of its product.

RESULTS AND DISCUSSION

Preparation of Initiator 4

VEM-HI adduct **4** was prepared by the treatment of VEM with HI in toluene at -78°C under dry nitrogen (eq. 2). The quantitative formation of **4** was proved as follows. Since adduct **4** was not stable enough to be isolated at room



[Eq.4]

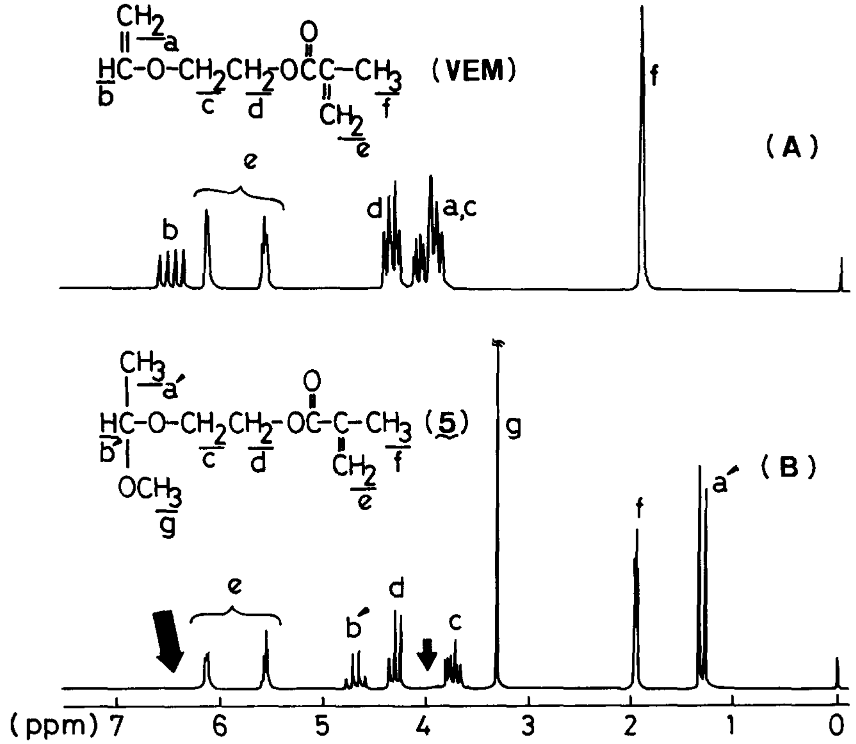


Figure 1. ^1H NMR spectra (A) VEM and (B) acetal 5 in $CDCl_3$.

temperature, it was converted in situ into a more stable acetal form (5) by quenching with methanol (eq. 4). The size exclusion chromatogram (SEC) of the product showed a sharp single peak; there was no peak assignable to VEM or polymeric by-products.

The ^1H NMR spectra of VEM and the acetalized product are shown in Figure 1, along with peak assignments. After the treatment of VEM with HI then with methanol, the absorption of the vinyloxyl group [ca. 6.4 ppm (=CH-O-)] of VEM disappeared completely, and methyl [1.3 ppm], methine [4.7 ppm], and methoxy [3.3 ppm] peaks appeared. In contrast to these changes, the methacrylate moiety [5.6 and 6.1 ppm] remained intact. In addition, the spectrum does not exhibit signals indicative of undesirable side reactions, e.g., the addition of HI or I_2 to the methacrylate group or HI-initiated polymerization via the vinyloxyl group. The formation of adduct 4 was also shown by ^{13}C NMR analysis: [δ(ppm); 166.6 (s,-COO-), 135.8 (s,=$\underline{C}$-CO-), 124.9 (t,CH_2=), 99.9 (d,-O-CH-O-), 63.5 and 62.1 (t,-O-CH_2CH_2-O-), 51.7 (q,-OCH_3), 18.5 (q,$\underline{C}H_3$-CH-O-), 17.6 (q,=C($\underline{C}H_3$)-CO-)]. These results show the selective addition of HI to the vinyloxyl group of VEM to form adduct 4.

