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Synthesis of α,ω-Bifunctional Linear Poly(divinylbenzene)

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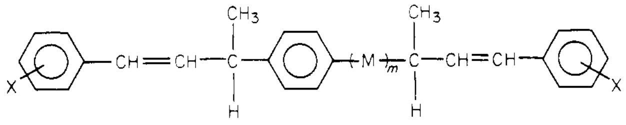
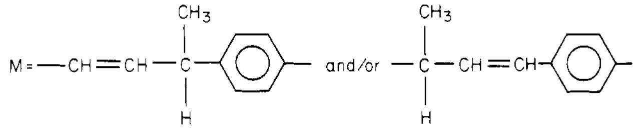
ABSTRACT: Linear poly(divinylbenzene) (I) having a variety of functional groups (X = acetoxyl, hydroxyl, and chloromethyl) at both chain ends was prepared by copolymerization of divinylbenzene (DVB) and a substituted styrene (Sts) catalyzed by acetyl perchlorate in benzene solvent at 70 °C. The molecular weight of polymer I ($\bar{M}_n = 3 \times 10^2$–$2 \times 10^3$) could be controlled by regulating the feed ratio of DVB and Sts. Polymer I of higher molecular weight ($>3 \times 10^3$) was also synthesized by the reaction of Sts with a linear poly(DVB) having vinyl termini. Polymer end-group analysis by ^{1}H NMR spectroscopy showed that the functionality of polymer I, obtained after quantitative reaction of DVB, is close to two for the three functional groups. The relative reactivities of DVB and Sts were also discussed on the basis of the end-group analysis.



I



α,ω-Bifunctional (telechelic) oligomers and polymers have elicited active interest among polymer chemists because of their versatility in elastomer synthesis, chain extension, network formation, and the like.[1] Conventional syntheses of telechelic polymers via cationic polymerization proceed through many steps, involving preparation of prepolymers and subsequent functionalization of their chain ends.[2] Careful and often cumbersome purification of the prepolymers is mandatory for the high functionality and yield of telechelic polymers. Another approach to the functionalized polymer synthesis is the "inifer" method,[2a] which, although simple and effective, is thus far confined to α,ω-*tert*-chlorinated polyisobutylene; introduction of other functional groups requires polymer reactions of the isolated polyisobutylene dichloride.[2a]

This paper presents a new, single-step synthesis of a series of α,ω-bifunctional linear poly(divinylbenzene) (I) by the cationic polymerization of divinylbenzene (DVB) in the presence of a substituted styrene (Scheme I). The synthesis is based on our recent finding[3] that DVB, in conjunction with acetyl perchlorate ($AcClO_4$) initiator, polymerizes without cross-linking to give linear polymer II (Scheme I). The key process of the linear DVB polymerization is the counteranion-assisted[4] facile β-proton elimination from the propagating cation. Because of this frequent chain transfer, each vinyl group of DVB monomer can undergo only "dimerization" to give a linear unsaturated polymer backbone (II) capped with vinyl groups at both ends.

It occurred to us that when such DVB polymerization was carried out in the presence of a substituted styrene, the resulting poly(DVB) would possess styrene units, instead of vinyl groups, at both termini (Scheme I). Once the propagating DVB cation reacts with the styrene (a monofunctional monomer) to form the styryl-type cation, it would quickly release its β proton,[4] yielding polymer I that lacks polymerizable vinyl groups. The ring substituent of the terminal styrene unit thus serves as an end-functional group. In view of the wide variety of substituted styrenes, our method outlined in Scheme I will enable the synthesis of telechelic poly(DVB)'s with various functional groups.

In this work we have prepared telechelic poly(DVB)'s having acetoxyl (I-AcO) and chloromethyl (I-ClMe) termini by the $AcClO_4$-initiated polymerization of DVB in the presence of the corresponding substituted styrenes.

