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after cooling. This indicated that appreciable rearrangement had not occurred in this sample. This same tube was reheated at 145 °C for an additional 18 h. After the tube cooled, a large amount of VIII precipitated.

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Synthesis of Linear Poly(divinylbenzene) through Proton-Transfer Polyaddition by Oxo Acids

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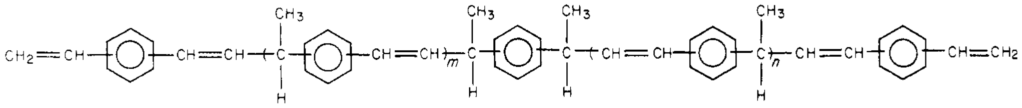
ABSTRACT: Polymerization of *p*- and *m*-divinylbenzenes to linear polymer took place without cross-linking with cationic oxygen-containing acid (oxo acid) catalysts such as CF_3SO_3H and $AcClO_4$ in nonpolar solvents above room temperature and at low monomer concentrations. The polymer was soluble in aromatic and halogenated hydrocarbons and consisted of trans olefinic and phenyl groups in the main chain with vinyl groups at both ends, that is



The molecular weight of the polymer increased with increasing conversion and further increased on sequential addition of monomer to the reaction mixture. The molecular weight of the polymer could be controlled in the range of about 10^2–10^4. A stepwise reaction mechanism is proposed for this linear divinylbenzene polymerization, in which the terminal vinyl group is protonated, the carbocation formed adds to another vinyl group, and a proton is immediately released to give an unsaturated linear backbone.

Linear polymers with carbon–carbon double bonds in the backbone and/or at chain ends are attractive as macromers because of the potential reactivity of the olefinic double bonds in the polymer chain and the end groups. Few examples have been reported which form unsaturated linear polymers from divinyl compounds with the exception of anionic and coordinative polymerization of conjugated 1,3-dienes (butadiene[1] and isoprene[2]). Polymers obtained from these monomers do not have terminal double bonds because the polymerizations are regular 1,4-addition reactions.

Divinylbenzene (DVB; diethenylbenzene) yields usually insoluble, cross-linked polymers in radical[3] and anionic[4] polymerizations. The cationic polymerization of DVB and its derivatives can give, under specific conditions, soluble polymers without cross-linking. In polymerizations of *o*-DVB,[5] the two vinyl groups in the monomer cannot propagate independently and cyclopolymerization occurs. Another example of a polymerization of divinylbenzene derivatives is the proton-transfer polyaddition of *p*-diisopropenylbenzene[6] and its derivatives,[7] forming cyclic structures with indan units in the main chain. The propagation of the sterically hindered isopropenyl group to form an indan structure proceeds no further than the dimer stage.[8] Polymerizations of α,ω-bis(4-vinylphenyl)alkenes also produce linear polymers.[9] However, no linear, unsaturated polymer has yet been prepared from DVB with cationic catalysts.

We have recently found that an unsaturated linear dimer (I) of styrene can be obtained in a very selective reaction with oxo acid catalysts, such as CF_3SO_3H and $AcClO_4$, via the reaction sequence shown in eq 1.[10–12]

It might be visualized that each vinyl group of DVB is capable of repeating the same reaction; if this type of reaction occurs instead of the conventional cationic addition polymerization, a linear unsaturated polymer III would be formed. (Scheme I; illustrated for *p*-DVB only for simplicity. The possible reactions of the cationic species are also omitted for simplicity.) The first process is the dimerization of DVB, analogous to eq 1, which yields a linear dimer II with two terminal vinyl groups. The dimer II can subsequently be protonated at either of the terminal vinyl groups, add to another DVB monomer, and release a proton to give a linear DVB trimer. Repetition

