

Reactions

Living Cationic Polymerization of Vinyl Ethers with a Functional Group

2. Polymerization of Vinyl Ethers with an Unsaturated Ester Pendant

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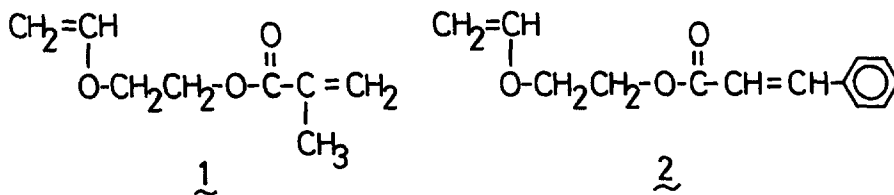
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SUMMARY

"Living" polymerizations of 2-vinyloxyethyl methacrylate and 2-vinyloxyethyl cinnamate were successfully performed with a mixture of hydrogen iodide and iodine (HI/I₂) as an initiating system in toluene at -15 to -40 °C. Although the two monomers have an unsaturated ester pendant group, their living polymerizations proceeded exclusively via the vinyloxy group without undesirable side reactions of the pendant group. The product polymers had a very narrow molecular weight distribution ($M_w/M_n \sim 1.1$), and M_n directly proportional to monomer conversion. For both vinyloxyethyl monomers, the addition of a new feed of monomer to a polymerization mixture led to an increase in polymer molecular weight which was again proportional to the conversion.

INTRODUCTION

Following our recent discovery of the perfectly "living" cationic polymerization of alkyl vinyl ethers initiated by a mixture of hydrogen iodide and iodine (HI/I₂ initiator) (1,2), the first paper of this series has shown that 2-acetoxyethyl vinyl ether (CH₂=CH-O-CH₂CH₂OCOCH₃), in spite of its polar ester pendant, can be cleanly polymerized by the same initiator to yield monodisperse living polymers (3). Encouraged by this breakthrough, we have now applied our HI/I₂ initiator to vinyl ethers having a reactive or polymerizable "unsaturated" ester group as pendant. This paper describes preliminary results on the HI/I₂-initiated living cationic polymerization of 2-vinyloxyethyl methacrylate (VEM; 1) and 2-vinyloxyethyl cinnamate (VEC; 2) in which, respectively, a methacryloyl and a cinnamoyl groups are connected to a vinyl ether moiety.



The methacryloyl group in VEM is, of course, radically or anionically polymerizable, whereas the cinnamoyl pendant in VEC readily undergoes four-centered photo-dimerization to form a cyclobutane ring. In view of the high cationic polymerizability of their vinyl ether moieties, these "functionalized" vinyl ethers are of interest as precursors of photoresists, curable coatings, etc. Besides these potential applications, they will provide, when cationically polymerized, an insight into the effects of polar and unsaturated ester groups on cationic vinyl polymerization in

general and "living" cationic polymerization in particular where unsaturated ester pendants may deteriorate the initiation and propagation processes.

VEM has been polymerized cationically (via the vinyloxy group) and anionically (via the methacryloyl group) to give soluble polymers (4). The cationically obtained poly(VEM) retained the methacryloyl groups intact and readily crosslinked on exposure to heat, light, or X-ray (5). Extensive studies by Kato et al. (6) on the cationic polymerization of vinyloxyethyl cinnamates including VEC led to high-performance photoresists now commercially available. The hitherto reported cationic polymerizations of VEM and VEC, however, are all non-living processes initiated by conventional Lewis-acid initiators, resulting in polymers with a broad, and uncontrolled molecular weight distribution (MWD). We have succeeded in living cationic polymerization of VEM and VEC with HI/I₂ initiator to obtain monodisperse polymers, as described below.

RESULTS AND DISCUSSION

Polymerization of 2-Vinyloxyethyl Methacrylate (VEM)

The possibility of living cationic polymerization of VEM was studied using HI/I₂ initiator in toluene at -15 to -40 °C. For comparison, boron trifluoride etherate (BF₃OEt₂) was also employed as initiator.

With both initiators the methacrylate derivative readily polymerized quantitatively to give soluble polymers. Figure 1A shows the MWD of the produced polymers at a 100 % conversion. BF₃OEt₂ yielded poly(VEM) with a broad (normal) MWD ($\bar{M}_w/\bar{M}_n = 2.46$), whereas HI/I₂ initiator led to a very narrow MWD ($\bar{M}_w/\bar{M}_n = 1.11$), similar to that of living poly(2-acetoxyethyl vinyl ether) ($\bar{M}_w/\bar{M}_n = 1.15$) produced by the same initiator (3).