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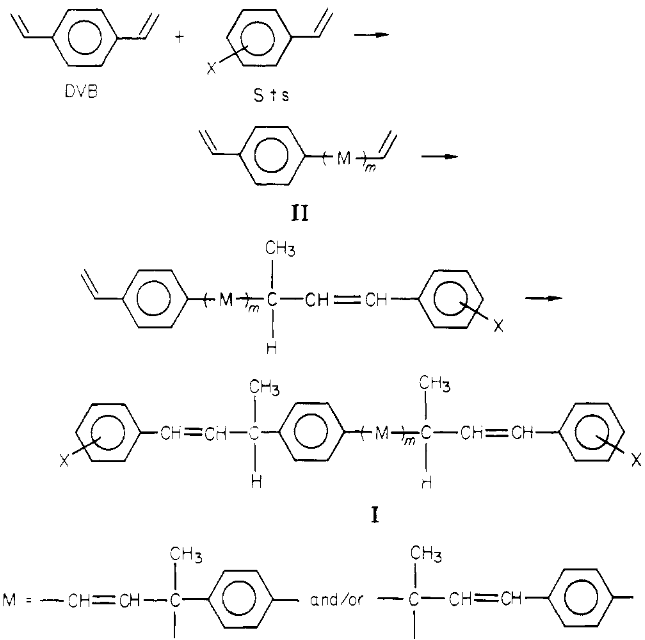
Scheme I



I-Me, X = p-CH_3
I-AcO, X = p-$OCOCH_3$
I-OH, X = p-OH
I-ClMe, X = p- or m-CH_2Cl

Quantitative hydrolysis of I-AcO gave the α,ω-dihydroxy derivative, I-OH. The relative reactivities of DVB and several styrenes in the cationic linear oligomerization were also evaluated on the basis of end-group analysis of these polymers.

Experimental Section

Materials. An isomeric mixture of DVB ([mDVB]/[pDVB] = 70/30) with ethylvinylbenzene and diethylbenzene (0.7% in total, by gas chromatography) was obtained by liquid chromatographic fractionation of commerical DVB as reported.[3] pDVB (purity >99%) was isolated from this mixture by the method of Storey et al.[5] The residual fraction was further separated by preparative liquid chromatography to give mDVB ([mDVB]/[pDVB] = 92/8).

p-Methylstyrene (pMeSt) was synthesized from p-methylacetophenone as reported.[6] p-Acetoxystyrene (pAcOSt; Maruzen Oil Co.) and (chloromethyl)styrene (ClMeSt; [m-ClMeSt]/[p-ClMeSt] = 2/1; Tokyo Kasei Co.) were obtained commercially. The three monomers were purified by distillation over CaH_2 under reduced pressure before use (gas chromatographic purity: pMeSt, >99%; pAcOSt, 97%; ClMeSt, 98%).

$AcClO_4$ was synthesized as described elsewhere.[7] Benzene as solvent was purified by distillation over CaH_2 at least twice before use.

Procedures. Polymerizations were carried out in a baked Erlenmeyer flask equipped with a three-way cock under a dry nitrogen atmosphere. The reaction was initiated by addition of the catalyst solution with a syringe into the monomer solution (a mixture of DVB and a substituted styrene). After the desired time, the polymerization was stopped by addition of methanol containing a small amount of aqueous ammonia. Conversions of DVB and Sts were determined from the residual monomer concentrations by gas chromatography, with bromobenzene as internal standard. The reaction solution after quenching was washed with water to remove the catalyst residue, and the products were recovered from the organic layer by evaporation of the unreacted monomers and solvent under reduced pressure.

The apparent molecular weight distribution of the product was determined by high-performance liquid chromatography (HLC; Jasco Triroter chromatograph, JSP-101 polystyrene gel column, 20-mm i.d. × 500 mm, $CHCl_3$ eluent, refractive index detector). When necessary, the fractions in the molecular weight range 2 × 10^2–10^3 were separated from the product by preparative liquid chromatography with recycling. The structure of the products was determined by ^{1}H NMR spectroscopy (60 and 90 MHz) in CCl_4 or $CDCl_3$ solution and by infrared (IR) spectroscopy (Shimadzu IR-27G). The number-average molecular weight ($\bar{M}_n$) was measured by vapor pressure osmometry (VPO; Hitachi 117 molecular weight apparatus) in benzene solution at 30 °C.