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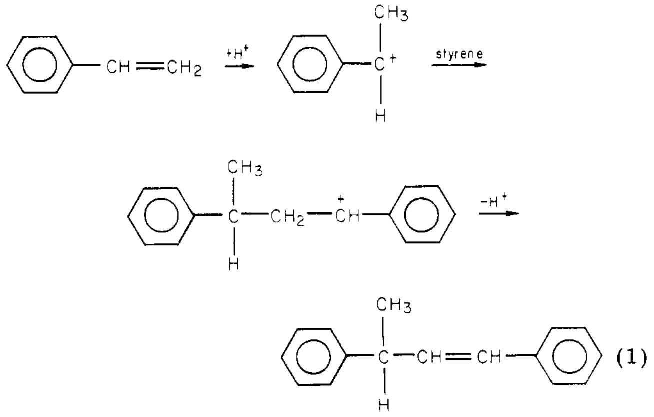


(1)

I

of such a protonation–propagation–transfer sequence involving only terminal vinyl groups eventually leads to polymer III; as can be seen from the equation, no cross-linking would be anticipated.

This paper describes the successful synthesis of a linear unsaturated polymer from DVB with an oxo acid catalyst such as CF_3SO_3H or acylium salts ($AcClO_4$). The new polymer III consists of a rigid polymer main chain composed of alternating olefinic and aromatic units and contains two terminal vinyl groups. Supporting evidence for Scheme I is presented and discussed.

Experimental Section

Materials. A commercial mixture of DVB (60%) and ethylvinylbenzene (40%) was washed with an aqueous alkali solution and was distilled over calcium hydride. The distillate was purified by preparative liquid chromatography with recycling (see below) to give an isomeric mixture of DVB ([*m*-DVB]/[*p*-DVB] = 70/30) with 0.7% ethylvinylbenzene (by gas chromatography). *p*-DVB was isolated from this mixture by the method of Storey et al.[13]

$AcClO_4$ was synthesized as described elsewhere.[14] $BF_3{\cdot}OEt_2$ was purified by distillation. CF_3SO_3H (Sumitomo 3M Co., purity ≥98%) was used without further purification. Solvents were purified as described[11] and were distilled over calcium hydride at least twice before use.

Polymerization Procedures. Polymerizations were carried out in an Erlenmeyer flask equipped with a three-way stopcock under a dry nitrogen atmosphere. The reaction was initiated by addition of the catalyst solution directly with a syringe into the monomer solution containing 0.10 M bromobenzene as an internal standard for gas chromatography. By this procedure the concentration of water in the solution was kept to less than 0.3 mM, as judged by independent water determination by Karl Fischer titration. After the desired time the polymerization was stopped by addition of methanol containing a small amount of aqueous ammonia. Conversion to polymers and oligomers was determined from the residual monomer concentration by gas chromatography.

After catalyst residues were removed from the reaction mixture by extraction with water, the product was isolated by removal of the unreacted monomer and the solvent under reduced pressure. When gelation occurred during the polymerization, the product was precipitated into methanol, the suspension was filtered, and the solid was washed several times with methanol and dried in vacuo.

When necessary, the fractions containing dimers to pentamers were separated from the isolated product by preparative liquid chromatography with recycling (JASCO TRIROTER chromatography; JSP-101 polystyrene gel column, 20-mm i.d. × 500 mm; chloroform eluent).

Characterization of Poly(divinylbenzene). The apparent molecular weight distribution of the product was determined by high-performance liquid chromatography (HLC), using a JASCO FLC-A700 apparatus with a refractive index detector and a polystyrene gel column (JSP-101 for $\bar{M}_n < 3 \times 10^3$ or Shodex GPC-A803 for $3 \times 10^2 < \bar{M}_n < 2 \times 10^5$). The number-average molecular weight ($\bar{M}_n$) was measured by vapor pressure osmometry (VPO; Hitachi Molecular Weight Apparatus 117) in benzene solution. Polymer structure was studied by ^1H NMR spectroscopy (60 and 100 MHz) in CCl_4 or $CDCl_3$ solution.