Polymerization of Ethyl Vinyl Ether by $4/I_2$ Initiator

To a toluene solution of adduct 4 prepared at -78°C was added ethyl vinyl ether and iodine in this order, and then the temperature of the reaction mixture was raised to -40°C. The polymerization by the $4/I_2$ system proceeded without an induction phase up to 100% at a rate comparable to that by HI/I_2, as shown in Figure 2.

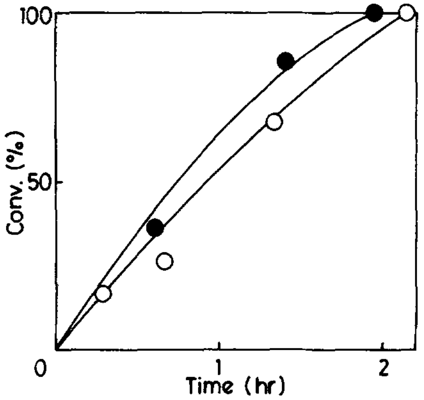


Figure 2. Time-conversion curves for the polymerization of ethyl vinyl ether in toluene at -40 °C and $[M]_0$= 0.50M. Initiator (mM): (●) HI/I_2, 10/5; (○) $4/I_2$, 10/5.

Figure 3 shows the MWDs of the products obtained at various feed ratios of ethyl vinyl ether to 4 ($[M]_0/[4]_0$= 5, 50, and 100; conversion ~100%). Every polymer has a very narrow MWD, the peak molecular weight of which is increasing progressively with increasing $[M]_0/[4]_0$ ratio. Furthermore, an increase of their molecular weight proportional to vinyl ether conversion (Figure 4) shows that 4, in conjunction with iodine, initiates the living polymerization of ethyl vinyl ether.

SEC analysis using refractometric and UV (λ= 255nm) dual detectors established that the samples contain methacrylate end groups over the whole range of their MWD.

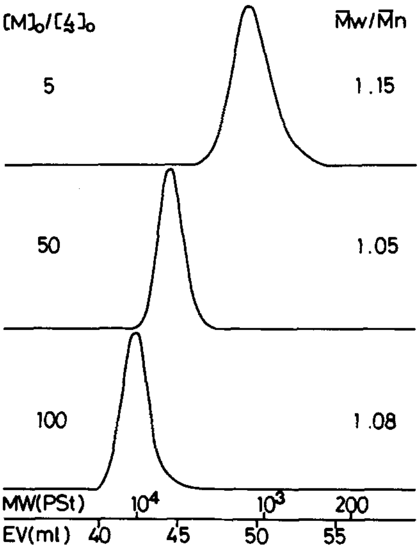


Figure 3. Effect of $[M]_0/[4]_0$ feed ratio on the MWD of macromer 1. See Table 1 for reaction conditions.

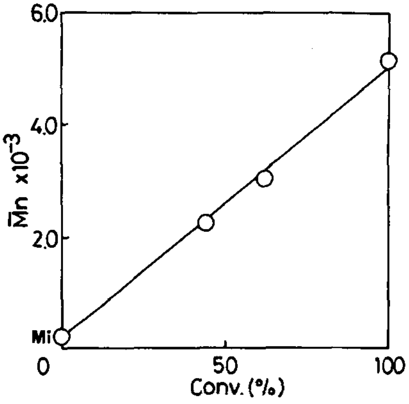


Figure 4. Relationship between conversion and $\overline{M}_n$ in the polymerization of ethyl vinyl ether by $4/I_2$ in toluene at -40 °C: $[M]_0$= 0.50M; $[4]_0/[I_2]_0$= 10/5 (mM). Mi indicates the molecular weight of initiator 4.