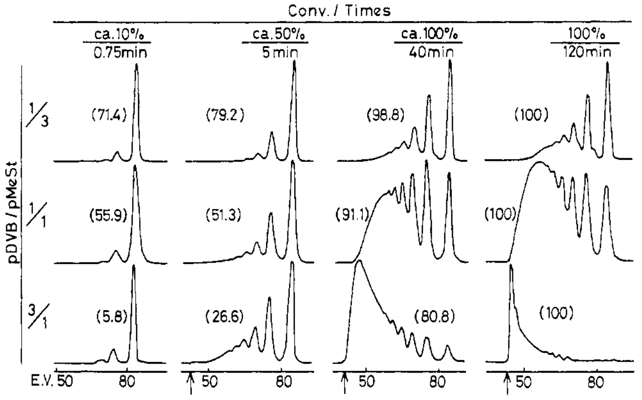


Figure 1. Effect of feed composition and conversion on the product distribution in the copolymerization of pDVB and pMeSt by $AcClO_4$ in benzene. The arrows indicate the exclusion limit of the HLC column. The values in parentheses indicate the percent of ring-substituted methyl groups in all end groups. $[pDVB]_0 + [pMeSt]_0 = 0.10$ M, $[C]_0 = 0.20$ mM; 70 °C.

The base-catalyzed hydrolysis of polymer I-AcO to I-OH was performed as follows.[8,9] A sample of I-AcO (0.3 g, ca. 2 equiv of $OCOCH_3$, $\bar{M}_n \simeq 600$) was dissolved in purified 1,4-dioxane (9.0 mL), and hydrazine hydrate (1.0 mL, 0.02 mol) was added. The mixture was stirred for 4 h at room temperature, neutralized with diluted hydrochloric acid, and washed with distilled water. The organic phase was evaporated to dryness and the residue was vacuum-dried overnight to give white polymer I-OH in quantitative yield; see Results and Discussion for the spectroscopic characterization of this product.

Results and Discussion

Copolymerization of pDVB with pMeSt: Orienting Experiments. To find out optimum conditions for the preparation of polymer I according to Scheme I, preliminary model experiments were performed on the copolymerization of pDVB with pMeSt that seems similar in reactivity to pDVB. The copolymerization was carried out with $AcClO_4$ initiator in benzene at 70 °C (a low monomer concentration). In the absence of pMeSt, pDVB polymerizes quantitatively to linear unsaturated polymers (II) under these conditions.[3]

Figure 1 shows the molecular weight distribution of the products obtained at various monomer feed ratios ($[pDVB]_0/[pMeSt]_0$) and conversions. At the same monomer feed ratio, the average molecular weight of the products increased gradually with increasing conversions of both monomers. Interestingly, higher oligomers and polymers further increased with reaction time even after pDVB was completely consumed. This tendency was more pronounced when pDVB was richer in the monomer feed. The average molecular weight at similar conversions increased with increasing pDVB feed. These increases in polymer molecular weight are due to chain extension via the vinyl groups of terminal DVB units.[3]

Figure 2 shows the ^{1}H NMR spectra of the copolymerization products together with the spectrum of a sample of linear homopoly(DVB) ($\bar{M}_n \sim 1000$).[3] The spectrum (Figure 2B) of the copolymerization product obtained at ca. 50% conversions of both monomers is quite similar to that of linear poly(DVB) (Figure 2A), which is characterized by the absorptions of vinyl (4.7–6.8 ppm) and aliphatic methyl (1.4 ppm) groups. In addition, Figure 2B