Scheme I

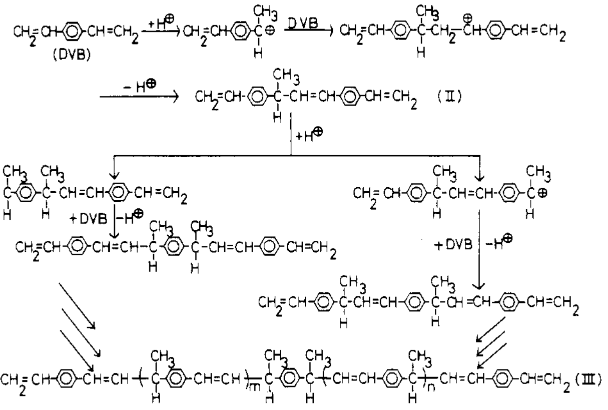


Table I
Molecular Weight ($\bar{M}_n$) and Solubility of Poly(divinylbenzene) Produced by Acid Catalysts ($[M]_0$ = 0.10 M, 70 °C)[a]

catalyst[b]	solvent	$\bar{M}_n$[c]	solubility[d] in $CHCl_3$	% conversion
$AcClO_4$	benzene	2000	soluble	98
$AcClO_4$[e]	benzene	4300	soluble	96
$AcClO_4$	$(CH_2Cl)_2$	3500	soluble	99
$BF_3{\cdot}OEt_2$	benzene	3500	soluble	90
$BF_3{\cdot}OEt_2$	$(CH_2Cl)_2$		insoluble	

[a] An isomeric mixture of DVB ([*m*-DVB]/[*p*-DVB] = 70/30) was used as monomer unless otherwise stated. [b] Catalyst concentration: $AcClO_4$, 0.50 mM; $BF_3{\cdot}OEt_2$, 5.0 mM (with 2.5 mM water as cocatalyst). [c] By VPO. [d] 100 mg of polymer/1 mL of $CHCl_3$, at room temperature. [e] With pure *p*-DVB.

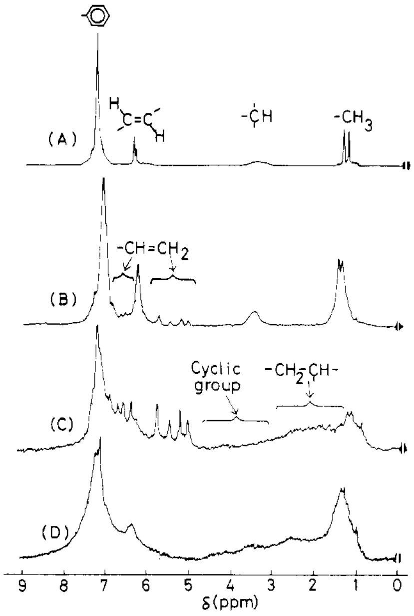


Figure 1. ^1H NMR spectra (60 MHz) of styrene dimer I (A) and poly(DVB) (B–D) obtained by acid catalysts ($[M]_0$ = 0.10 M, 70 °C). Catalyst and solvent: (A) $AcClO_4$, benzene; (B) $AcClO_4$, benzene; (C) $BF_3{\cdot}OEt_2$, benzene; (D) $AcClO_4$, $(CH_2Cl)_2$.

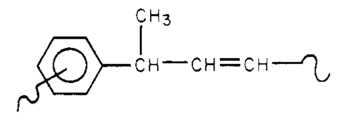
Results and Discussion

A. Cationic Polymerization of Divinylbenzene. 1. Reaction Conditions and Structure of the Products.

To examine the possibility of the formation of linear unsaturated polymers (Scheme I), we polymerized DVB ([*m*-DVB]/[*p*-DVB] = 70/30) with $AcClO_4$ or $BF_3{\cdot}OEt_2$ catalysts at low monomer concentration (0.10 M) above room temperature (70 °C). Under these conditions styrene yields primarily the linear dimer (eq 1).[12]