In addition to the monodisperse MWD, analysis of polymer molecular weight (\bar{M}_n) demonstrated the living character of the HI/I₂-initiated polymerization of VEM (Table 1 and Figure 2). Thus, the \bar{M}_n of obtained poly(VEM) increased proportionally to the monomer-to-initiator feed ratio ($[M]_0/[HI]_0$) (Table 1, entries 3-6) and to monomer conversion (Figure 2). Addition of a fresh VEM feed to a polymerized solution led to a second-

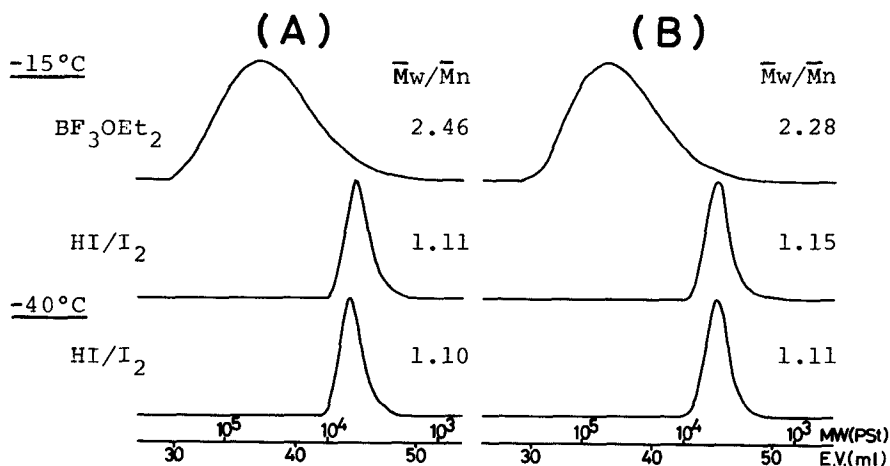


Figure 1. MWDs of poly(VEM) (A) and poly(VEC) (B) obtained in toluene at -15 and -40 °C: A (from top), samples 1, 2, and 3, Table 1; B (from top), samples 7, 8, and 9, Table 1. See also Table 1 for reaction conditions.

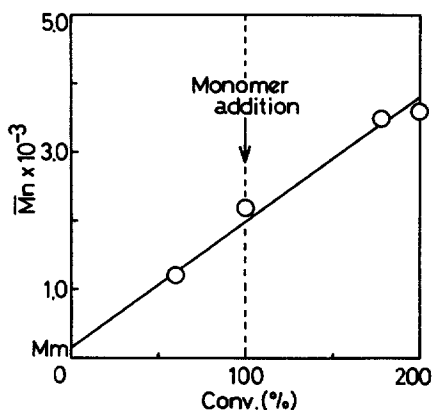


Figure 2. Relationship between conversion and \bar{M}_n before and after the monomer addition in the VEM polymerization by HI/I₂ in toluene at -40 °C: $[M]_0 = [M]_{\text{add}} = 0.16$ M; $[HI]_0/[I_2]_0 = 21/20$ (mM). Mm indicates the molecular weight of VEM monomer.

Table 1
Cationic Polymerization of VEM and VEC in Toluene^a

No.	Monomer	Initiator (mM)	$[M]_0$ (M)	Temp. (°C)	Time (hr)	\bar{M}_n^b $\times 10^{-3}$	$\frac{\bar{M}_w^b}{\bar{M}_n}$
1	VEM	BF ₃ OEt ₂ (2.0)	0.32	-15	0.25	22	2.46
2	VEM	HI/I ₂ (11/10)	0.32	-15	2.5	5.0	1.11
3	VEM	HI/I ₂ (10/10)	0.32	-40	31.7	5.9	1.10
4	VEM	HI/I ₂ (5/5)	0.32	-40	233	9.9	1.16
5	VEM	HI/I ₂ (23/20)	0.32	-40	7.5	3.1	1.09
6	VEM	HI/I ₂ (5/5)	0.64	-40	650	14	1.17
7	VEC	BF ₃ OEt ₂ (4.0)	0.21	-15	0.50	29	2.28
8	VEC	HI/I ₂ (10/10)	0.21	-15	1.3	4.5	1.15
9	VEC	HI/I ₂ (11/10)	0.21	-40	9.7	4.8	1.11
10	VEC	HI/I ₂ (3/3)	0.21	-40	700	12	1.28
11	VEC	HI/I ₂ (20/20)	0.21	-40	1.5	2.9	1.11
11A ^c	VEC	HI/I ₂ (20/20)	0.21 +0.21	-40	7.0	5.6	1.18

a) Conversion ~ 100 %.