Table I
End-Group Ratios ($-C{=}C/-C_6H_4CH_3$) for Polymer I-Me[a]

reaction time, min	conv, %	[*p*DVB]/[*p*MeSt]	($-C{=}C/-C_6H_4CH_3$)				
			$n^b = 2$	$n = 3$	$n = 4$	$n = 5$	overall
5	ca. 50	1/1	1.06	0.88	0.90	0.97	0.95
		3/1	3.07	2.47	2.55	2.92	2.76
40	ca. 100	1/1	0.08	0.10	0.08	0.07	0.10
		3/1	0.12	0.22	0.23	0.24	0.24
120	100	1/1	0.00	0.00	0.00	0.00	0.00
		3/1	0.00	0.00	0.00	0.00	0.00

[a] $[pDVB]_0 + [pMeSt]_0 = 0.1$ M, catalyst $AcClO_4$, $[C]_0 = 0.2$ mM, solvent benzene, 70 °C. [b] The number of monomer units (*p*DVB and/or *p*MeSt); e.g., the fraction with $n = 3$ contains DVB-DVB-DVB, DVB-DVB-Sts, and Sts-DVB-Sts.

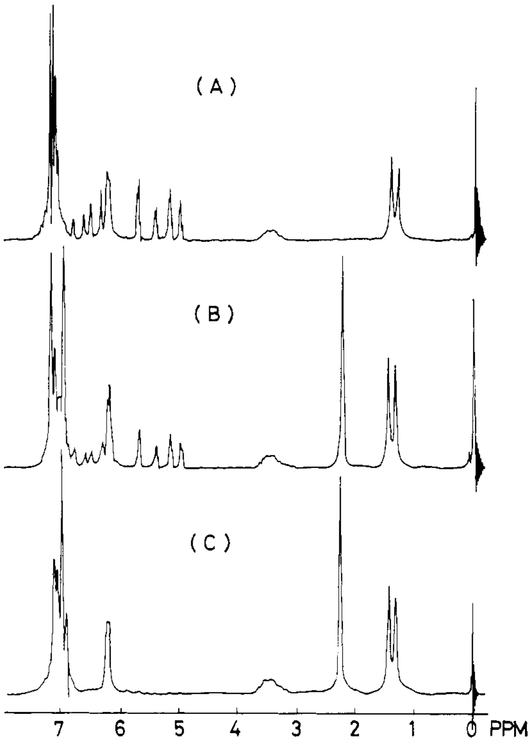


Figure 2. ^1H NMR spectra of linear poly(DVB) (A; from ref 1) and *p*DVB-*p*MeSt copolymerization products (B and C) obtained by $AcClO_4$ initiator in benzene at 70 °C. Reaction time: (A) 10 min; (B) 5 min; (C) 40 min. Conversion: (A) ca. 70%; (B) ca. 50% (both *p*DVB and *p*MeSt); (C) ca. 100%. $[pDVB]_0 = [pMeSt]_0 = 0.050$ M, $[C]_0 = 0.20$ mM.

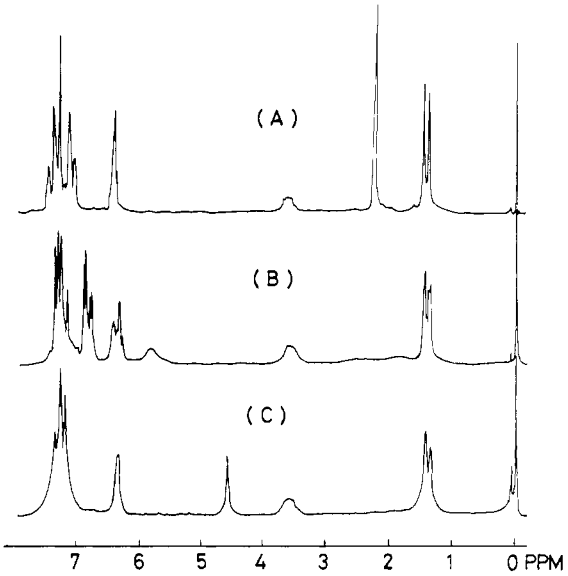


Figure 3. ^1H NMR spectra of polymer I-AcO (A), I-OH (B), and I-ClMe (C) obtained by $AcClO_4$ in benzene at 70 °C: $[pDVB]_0 + [Sts]_0 = 0.10$ M, $[C]_0 = 0.20$ mM. (A) $[pDVB]_0/[pAcOSt]_0 = 1/3$; (C) $[pDVB]_0/[ClMeSt]_0 = 1/1$.