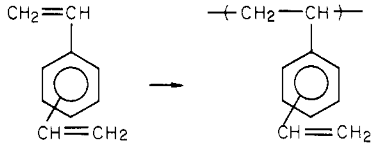
Table I shows the molecular weight ($\bar{M}_n$) and the solubility of the products. The $AcClO_4$–benzene system gave a polymer soluble in a number of aromatic or chlorinated hydrocarbons (benzene, toluene, CCl_4, $CHCl_3$, etc). In the $BF_3{\cdot}OEt_2$–$(CH_2Cl)_2$ system, on the other hand, gelation occurred to form an insoluble, cross-linked polymer. Polymers obtained with the $AcClO_4$–$(CH_2Cl)_2$ or the $BF_3{\cdot}OEt_2$–benzene systems needed longer times to dissolve in organic solvents than the products of similar molecular weights from the $AcClO_4$–benzene system because they were apparently partially cross-linked (see below).

Figure 1 shows the NMR spectra of the soluble polymers and the linear styrene dimer I. Spectrum A is the spectrum for the styrene dimer I. Spectrum B is that of the product obtained by the $AcClO_4$–benzene system which is very similar to that of A. Four major signals, i.e., phenyl, trans olefin, methine, and methyl, were observed and their intensity ratio was about 4:2:1:3. On the basis of the comparison of spectra A and B it appears that the polymer produced by polymerization of DVB with the $AcClO_4$–benzene system contains a linear unsaturated unit IV



IV

The small peaks at 5–7 ppm are characteristic of vinyl protons that may be present as either pendent (unit V in eq 2) or terminal (polymer III in Scheme I) groups. The absence of saturated methylene signals (1.5–3 ppm) (within the detectable limit of ~2%) for unit V indicates that the vinyl groups of the polymer are in the terminal position. The spectral data thus indicate the formation of the linear polymer III in the $AcClO_4$–benzene system.



V

(2)

Spectrum C for the product in the $BF_3{\cdot}OEt_2$–benzene system showed peaks which we attribute to the vinyl and $-CH_2CH<$ protons of unit V. Broad absorptions at 3–5 ppm distinguishable from the background noise are associated with cyclic structures[15,16] formed by intramolecular reactions of pendent vinyl groups. It is concluded that, in this system, addition polymerization of DVB (eq 2) occurred and that about 30% of the pendent vinyl groups were consumed by cross-linking and intramolecular cyclization.

In spectrum D for the product of DVB reaction in the presence of $AcClO_4$–$(CH_2Cl)_2$, a small signal (~6.3 ppm) indicating olefinic protons of unit IV is seen as well as peaks characteristic for cyclic units (3–5 ppm). In addition, proton chemical shifts at 1.5–3.0 ppm indicative of unit V ($-CH_2CH<$) were observed. It can be concluded that two reaction paths, stepwise linear polymerization (Scheme I) and conventional addition polymerization (eq 2), proceeded concurrently in this system.

Polymerization of DVB with oxo acid catalysts (CF_3SO_3H and p-$CH_3C_6H_4SO_3H$) in benzene at 70 °C also produced linear polymer III.

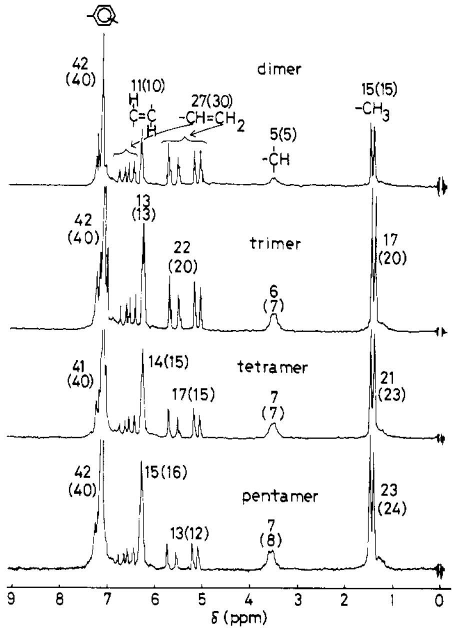


Figure 2. ^1H NMR spectra (90 MHz) of oligo(DVB) produced by $AcClO_4$ in benzene ($[M]_0$ = 0.10 M, 70 °C).

