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Living Cationic Polymerization

Living Cationic Polymerization of Vinyl Ethers with a Functional Group
3. Polymerization of Vinyl Ethers with Acrylate or Sorbate Pendant

Sadahito Aoshima, Osamu Hasegawa, and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto, 606 Japan

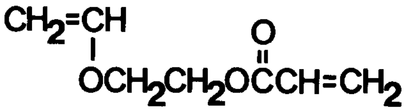
SUMMARY

Two unsaturated ester-containing vinyl ethers, 2-vinyloxyethyl acrylate (1) and sorbate (2), were polymerized by the hydrogen iodide/iodine (HI/I_2) initiating system in toluene at -15 or -40°C, to give "living" polymers, having a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$=1.10-1.15) and crosslinkable via their pendant C=C double bonds. The number-average molecular weight of the polymers increased in direct proportion to conversion, and further increased on addition of a new monomer feed to a polymerized reaction mixture. According to ^1H and ^{13}C NMR structural analysis, the polymerization proceeds exclusively via the vinyloxyl group of the potentially bifunctional monomers without undesirable side reactions of the unsaturated ester pendants.

INTRODUCTION

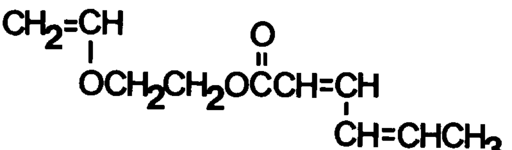
Recently, we have shown that the hydrogen iodide/iodine (HI/I_2) initiator, under appropriate conditions, induces living polymerization of vinyl ethers (1), including those with a variety of functional pendants such as ester, phenyl, and olefinic groups (2, 3). The HI/I_2-initiated living process thus provides new routes for the synthesis of functionalized polymers with a controlled molecular weight and structure, for the first time in the field of the cationic polymerization of vinyl compounds.

In this work, we examined the possibility of the living cationic polymerization of two unsaturated ester-containing vinyl ethers, 2-vinyloxyethyl acrylate (VEA; 1) and 2-vinyloxyethyl sorbate (VES; 2) in which, respectively, the simplest unsaturated ester (acrylate) and a conjugated dienyl ester (sorbate) groups are connected to a vinyl ether moiety. The preceding paper of this series (3) described the living polymerization of 2-vinyloxyethyl methacrylate and cinnamate, both having a sterically hindered C=C double bond (due to the α-methyl or β-phenyl group) in the ester pendant. When compared with these monomers, VEA and VES have a less crowded or "naked" double bond in the ester pendant, which is, therefore, more accessible to the propagating species and may be detrimental to living cationic polymerization. In addition,



$CH_2{=}CH{-}OCH_2CH_2OC({=}O)CH{=}CH_2$

1



$CH_2{=}CH{-}OCH_2CH_2OC({=}O)CH{=}CH{-}CH{=}CHCH_3$

2

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* To whom offprint requests should be sent

the reactive diene unit involved in VES may cause other side reactions. The cationic polymerization of VEA and VES have been performed by Nishikubo et al. (4) for the synthesis of resist materials crosslinkable by heat, light, or X-ray (5). Since they employed a metal halide initiator (BF_3OEt_2), however, they were unable to prepare living polymers, with a narrow molecular weight distribution (MWD). Using HI/I_2 initiator, we succeeded in the living cationic polymerization of VEA and VES and obtained poly(vinyl ethers) with a narrow MWD, controlled molecular weight, and unsaturated ester pendant.

RESULTS AND DISCUSSION

Cationic Polymerization of 2-Vinyloxyethyl Acrylate and Sorbate

To examine whether the unsaturated substituent of VEA and VES affects "living" cationic polymerization of vinyl ethers, these vinyloxyethyl monomers were polymerized by HI/I_2 initiator in toluene at -15 or -40 °C ($[M]_0$= 5vol%). For comparison, boron trifluoride etherate (BF_3OEt_2) and iodine (I_2) were also employed as initiators. BF_3OEt_2 is known to be effective for the synthesis of high-molecular-weight polymers in cationic polymerization; iodine is known to generate long-lived poly(vinyl ethers) but to initiate slowly vinyl ether polymerization (6).

With all the initiators, the polymerizations of both monomers proceeded quantitatively without an induction period, to give soluble products. Figure 1 shows the time-conversion curves for the polymerization of VEA as typical examples.