exhibits a sharp singlet (2.3 ppm) due to the ring-methyl group. These results show that the copolymerization product has the expected linear unsaturated structue I-CH_3 (Scheme I) and that the polymer is capped with either the *p*DVB or *p*MeSt unit. On the other hand, the absorption of the vinyl group completely disappeared in the spectrum (Figure 2C) for the product at the end of the reaction. This final product possesses, therefore, *p*MeSt terminal units only. The absence of signals due to the $-CH_2CH<$ group in both spectra 2B and 2C demonstrates that under our conditions neither *p*DVB nor *p*MeSt undergoes conventional vinyl polymerization. Thus, it was confirmed that polymer I could be obtained by the reaction shown in Scheme I, which proceeds via repetition of the "dimerization" of the vinyl groups of DVB (and/or its oligomers) and terminates when *p*MeSt is incorporated in the polymer chain.

The ^1H NMR spectra of the lowest six oligomer fractions (molecular weight 2×10^2–10^3; cf. Figure 1) isolated by HLC were all consistent with the structure of I-CH_3 (Scheme I). The number of terminal vinyl and/or methyl groups per oligomer was determined from the integrated peak area ratio of vinyl and ring-methyl protons to phenyl protons. This number was approximately 2 for all fractions.

Table I shows the relative numbers of the terminal vinyl to ring-methyl groups in each oligomer fraction. This ratio was dependent on the monomer feed composition and conversion but independent of the molecular weight of the oligomers provided they were formed under the same reaction conditions. The number of vinyl end groups decreases with decreasing DVB feed or at high conversion and completely disappears at 100% conversion.

α,ω-Diacetoxypoly(divinylbenzene) (I-AcO). To introduce acetoxyl groups (AcO) into both ends of linear poly(DVB), *p*DVB and *p*AcOSt were copolymerized by $AcClO_4$ in benzene at 70 °C ($[pDVB]_0 + [pAcOSt]_0 = 0.10$ M, $[pDVB]_0/[pAcOSt]_0 = 1/1$). *p*DVB was quantitatively consumed within 1 h, but the polymerization solution was allowed to stand another hour for complete reaction of the terminal vinyl groups with *p*AcOSt.

Figures 3A and 4A show, respectively, the ^1H NMR spectrum and the molecular weight distribution of the product obtained at quantitative conversion of *p*DVB and *p*AcOSt. The spectrum exhibited the sharp singlet (2.2 ppm) characteristic of the acetoxyl group and all signals due to the linear poly(DVB) backbone; absorptions of a terminal vinyl group were absent. The IR spectrum also showed the presence of the acetoxyl group [1760 ($\nu_{C=O}$) and 1200 cm^{-1} ($\nu_{C-C=O}$)]. Therefore, the copolymerization product is of structure I-AcO and its acetoxyl functionality is close to 2.0. This conclusion was supported by ^1H NMR