Some experiments to polymerize pure *p*-DVB with $AcClO_4$ in benzene (Table I), instead of the isomeric DVB mixture, were carried out. It was found that the overall reaction rate of the pure para isomer was greater than that of the meta/para mixture. The polymer from pure *p*-DVB was also of higher molecular weight than the polymer produced from the isomeric mixture. The ^1H NMR spectrum of the polymer of pure *p*-DVB was identical with spectrum B in Figure 1. Therefore, for most of our studies, the more easily available meta/para mixture was used.

2. Structure of Divinylbenzene Oligomers. The structures of DVB oligomers (dimer to pentamer) produced in the $AcClO_4$–benzene system were studied by ^1H NMR (Figure 2). The pure oligomers were isolated by HLC from a reaction product of DVB in the $AcClO_4$–benzene system at 65% DVB conversion (see Figure 4B). The ^1H NMR spectra of the oligomers were consistent with the structure of linear oligomer III. The numbers in Figure 2 indicate the relative signal intensities in percent determined from peak area; those in parentheses show the corresponding values based on the values calculated for structure III. The observed and calculated values were in good agreement, indicating that the polymer produced by $AcClO_4$ in benzene has the linear unsaturated structure III. It should be noted that no signals assignable to other units could be detected.

B. Polymerization with $AcClO_4$—Reaction Pathway. 1. Effect of Conversion. Figure 3 shows the relationship between $\bar{M}_n$ and conversion or reaction time for the polymerization with $AcClO_4$ in benzene ($[M]_0$ = 0.10 M, 70 °C). $\bar{M}_n$ increased gradually from ca. 300 to ca. 700 in the range of 0–80% conversion. The products obtained at this stage were oily materials. At higher conversion a steep increase of $\bar{M}_n$ was observed and white powdery polymers were isolated. The time–$\bar{M}_n$ plot gave a straight line. These time-course data suggest that the overall process of the DVB polymerization with $AcClO_4$ catalyst is kinetically similar to a step-growth reaction, such as polycondensation, rather than to a conventional addition polymerization.

These effects of conversion on the molecular weight distribution and the structure of the products are shown

Table II
Comparison between the Dimerization of Styrene with Polymerization of DVB[a] by Acid Catalysts

catalyst[b]	solvent	$[M]_0$, M	temp, °C	styrene dimer % yield[c]	structure of poly(DVB)[d]
$AcClO_4$	benzene	0.10	70	89	IV
$AcClO_4$	benzene	0.50	70	70	IV (major) + V (minor)
$AcClO_4$	benzene	0.10	5.0	70	IV (major) + V (minor)
$AcClO_4$	$(CH_2Cl)_2$	0.10	70	50	IV + V[e]
$BF_3 \cdot OEt_2$	benzene	0.10	70	10	V[f]
$BF_3 \cdot OEt_2$	$(CH_2Cl)_2$	0.10	70	2	V[e]

[a] [*m*-DVB]/[*p*-DVB] = 70/30. [b] Catalyst concentration: $AcClO_4$, 0.50 mM; $BF_3 \cdot OEt_2$, 5.0 mM (with 2.5 mM water as cocatalyst in benzene). [c] Reference 12. [d] Determined by ^1H NMR. For IV and V, see text. [e] Mostly cross-linked or cyclized. [f] Partially cross-linked or cyclized.

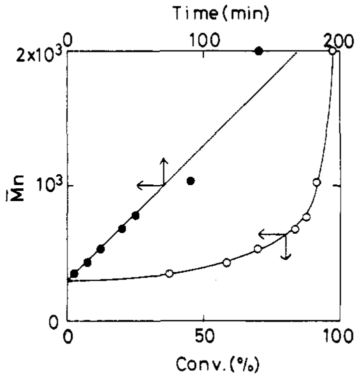


Figure 3. Dependence of polymer molecular weight on conversion (○) and reaction time (●) in the DVB polymerization by $AcClO_4$ in benzene ($[M]_0$ = 0.10 M, 70 °C).

in Figures 4 and 5, respectively. The oligomeric products at low DVB conversion contained a large amount of linear dimer II (Figure 4A). All the oligomers, irrespective of their molecular weight, gave ^1H NMR spectra (Figure 5) with a phenyl–trans olefin–methine–methyl ratio of 4:2:1:3 with a confidence limit of less than 5%. No signals indicative of oligomers or polymers formed by cyclization or cross-linking were observed.