Characterization of Macromer

The structure and olefinic end functionality (Fn) of the macromers have been determined by ^1H and ^{13}C NMR spectroscopy. Figure 5 shows the ^1H NMR spectra of the macromers having 5 (Fig. 5A) and 100 (Fig. 5B) ethyl vinyl ether units in the pendant. The signals of the head methacrylate group [2.0 ($=C(CH_3)CO-$), 4.2 ($-COO-CH_2-$), and 5.6 and 6.1 ppm ($CH_2=$)] and the end acetal group [3.3 ($-OCH_3$) and 4.6 ppm ($-O-\underset{|}{C}H-O-$)] are clearly seen, together with the large three signals due to the poly(ethyl vinyl ether) chain [1.2 ($-OCH_2CH_3$), ~1.6 ($\leftarrow\!\!CH_2\text{-}\underset{|}{C}H\!\!\rightarrow_n$), and ~3.5 ppm ($-\underset{|}{C}H-O-CH_2-$)]. The numbers in Figure 5A indicate the relative signal intensities in percent determined from integrated peak areas; those in parentheses show the corresponding calculated values based on the assigned structure **6**. The agreement between the calculated and observed values is satisfactory, and no peaks assignable to other structures were detected. The ^{13}C NMR spectra of the macromers (e.g., Figure 6) also confirmed their expected structure **1**.

The number of the terminal methacrylate per polymer molecule (Fn) for macromer **1** was determined from the ratio of the integrated ^1H-NMR peak areas in Figure 5: a/2k = (methacrylate olefin)/(acetal end). The a/2k value directly gives the end functionality Fn. In addition, the a/c ratio [=(methacrylate olefin)/(VEM residue)] indicates the number of methacrylate olefins per VEM head group and should be unity when methacrylate-consuming side reactions are absent in the macromer synthesis. Table 1 shows these ratios for a series of macromer **1** with three molecular weights. The a/2k (Fn) and a/c values for all macromers are very close to unity within the experimental error, indicating that they carry one methacrylate function per one molecule.

The macromer synthesis route illustrated in eqs. 2 and 3 is applicable to vinyl ethers other than ethyl vinyl ether, including those with a functional group, which undergo living polymerization in the presence of HI/I_2.

Radical homopolymerization of macromer **1** and its copolymerization with methyl methacrylate were carried out in bulk or in benzene solution with azobisisobutyronitrile (AIBN) as an initiator, to yield high molecular weight polymers. Further studies in this line are now in progress.

TABLE 1

Synthesis of Macromer **1** in Toluene at -40°C [a]

Samples No.	$[M]_0$ (M)	$[\mathbf{4}]_0$ (M)	$[M]_0/[\mathbf{4}]_0$	Time (hr)	$\bar{M}_n$ [b] $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$ [b]	a/2k[c] (Fn[d])	a/c[c]
1	0.1	0.02	5	0.5	1.2	1.15	0.99	0.97
2	0.5	0.01	50	2	5.4	1.05	1.05	0.97
3	1.0	0.01	100	3	9.7	1.08	0.99	1.06

a) $[I_2]_0$= 0.005M; conversion ~100%.
b) Measured by SEC.
c) ^1H NMR peak intensity ratio; see Figure 5 and text.
d) Number-average end functionality of macromer **1**.