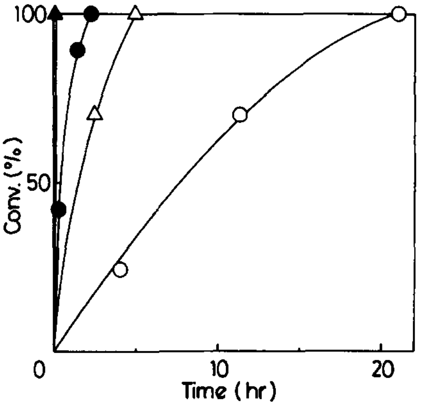


Figure 1. Time-conversion curves for the polymerization of VEA in toluene at -15 °C and $[M]_0$= 0.36M (5vol%). Initiator,mM: (▲)BF_3OEt_2,2; (△)I_2,20; (●)HI/I_2,12/10; (○)HI/I_2,12/10,(-40°C).

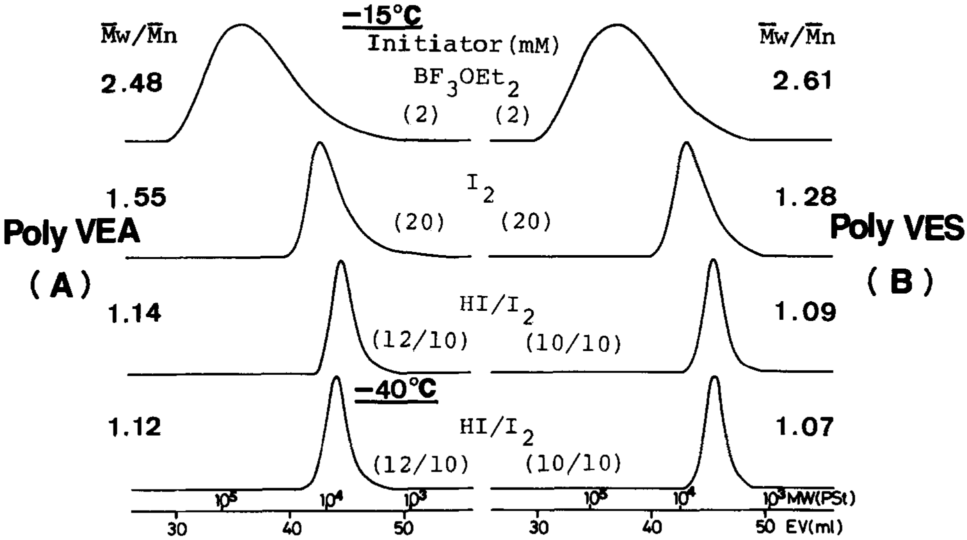


Figure 2. MWDs of poly(VEA) (A) and poly(VES) (B) obtained in toluene at -15 and -40 °C: see Table 1 for the $\overline{M}_n$ data and reaction conditions.

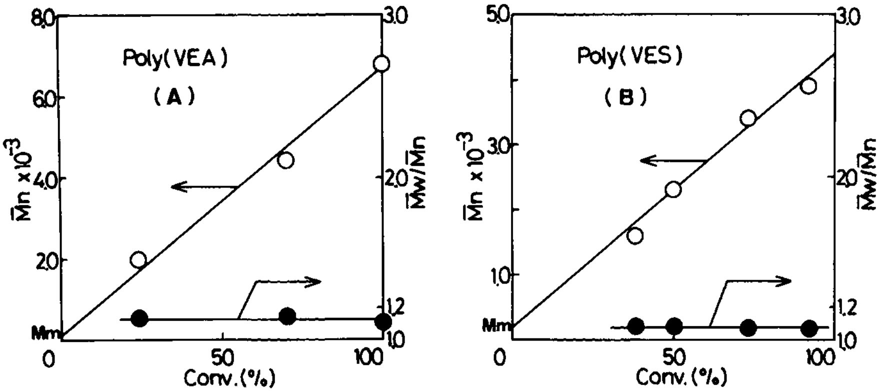


Figure 3. Relationships between conversion and $\overline{M}_n$ or $\overline{M}_w/\overline{M}_n$ ratio in the polymerization of VEA (A) and VES (B) by HI/I_2 in toluene at -40°C: A, $[M]_0 = 0.36M(5vol\%)$, $[HI]_0/[I_2]_0 = 12/10(mM)$; B, $[M]_0 = 0.27M(5vol\%)$, $[HI]_0/[I_2]_0 = 10/10(mM)$. Mm indicates the molecular weight of each monomer.