The relative amount of vinyl protons decreased with increasing molecular weight of the products. The $\bar{M}_n$ values calculated from the ratio of phenyl to vinyl protons on the basis of linear structure III were in reasonable agreement with those determined by VPO (e.g., calcd 1700, obsd 2000, for the oligomer of Figure 4C). We conclude, therefore, that the propagation of DVB polymerization with $AcClO_4$ catalsyt in benzene proceeds by a step-growth reaction of the terminal vinyl groups as shown in Scheme I.

2. Effects of Monomer Concentration and Temperature. Figure 6 shows the NMR spectra of the polymers obtained at a high $[M]_0$ (0.50 M) (A) and a lower temperature (5.0 °C) (B). Both products were easily soluble in organic solvents and mainly consisted of oligomers and polymers containing linear unsaturated unit IV. However, the signals (1.5–3 ppm) assigned to methylene protons show the presence of unit V; i.e., conventional vinyl polymerization (eq 2) also takes place under these conditions.

Table II summarizes the dependence of the structure of poly(DVB) on reaction conditions. The successful synthesis of polymer III requires the use of $AcClO_4$ and a nonpolar solvent above room temperature and at a low $[M]_0$. Table II also lists the yield of dimer I in the styrene polymerization under the same conditions.[12] Note that the linear dimerization of styrene (eq 1) is mechanistically equivalent to Scheme I. The content of linear polymer of DVB (III) correlated closely with the dimer yield. This also seems to support the proposed pathway (Scheme I) for the formation of III.

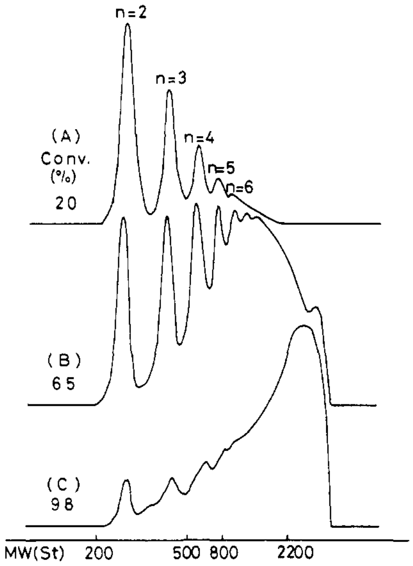


Figure 4. Effect of conversion on the molecular weight distribution of poly(DVB) obtained by $AcClO_4$ in benzene ($[M]_0$ = 0.10 M, 70 °C). The numbers on the peaks indicate the degree of polymerization. MW(St) means molecular weight based on a polystyrene calibration.

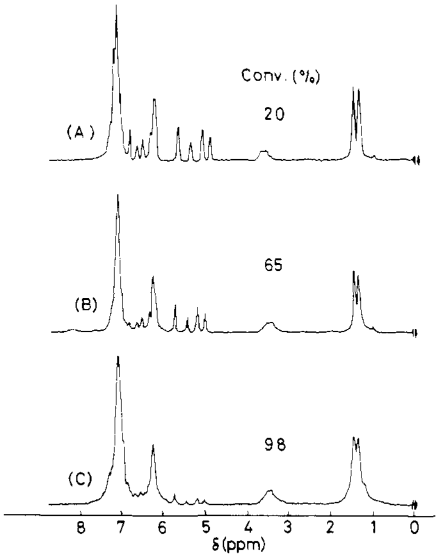


Figure 5. ^1H NMR spectra of poly(DVB) obtained by $AcClO_4$ in benzene at various conversions ($[M]_0$ = 0.10 M, 70 °C).