b) Determined by size exclusion chromatography (polystyrene calibration).

c) Monomer addition experiment for run 11. To the completely polymerized reaction mixture of this run (1.5 hr after initiation) was added the same molar amount of fresh VEC (neat) as in the first-stage polymerization. The second dose of VEC polymerized quantitatively after 5.5 hr.

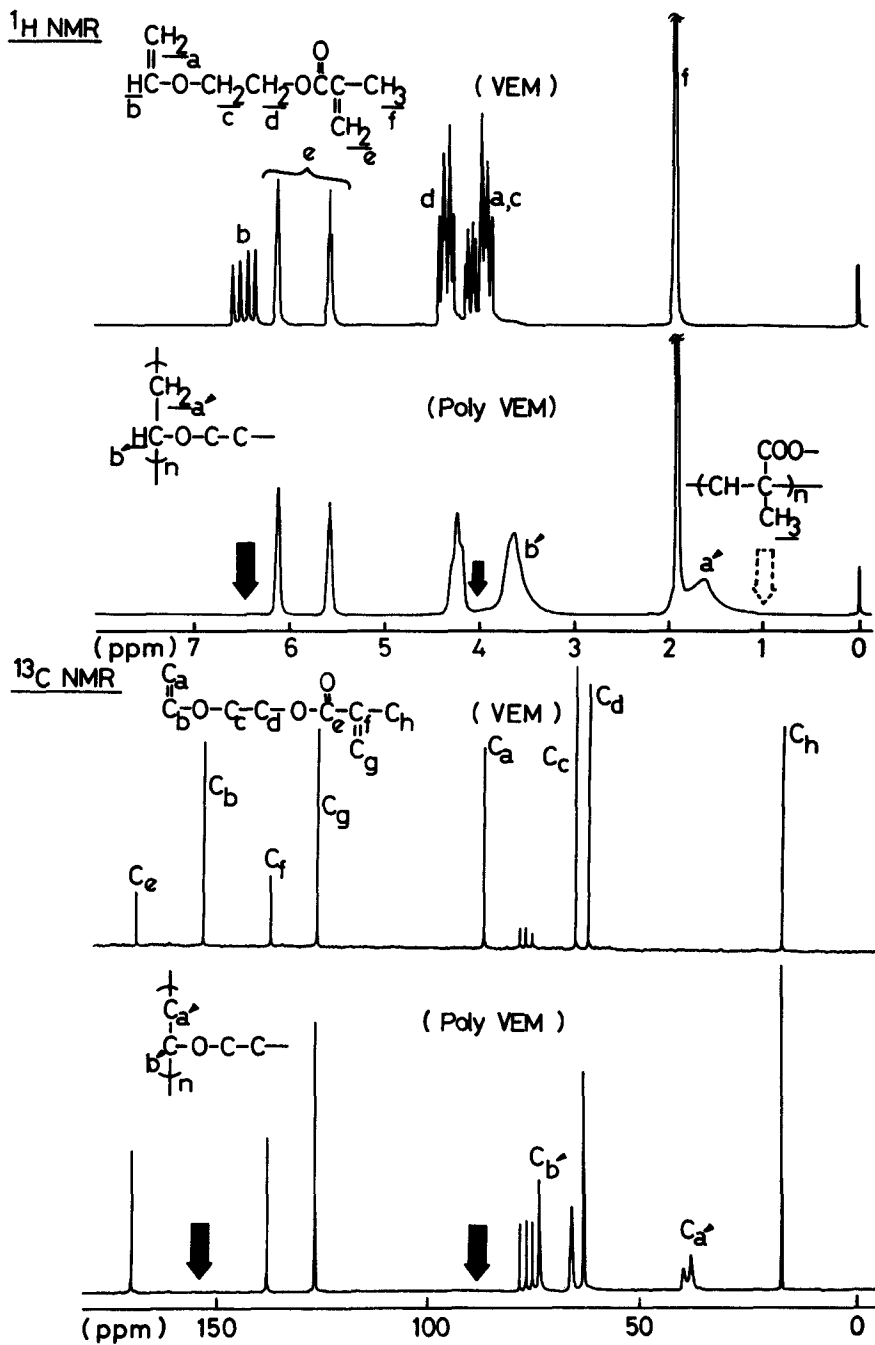


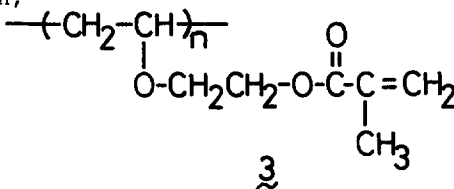
Figure 3. ¹H and ¹³C NMR spectra of VEM and poly(VEM) obtained with HI/I₂ in toluene at -40 °C (sample 6, Table 1).

stage polymerization in which the M_n of the polymers again increased with monomer conversion; the linear M_n -conversion plot passing the origin was retained before and after the monomer addition (Figure 2).

Figure 3 illustrates the 1H and ^{13}C NMR spectra of VEM monomer and its polymer produced by HI/I_2 . Comparison of the spectra shows that the poly-(VEM) is free from vinyloxy groups [1H NMR: ca. 6.4 ppm (=CH-O-); ^{13}C NMR: 86.5 and 151.2 ppm ($CH_2=CH-O-$)] but retains methacryloyl functions [1H NMR: 2.0 ppm ($=C(CH_3)-CO-$) 5.6 and 6.1 ppm ($CH_2=$); ^{13}C NMR: 17.7 (CH_3), 125.2 ($=C-CO-$), and 135.7 ppm ($CH_2=$)]. The absence of signals assignable to poly(methacrylate) units (e.g., 1H NMR, ca. 1 ppm for the methyl group) further excludes the possibility of side-reactions on the methacryloyl groups such as crosslinking, cyclization, and the addition of hydrogen iodide.

All these facts show that the HI/I_2 -initiated polymerization of VEM proceeds exclusively via its vinyloxy (vinyl ether) group to yield polymer 3.

When heated, the monodisperse poly(VEM) readily crosslinked to form an insoluble network.