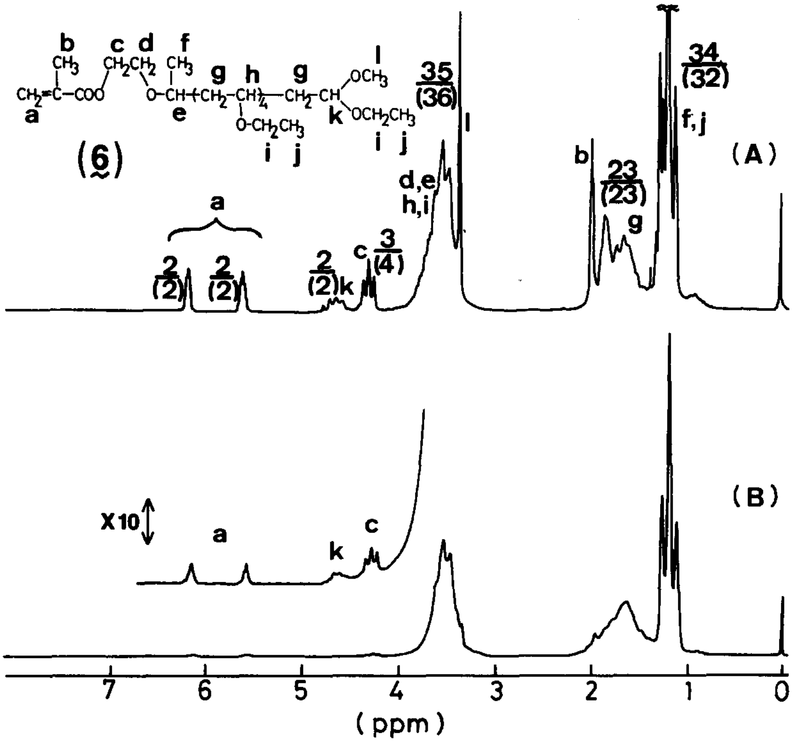


Figure 5. ^{1}H NMR spectra of macromers 1 having 5 (A) and 100 (B) ethyl vinyl ether units (samples 1 and 3, Table 1, respectively).

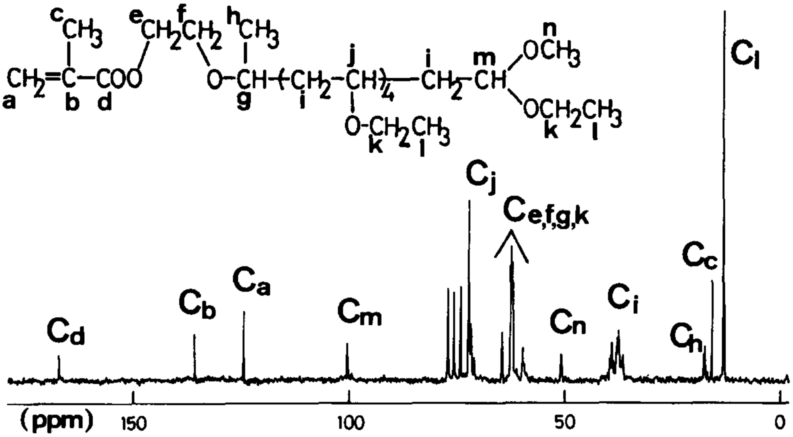


Figure 6. ^{13}C NMR spectrum of macromer having 5 ethyl vinyl ether units (sample 1, Table 1).

EXPERIMENTAL

The monomers, solvents, and initiators were prepared and/or purified as reported (1, 2). Polymerizations were carried out under dry nitrogen.

A typical example of the synthesis of macromer **1** having 50 ethyl vinyl ether units was as follows. In a baked vessel equipped with a three-way cock, 0.046 ml (0.3 mmol) VEM in toluene (24.6 ml) was treated with an equimolar amount of HI in hexane (330 mM, 0.9 ml) at -78 °C, to yield quantitatively adduct **4**. To this initiator solution was added, successively, ethyl vinyl ether (1.43 ml, 15 mmol) and iodine in toluene (50 mM, 3 ml) and the mixture was then kept at -40 °C. After 2hr, when the monomer had been consumed almost completely, the reaction was terminated with prechilled ammoniacal methanol. The quenched reaction mixture was washed with 10% sodium thiosulfate solution and then water to remove the iodine residues, and evaporated to dryness under reduced pressure to give the product macromer.

The MWD of the macromers was measured by SEC using polystyrene gel columns (1, 2). The $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ ratios were calculated from SEC curves on the basis of a polystyrene calibration. The ^{1}H and ^{13}C NMR spectra of the polymers were recorded on a JEOL FX-90Q spectrometer in $CDCl_3$.

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