Separate experiments showed that the rate of homopolymerization of unsaturated ester-containing vinyl ethers by HI/I_2 initiator decreases in the order VES > VEA > 2-vinyloxyethyl methacrylate.

HI/I_2-Initiated Living Polymerization

Figure 2 shows the MWDs of the polymers obtained by the three initiators at -15°C (conversion ~100%; see also Table 1 for detailed data). BF_3OEt_2 gave higher molecular weight polymers with a broad MWD ($\overline{M}_w/\overline{M}_n \sim 2.5$). With iodine the MWD was narrower ($\overline{M}_w/\overline{M}_n = 1.3\text{-}1.6$) but consisted of a tailing in the lower molecular weight side. HI/I_2 initiator, in contrast, gave a very narrow MWD ($\overline{M}_w/\overline{M}_n = 1.10\text{-}1.15$); even at -40 °C where the polymerization was so slow as to reach a 100% conversion in 40-72 hrs, nearly monodisperse MWDs were obtained without undesired crosslinking of the unsaturated ester pendants.

Figure 3 illustrates the $\overline{M}_n$-conversion relationships for poly(VEA) and poly(VES) obtained with HI/I_2 initiator in toluene at -40°C. The $\overline{M}_n$ of the polymers linearly increased with the progress of the reaction, keeping the MWD very narrow. To obtain further evidence for the living nature of the HI/I_2-initiated processes, a new portion of VEA or VES (equimolar to the initial charge) was added to the polymerization mixture at a nearly 100% conversion. Figure 4 compares the MWDs of the polymers thus obtained before and after the monomer addition. After the monomer addition, the polymer molecular weight was doubled without any broadening in MWD nor producing by-products due to

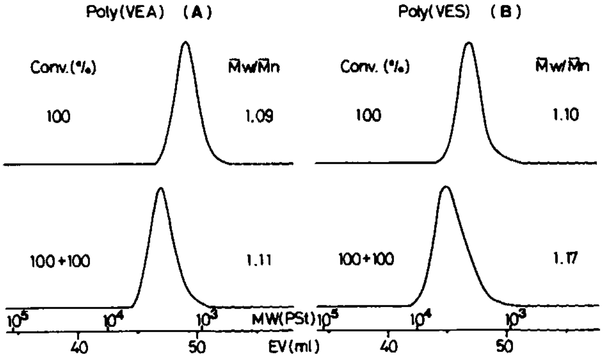


Figure 4. MWDs of poly(VEA) (A) and poly(VES) (B) obtained in monomer-addition experiments in the polymerization by HI/I_2 in toluene at -40°C: A, samples 7 and 7A, Table 1; B, samples 15 and 15A, Table 1: See also Table 1 for reaction conditions.

TABLE 1

Cationic Polymerization of VEA and VES in Toluene[a]

No.	Monomer	Initiator(mM)	$[M]_0$ (M)	Temp. (°C)	$\bar{M}_n$[b] $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$[b]
1	VEA	BF_3OEt_2 (2.0)	0.36	-15	25	2.48
2	VEA	I_2 (20)	0.36	-15	5.9	1.55
3	VEA	HI/I_2 (12/10)	0.36	-15	5.3	1.14
4	VEA	HI/I_2 (6/5)	0.71	-15	14	1.23
5	VEA	HI/I_2 (5/5)	0.36	-40	9.2	1.15
6	VEA	HI/I_2 (12/10)	0.36	-40	6.8	1.12
7	VEA	HI/I_2 (21/20)	0.18	-40	1.4	1.09
7A	VEA	HI/I_2 (21/20)	0.18 +0.18	-40	2.5	1.11
8	VES	BF_3OEt_2 (2.0)	0.27	-15	22	2.61
9	VES	I_2 (20)	0.27	-15	5.7	1.28
10	VES	HI/I_2 (10/10)	0.27	-15	3.9	1.09
11	VES	HI/I_2 (6/5)	0.54	-15	11	1.19
12	VES	HI/I_2 (5/5)	0.27	-40	8.0	1.19
13	VES	HI/I_2 (10/10)	0.27	-40	3.9	1.07
14	VES	HI/I_2 (22/20)	0.27	-40	2.2	1.09
15	VES	HI/I_2 (22/20)	0.27	-40	2.6	1.10
15A	VES	HI/I_2 (22/20)	0.27 +0.27	-40	4.0	1.17

a) Conversion ~100%.