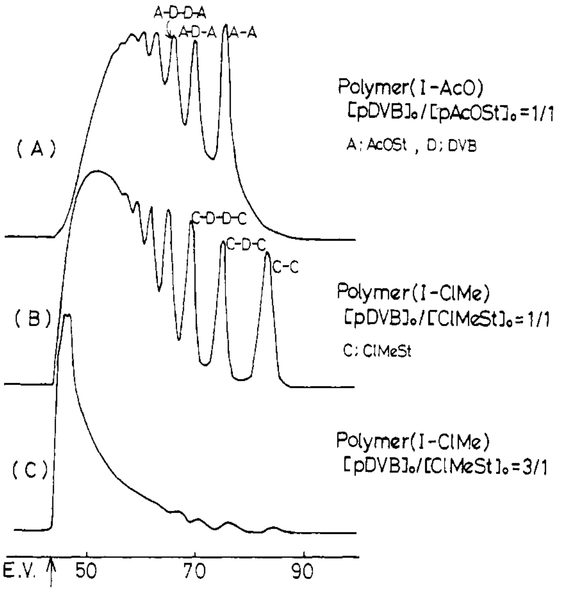


Figure 4. Molecular weight distributions of polymer I-AcO (A) and I-ClMe (B and C) obtained by $AcClO_4$ in benzene at 70 °C $[p\text{DVB}]_0 + [\text{Sts}]_0 = 0.10$ M, $[\text{C}]_0 = 0.20$ mM. The arrow indicates the exclusion limit of the HLC column.

analysis of the oligomers separated from the same product.

α,ω-Dihydroxypoly(divinylbenzene) (I-OH). Polymer I-OH was prepared by the base-catalyzed hydrolysis of polymer I-AcO (see Experimental Section). Figure 3B shows the ^{1}H NMR spectrum of the product after the hydrolysis. On hydrolysis the absorption of the acetyl group (~2.2 ppm; see Figure 3A) disappeared completely, and the hydroxyl peak (~5.8 ppm) was observed; the multiplet of a terminal vinyl group was not detected. Similarly, in the IR spectrum the bands due to the acetoxyl group were replaced by the hydroxyl absorption [3300 cm^{-1} ($\nu_{\text{O-H}}$)]. Therefore, the product was confirmed to have structure I-OH.

Attempts to prepare polymer I-OH directly by copolymerization of *p*-hydroxystyrene and DVB remained unsuccessful because of the very high cationic polymerizability of the former.

α,ω-Bis(chloromethyl)poly(divinylbenzene) (I-ClMe). This polymer was synthesized by copolymerization of ClMeSt and DVB. The copolymerization was effected by $AcClO_4$ in benzene at 70 °C for 2 h ($[p\text{DVB}]_0 + [\text{ClMeSt}]_0 = 0.10$ M, $[p\text{DVB}]_0/[\text{ClMeSt}]_0 = 1/1$ and 3/1; conversions of both monomers ~100%).

The copolymerization products had the expected ^{1}H NMR spectra (e.g., Figure 3C) with the absorption of the chloromethyl group (~4.5 ppm) and resonances characteristic of the linear poly(DVB) backbone; no vinyl end groups were detected by NMR. The spectral pattern did not depend on the $[\text{DVB}]_0/[\text{ClMeSt}]_0$ ratio. Therefore the products were identified as polymer I-ClMe (Scheme I).

Traces B and C of Figure 4 compare the molecular weight distributions of polymer I-ClMe obtained at two monomer feed ratios. Oligomer fractions were clearly reduced at the higher *p*DVB concentration. This indicates that the molecular weight of polymer I-ClMe can be controlled by regulating the starting monomer composition ($[p\text{DVB}]_0/[\text{ClMeSt}]_0$), with polymer structure being unchanged.

Comparison of traces A and B of Figure 4 suggests that the molecular weight of polymer I changes with the reactivity of Sts. That is, ClMeSt, which is less reactive than *p*AcOSt (see below), leads to polymer I of higher molecular weight.

The results described above thus show that linear poly(DVB)'s with a variety of end functional groups and molecular weights can be obtained easily by copolymerization of DVB with substituted styrenes.

Synthesis of α,ω-Bifunctional Poly(DVB) with Higher Molecular Weight. As Figures 1 and 4 show, it was rather difficult to obtain polymer I with high molecular weight in the copolymerization of a substituted styrene and DVB, because the reactivities of both monomers are close (see Table III). For the preparation of such polymer I, linear poly(DVB) (II) with a high molecular weight was synthesized first, to which functional end groups were introduced in situ by the reaction of the terminal vinyl groups of II with a substituted styrene.