3. Linear Polymer of Divinylbenzene of High Molecular Weight. The polymerization of DVB to linear polymer described above was usually done at low monomer concentration ($[M]_0$ = 0.10 M); consequently the molecular

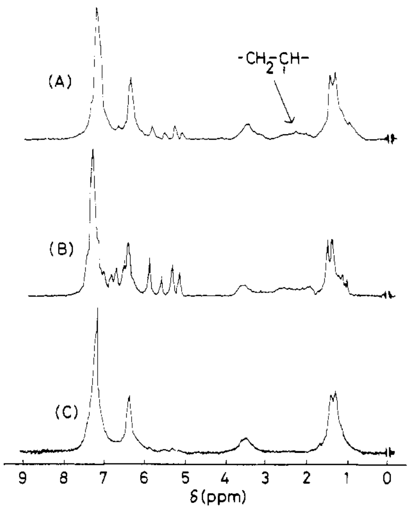


Figure 6. ^1H NMR spectra of poly(DVB) produced by $AcClO_4$ in benzene under different conditions: (A) $[M]_0 = 0.50$ M, at 70 °C; (B) $[M]_0 = 0.10$ M, at 5.0 °C; (C) after the sequential monomer addition was repeated seven times, at 70 °C (cf. Figure 7).

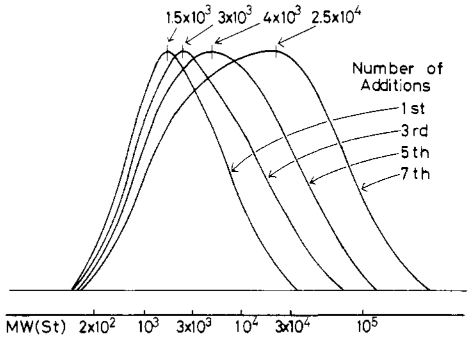


Figure 7. Effect of sequential monomer addition on the molecular weight distribution of poly(DVB) obtained with $AcClO_4$ in benzene at 70 °C: DVB concentration for each addition was 0.1 M. MW(St) indicates the molecular weight based on a polystyrene calibration. New monomer feeds were added every 45 min.

weight of the polymer of DVB (III) was at most 2000 (Figure 3). Polymerization at high $[M]_0$ gave higher molecular weight products but they contained not only the linear unit IV but also pendent vinyl groups which caused cross-linking (Figure 6).

For the preparation of the linear polymer of DVB (III) with high molecular weight, new monomer had to be repeatedly added to the reaction mixture when 70–80% of the previously supplied DVB had been consumed. This sequential monomer addition (repeated up to seven times) allowed the polymerization of large quantities of DVB while its concentration was kept at low concentration of below 0.1 M. Polymerization occurred readily when new monomer was added. The molecular weight of the polymers increased with the number of monomer additions (Figure 7). After the seventh monomer addition, the apparent peak molecular weight of the polymer of DVB judged by the GPC curve (polystyrene calibration) reached 2.5×10^4. The polymer was still easily soluble in common organic solvents and its ^1H NMR spectrum (Figure 6C) was very similar to that of the polymer of structure III (Figure 1B). Thus, the repeated monomer addition provided a new method for synthesizing linear polymers of DVB III of high molecular weight.

In this paper we reported for the first time the step-growth polymerization of DVB to linear polymers by acid catalysts. Structural analyses, primarily by ^1H NMR spectroscopy of the products, have indicated that the most likely reaction pathway is that shown in Scheme I for the preparation of these novel linear polymers or oligomers of DVB which have alternating olefinic and aromatic units (IV) in the main chain and two terminal vinyl groups. Preliminary experiments revealed that these polymers can still undergo further reactions and gave insoluble materials on heating at 100 °C or on treatment with $BF_3{\cdot}OEt_2$ in $(CH_2Cl)_2$ at room temperature. Studies on various reactions of the linear polymer of DVB (III) are in progress.

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