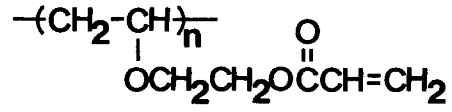
b) Determined by size exclusion chromatography (polystyrene calibration).

inactivation of the living ends and/or initiation of new shorter chains.

Table 1 summarizes the effects of reaction conditions on the polymerizations of VEA and VES in toluene. With HI/I_2 initiator, the $\bar{M}_n$ of polymer can be readily controlled by regulating the feed ratio of monomer to HI ($[M]_0/[HI]_0$).

Polymer Structure

Figure 5 compares the ^{1}H and ^{13}C NMR spectra of VEA monomer and its polymer obtained by HI/I_2 initiator, along with peak assignments. After polymerization, the absorptions of the vinyloxyl group of the monomer [^{1}H NMR: ca. 6.4 ppm (=CH-O-); ^{13}C NMR: 86.8 and 151.2 ppm (CH_2=CH-O-)] completely disappeared and, in turn, those of the main-chain methylene and methine groups [^{1}H NMR: ~1.7 and ~3.7 ppm ($(CH_2\text{-}CH)_n$); ^{13}C NMR: 39.0 and 40.6 (-CH_2-), 74.0 ppm (-CH-)] appeared. On the other hand, the absorptions of the acrylic olefin [^{1}H NMR: 5.8-6.6ppm; ^{13}C NMR: 127.9 and 130.5 ppm] remained unchanged. The two pendant methylene units (O-CH_2CH_2-OCO) are also observable in the polymer spectra with some broadening. Importantly, signals indicative of side reactions of the acrylate group (cross-linking, cyclization, and the addition of HI or I_2) are absent at all. These observations demonstrate that the polymerization of VEA by HI/I_2 initiator proceeds exclusively via its vinyloxyl group to yield polymer 3.



$$-\!\!(CH_2\text{-}\underset{OCH_2CH_2OCCH=CH_2}{\underset{|}{CH}})_n\!\!- \qquad \overset{O}{\overset{\|}{C}}$$