For instance, DVB (0.05 M) was polymerized by $AcClO_4$ initiator in benzene at 70 °C up to 98% conversion ($\bar{M}_n$ of the poly(DVB) ~2000), and *p*AcOSt (0.05 M) was added to the polymerization solution. The reaction was stopped when ca. 50% of *p*AcOSt reacted. The main portion of the product consists of polymers, the molecular weights of which apparently exceed the exclusion limit (ca. 2×10^3) of our HLC column. The byproduct eluting at the largest elution volume is the linear *p*AcOSt dimer[8] that can be readily separated from the polymers by extraction with methanol. The polymers thus purified showed ^{1}H NMR spectra fully consistent with acetoxy-capped polymer I-AcO. Thus the successive reaction of DVB and *p*AcOSt can lead to a much higher molecular weight of polymer I-AcO than their simultaneous reaction (copolymerization) does.

We previously reported that linear poly(DVB) with high molecular weight ($\bar{M}_n \geq 10^4$) can be prepared by sequential DVB addition.[3] Therefore, the reaction of such poly(DVB) with a substituted styrene will yield α,ω-bifunctional polymer I with a high molecular weight.

Relative Reactivity of DVB and Substituted Styrenes. An interesting spin-off of this study, as described below, is that we can evaluate the reactivity of DVB relative to styrenes on the basis of end-group analysis on polymer I.

In the linear DVB polymerization in the presence of a substituted styrene (Sts), produced polymers can be classified into the following three types: DVB–$(\text{DVB})_{n-2}$–DVB (DD), DVB–$(\text{DVB})_{n-2}$–Sts (DS), and Sts–$(\text{DVB})_{n-2}$–Sts (SS). DD and SS are capped at both ends with DVB and Sts units, respectively; DS has a DVB unit at one end and a Sts unit at the other. The probabilities of obtaining these three polymers with the degree of polymerization n are as follows: DD, r^{n-1}; DS, $r^{n-2}(1 - r)$; and SS, $r^{n-3}(1 - r)^2$ (where r is the probability that poly(DVB) reacts with the vinyl groups of DVB monomer and oligomers). The probability r was assumed to be independent of n. This process involves addition of poly(DVB) cation or protonated DVB to a vinyl group and subsequent deprotonation from the resulting carbocation.

The probability r is given by

$$r = \frac{k_{\text{D}}[\text{-C=C}]^2}{k_{\text{D}}[\text{-C=C}]^2 + k_{\text{S}}[\text{-C=C}][\text{Sts}]} = \frac{1}{1 + k_{\text{S}}[\text{Sts}]/k_{\text{D}}[\text{-C=C}]} \quad (1)$$

where [Sts] indicates the concentration of unreacted Sts monomer, and [–C=C] is that of the vinyl groups in the unreacted DVB monomer and its oligomers. k_{D} and k_{S} represent the overall rate constants for the incorporation of DVB and Sts units, respectively, into the chain end of poly(DVB). $k_{\text{D}}/k_{\text{S}}$ indicates the relative reactivity of DVB and Sts toward poly(DVB).

Table II
Effect of Monomer Composition on k_D/k_S in the Copolymerization of *p*DVB and *p*MeSt by $AcClO_4$ in Benzene[a]

[*p*DVB]/[*p*MeSt]	(-C=C/-$C_6H_4CH_3$)	r	k_D/k_S
1/3	0.26	0.26	1/2.0
1/1	0.95	0.49	1/2.2
3/2	1.11	0.50	1/3.2
3/1	2.76	0.68	1/3.2
7/1	7.62	0.83	1/3.1

[a] $[pDVB]_0 + [pMeSt]_0 = 0.10$ M, $[C]_0 = 0.2$ mM, 70 °C.