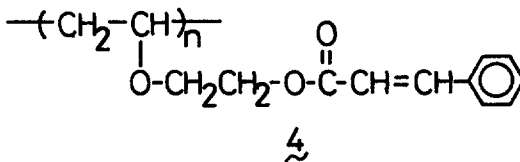


Polymerization of 2-Vinyloxyethyl Cinnamate (VEC)

Under reaction conditions similar to those for VEM, this cinnamate monomer was polymerized in toluene at -15 to -40 °C with HI/I_2 and BF_3OEt_2 as initiators. Figure 1B shows the MWD of the product polymers.

The polymerization by HI/I_2 initiator gave soluble polymers with a sharp MWD ($M_w/M_n = 1.11$). The M_n of the polymers increased proportionally to monomer conversion, and further increased on the addition of a fresh VEC feed to a polymerized reaction mixture (Table 1, entries 11 and 11A); the monodisperse MWD was retained for the polymers formed after the monomer addition. The polymer molecular weight can also be controlled by regulating the $[M]_0/[HI]_0$ feed ratio (Table 1, entries 9-11).

Figure 4 presents the 1H and ^{13}C NMR spectra of VEC monomer and poly-(VEC) obtained by HI/I_2 initiator, along with peak assignments. The spectra of the poly(VEC) lacked the signals due to vinyloxy groups but exhibited those of cinnamoyl groups; absorptions indicative of cyclobutane rings (1H NMR, ca. 5 ppm) (7) were absent. Therefore, the VEC polymerization with HI/I_2 occurs exclusively on the vinyloxy unit to give polymer 4, in the absence of any side reactions such as the cyclo-dimerization of the cinnamoyl groups.



EXPERIMENTAL

Materials

VEM and VEC were prepared by the phase transfer-catalyzed condensation of 2-chloroethyl vinyl ether with sodium methacrylate and cinnamate, respectively, in the presence of a catalytic amount of tetrabutylammonium iodide (6). The monomers, solvents (toluene and *n*-hexane), initiators, and other chemicals were purified as described (1,3).