3

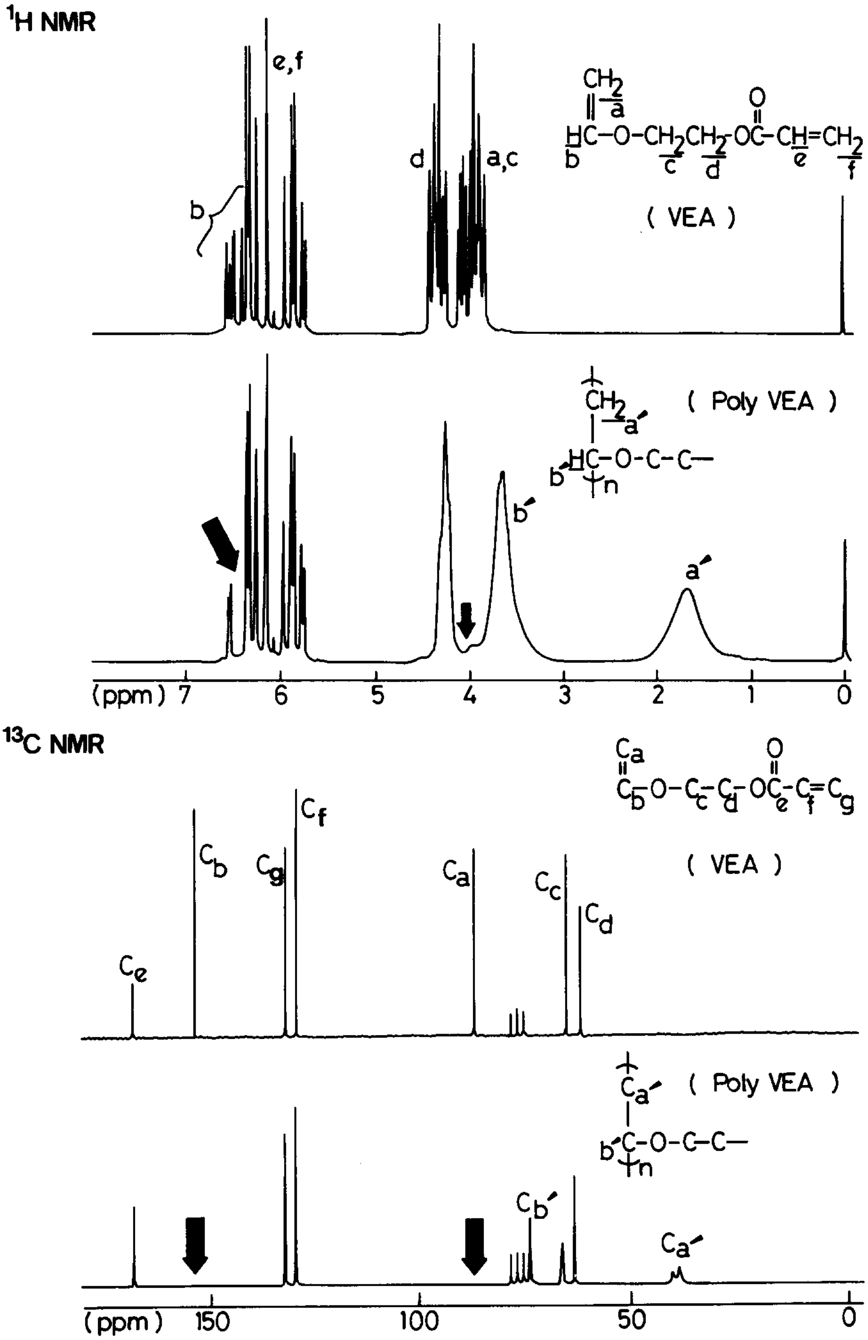


Figure 5. ^{1}H and ^{13}C NMR spectra of VEA and poly(VEA) obtained with HI/I$_2$ in toluene at -40 °C (sample 5, Table 1).

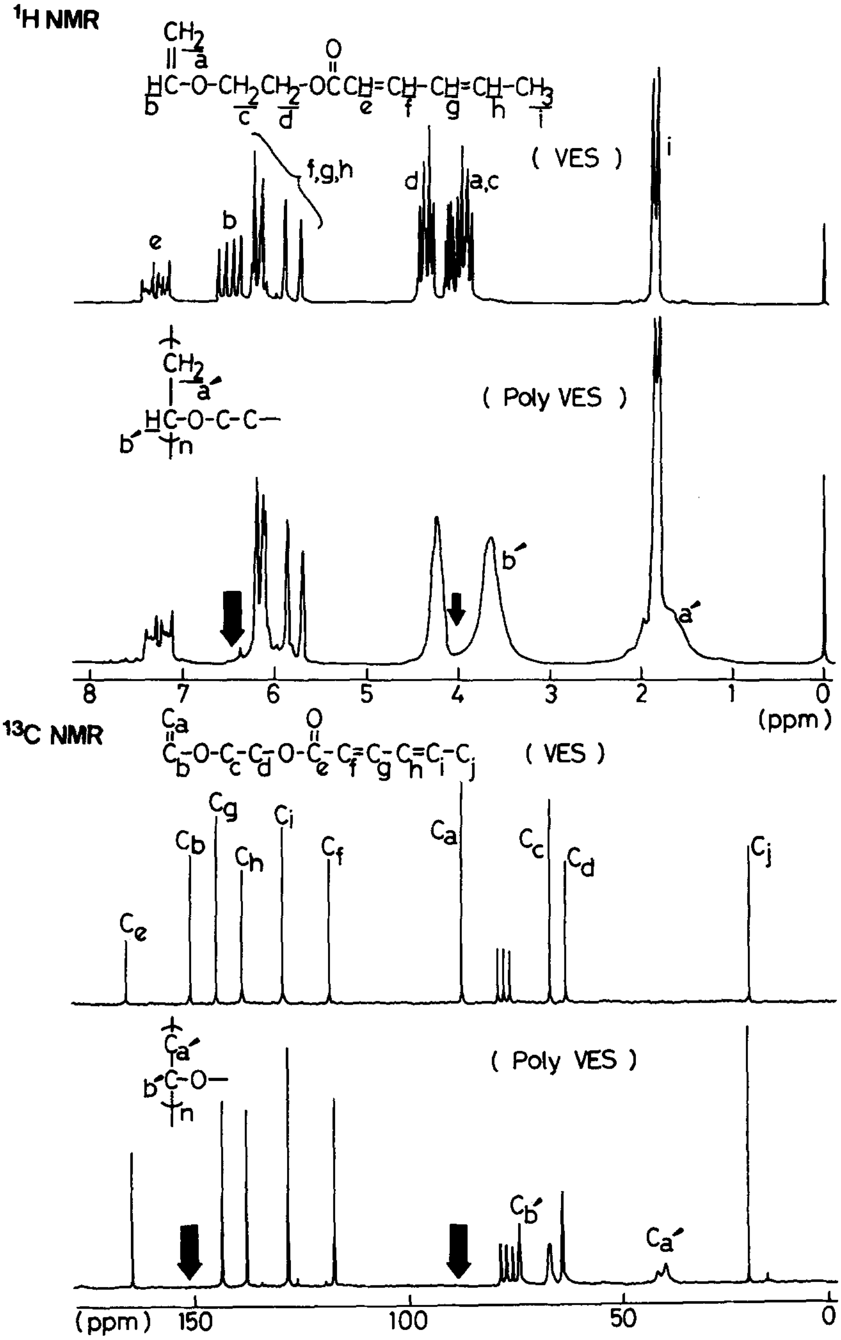
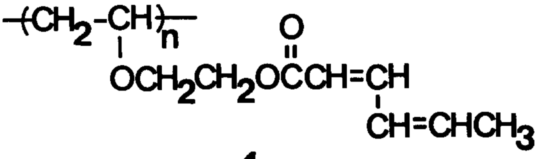