Table III
Relative Reactivity (k_D/k_S) of DVB in the Copolymerization with Substituted Styrenes (Sts) by $AcClO_4$ in Benzene[a]

monomer (1/1)	-C=C/-C_6H_4X	r	k_D/k_S
[*m*DVB]/[*p*MeSt]	0.52	0.38	1/3.7
[*p*DVB]/[*p*MeSt]	0.95	0.49	1/2.2
[*p*DVB]/[*p*AcOSt]	1.93	0.62	1/1.3
[*p*DVB]/[ClMeSt]	7.44	0.83	1/0.4

[a] $[DVB]_0 = [Sts]_0 = 0.05$ M, $[C]_0 = 0.2$ mM, 70 °C, conversion ca. 50%.

Experimentally, r and hence k_D/k_S can be determined from the relative numbers (C=C/X) of terminal DVB and Sts units in a product on the basis of the equation

$$\frac{C{=}C}{X} = \frac{2[DD] + [DS]}{2[SS] + [DS]} = \frac{r^2 + r}{r^2 - 3r + 2} \qquad (2)$$

where the brackets mean the relative amount of the indicated polymer. Equation 2 requires that the end-group ratio C=C/X be independent of n, which was actually the case (Table I).

Table II lists end-group ratios (C=C/X) for polymer I-CH_3 at various monomer feed ratios together with r and k_D/k_S values calculated by eq 2 and 1. These data are for the products obtained at ca. 50% conversion of both *p*DVB and *p*MeSt, so that on calculation of k_D/k_S ratios, the monomer concentrations in eq 1 were taken as the means of the corresponding initial and final concentrations.

In spite of the large changes in the end-group ratio (or r), the k_D/k_S values remained practically constant over a wide range of the monomer feed ratio. This constancy strongly supports the reasonableness of our treatment and the k_D/k_S values. Table II indicates that each vinyl group of *p*DVB is 2–3 times less reactive than that of *p*MeSt.

Table III summarizes the reactivity ratios (k_D/k_S) for *p*DVB, *m*DVB, and various styrenes obtained by our method. The relative reactivities of the five monomers are in the order *p*MeSt > *p*AcOSt > *p*DVB > *m*DVB ≥ ClMeSt (*m*, *p*). *p*DVB is about 1.7 times as reactive as *m*DVB. The order found for *p*MeSt, *p*AcOSt, and ClMeSt agrees with that hitherto known in their conventional cationic polymerizations. For a given DVB/Sts pair, it may be possible to prepare polymer I of desired molecular weight by regulating the monomer feed ratio $[DVB]_0/[Sts]_0$ according to the k_D/k_S, because the molecular weight of polymer I is critically dependent upon the feed ratio and the DVB/Sts pair (k_D/k_S) (see Figure 4).

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Polymerization of 2,2-Dimethyloxacyclobutane

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ABSTRACT: The polymerization of 2,2-dimethyloxacyclobutane has been studied in bulk as well as in CH_2Cl_2 solution in the temperature range −25 to −78 °C using the cationic initiators PF_5 and Et_3OPF_6. Extensive transfer reactions result in the formation of only low polymers and oligomers. The end-group structures have been identified as isopropenyl and primary hydroxyl, respectively. A mechanistic scheme is presented that accounts for the formation of these structures, and it is proposed that oxonium ion and carbenium ion species are present and active during the course of the polymerization. The ring-opening reaction is found to occur by bond breakage between carbon C-2 and oxygen.

Introduction

Initially, oxacyclobutane (oxetane) and various derivatives of this four-membered cyclic ether were found to undergo polymerization under the influence of cationic initiators.[1,2] Later, the kinetics of polymerization of the derivatives substituted at the 3-position were investigated[3,4] as well as the kinetics of the oligomerizations that often accompany the polymerizations.[5–7] These monomers also undergo polymerization when the coordination initiators developed by Vandenberg are used.[8] Less attention has been paid to derivatives substituted at the 2-position although recently, structural aspects of the cationic ring-

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