Procedures

Polymerization by HI/I_2 was carried out under dry nitrogen. It was

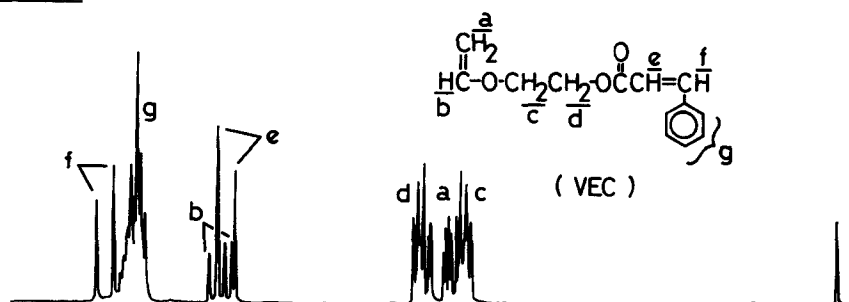
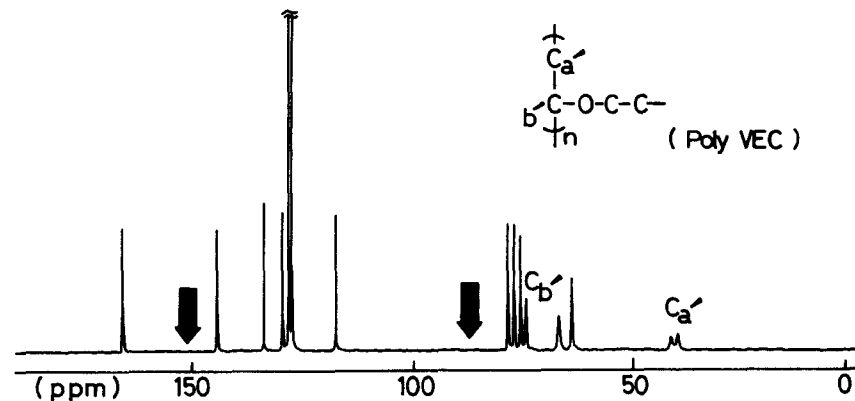
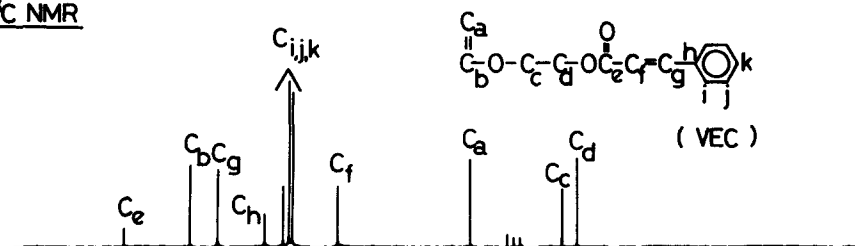
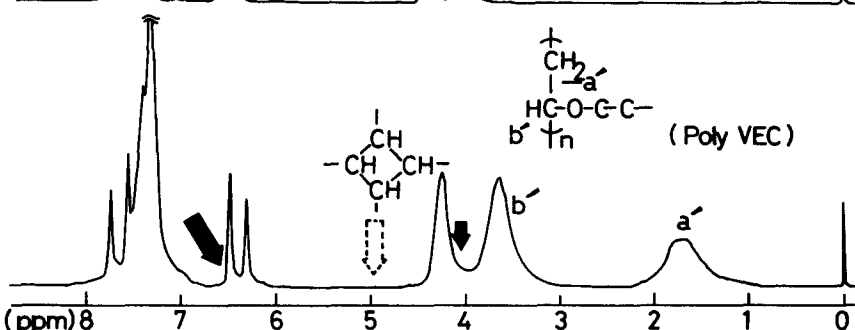
^1H NMR ^{13}C NMR

Figure 4. ^1H and ^{13}C NMR spectra of VEC and poly(VEC) obtained with HI/I_2 in toluene at -40°C (sample 10, Table 1).

initiated by adding, successively, a hydrogen iodide solution in *n*-hexane and an iodine solution in toluene to a monomer solution in toluene, and terminated with prechilled methanol containing a small amount of ammonia. The quenched reaction mixture was washed with 10 % aqueous sodium thiosulfate solution and then water to remove the initiator residues, followed by evaporation under reduced pressure to give the products. The MWD of the polymers was measured by size exclusion chromatography on a JASCO Trirotar-II chromatograph equipped with three polystyrene gel columns [Shodex A-802 and A-804 ($\times 2$)]. The \bar{M}_n and \bar{M}_w/\bar{M}_n ratios were calculated from size exclusion chromatograms on the basis of a polystyrene calibration. ^1H and ^{13}C NMR spectra were recorded on a JOEL FX 90Q spectrometer in CDCl_3 .

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Accepted March 5, 1985