Figure 6. ^{1}H and ^{13}C NMR sprctra of VES and poly(VES) obtained with HI/I_2 in toluene at -40 °C (sample 12, Table 1).

Figure 6 shows the ^{1}H and ^{13}C NMR spectra of VES monomer and poly(VES) produced by HI/I$_2$ initiator. The spectra of the poly(VES) are free from vinyloxyl signals expected at ~6.4 ppm (^{1}H) and 86.9, 151.3 ppm (^{13}C) but clearly exhibit the sorbate absorptions [^{1}H NMR: 1.8, 5.7-6.2 and 7.1-7.4 ppm; ^{13}C NMR: 18.2, 118.4, 129.6, 139.1, 145.2, and 166.6 ppm], indicating the expected polymer structure **4**. In the ^{13}C NMR spectrum, however, small additional absorptions were detected in the aliphatic (13.7 ppm) and olefinic regions (120.2, 127.0, and 135.6 ppm). On the basis of the ^{13}C NMR analysis on a mixture of poly(VES) or its model compound for side chain (methyl sorbate) and iodine, these signals were assigned to the pendant diene groups of poly(VES) (**4**) complexing with molecular iodine. The complexation most likely takes place during not the living polymerization but the work-up of the polymer solution where iodine may be regenerated from the initiator residues.



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These investigations demonstrate that vinyl ethers VEA and VES can be polymerized by HI/I$_2$ initiator without side reactions to yield linear living polymers with a poly(vinyl ether), backbone carrying radical-sensitive unsaturated pendants. These polymers readily crosslink into an insoluble network, on heating [poly(VEA)] or even at room temperature [poly(VES)], without a radical initiator.

EXPERIMENTAL

VEA and VES were prepared by the reaction of 2-chloroethyl vinyl ether with the sodium salts of the corresponding carboxylic acids in the presence of small amounts of tetrabutylammonium iodide as a phase-transfer catalyst and *p-tert*-butyl catecol as a radical inhibitor; isolated yield 30-50%. The monomers, solvents, initiators, and other materials were purified and used as previously described (1-3).

Polymerization was carried out in a baked Shlenk tube equipped with a three-way stopcock under dry nitrogen. The reaction was initiated by adding an initiator solution with a syringe to a monomer solution and, after a certain period, quenched by adding ammoniacal methanol. Conversion to polymers was determined from the residual monomer concentration by gas chromatography. The $\bar{M}_n$ and MWD of the polymers were measured by size exclusion chromatography using a set of polystyrene gel columns calibrated against polystyrene standard samples (3).

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