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## SYNTHESIS OF SOLUBLE POLY(DIVINYLBENZENE) THROUGH ANIONIC POLYMERIZATION<sup>†</sup>

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### ABSTRACT

Lithium diisopropylamide (LDA), in the presence of diisopropylamine (DPA), initiates the polymerization of 1,4-, or 1,3-divinylbenzene (DVB) to form a soluble poly(divinylbenzene). Initiation was confirmed to take place by addition of an alkylamino group to the DVB molecule. The population of the triad tacticity of the soluble poly(DVB) suggests the steric course of the polymerization reaction to proceed according to Bernoullian statistics with respect to the diad placements, *m* and *r*. The chain-transfer reaction was found to take place through proton transfer from DPA to the growing chain end. A kinetic study of the reaction between lithium alkylamide and poly(DVB) was carried out for comparison with some other styrene derivatives. The second-order rate constant (*k*) of the reaction between lithium diethylamide and the vinyl group of poly(DVB) was  $1.19 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , which is only about one-fiftieth of that for 1,4-DVB. LDA was found to metalate the methyl group of 4-methylstyrene to form 4-vinylbenzylolithium without any side reaction. This carbanion has the structure of  $10\pi$ -conjugation and is stable in the reaction system for more than 30 min. The vinylbenzyl anion is regarded as a model for the growing end of poly(DVB). On the

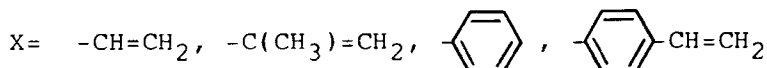
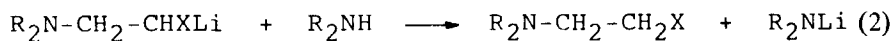
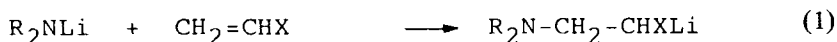
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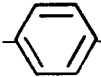
<sup>†</sup>Parts of this study were published in References 7, 10, and 11.

basis of these results, the reason for formation of soluble poly(DVB) in the LDA-induced DVB polymerization is summarized as follows: (i) Relatively short life time of the growing carbanion owing to chain transfer by DPA; (ii) lower reactivity of the pendent vinyl groups of the soluble poly(DVB) compared with those of DVB monomer; and (iii) lowered reactivity of the growing carbanion, which has a stabilized  $10\pi$ -conjugation.

### INTRODUCTION

We have long been studying addition reactions of lithium alkylamide toward conjugated olefins. For example, lithium dialkylamide reacts with diene or styrenes to form 1:1 addition product selectively (Eqs. 1 and 2) [1-5].



In the reaction with 1,4-divinylbenzene (DVB, X: ) ,

in cyclohexane at  $50^\circ\text{C}$ , the rate of the first step was 20 times as high as that of the second step, so that the reaction was applied to the synthesis of a variety of amino-containing styrene monomers [4, 5] and macromonomers [6].

Reactivities of lithium alkylamide are strongly dependent on the structure of the alkyl substituents. For example, lithium diisopropylamide (LDA) has much lower reactivity than lithium diethylamide. Actually, no reaction takes place between LDA and dienes or styrenes [1, 3]. In contrast with dienes or styrenes, DVB exhibited a unique behavior toward LDA which induced the polymerization of DVB to a soluble polymer [7].

This paper reviews a series of studies of the LDA-induced anionic polymerization of DVB plus the addition of some new results.

## EXPERIMENTAL

All procedures, such as distillation, polymerization, and anionic addition reaction, were carried out under purified nitrogen to eliminate oxygen and moisture.

### Materials

Commercial tetrahydrofuran (THF), diisopropylamine (DPA), and diethylamine were purified by conventional methods [8]. 1,4- and 1,3-Divinylbenzene (DVB, supplied by Asahi Chemical Industry Co.) were purified by fractional distillation over calcium hydride under vacuum. Butyllithium (BuLi, supplied by Asahi Chemical Industry Co.) was used as the cyclohexane solution, the concentration of which was determined by Gilman's double titration method [9].

### Polymerization Procedure [7]

One of the representative procedures of DVB polymerization initiated with LDA is as follows: To a stirred THF solution (52 mL) of diisopropylamine (100 mmol) in a round-bottomed flask, a cyclohexane solution of butyllithium (2 mmol) was added. After a few minutes of agitation to complete the formation of lithium diisopropylamide, DVB (14 mmol) was added to the mixture. The mixture was allowed to react for 15 min at 20°C with stirring, and then a small amount of methanol was added to stop the reaction. The mixture was poured into a large excess of methanol, and the precipitates were purified by threefold reprecipitation from THF solution into methanol. Polymer samples collected after precipitations were finally refined by freeze-drying with benzene or 1,4-dioxane. The molecular weight of the poly(DVB) formed in this reaction was about 20 000. Results obtained in a series of DVB polymerization are summarized in Table 1.

### Amination Reaction of Poly(1,4-Divinylbenzene) by Lithium Alkylamide

One of the representative procedures of the addition reaction between lithium alkylamides and poly(1,4-DVB) is as follows: To a stirred THF solution of poly(DVB) in a 100-mL round-bottomed flask, a mixture of lithium amide, amine, and THF was added (initial concentration of vinyl groups of poly(DVB) =  $[\Delta\text{NH}]_0 = 0.25 \text{ mol/L}$ ;  $[\Delta\text{NH}]_0 / [\Delta\text{NLi}]_0 = 10$ ). The mixture

TABLE 1. Anionic Polymerization of Divinylbenzene (DVB) Initiated with Lithium Diisopropylamide (LDA) in the Presence of Diisopropylamine (DPA)<sup>a,b</sup>

Run	Monomer	$10^2 \cdot [\text{DVB}]_0$ , mol/L	$10^2 \cdot [\text{LDA}]_0$ , mol/L	$[\text{DPA}]_0$ , mol/L	Time, min	Yield, %	$10^{-3} \bar{M}_n^c$
1	1,4-DVB	35.0	2.5 <sup>d</sup>	0	1	100	(Gel)
2	1,3-DVB	35.0	2.5 <sup>d</sup>	0	5	98	(Gel)
3	1,4-DVB	35.0	5.0	0.35	5	87	100 <sup>e</sup>
4	1,4-DVB	35.0	5.0	0.55	60	90	90 <sup>e</sup>
5	1,4-DVB	23.3	1.11	0.50	10	72.8 <sup>f</sup>	20.3
6	1,4-DVB	2.33	3.33	1.00	30	38.7 <sup>f</sup>	3.00
7	1,4-DVB	2.33	3.33	3.00	120	28.8 <sup>f</sup>	1.47
8	1,3-DVB	35.0	2.5	0.025	240	36	60 <sup>e</sup>
9	1,3-DVB	35.0	2.5	0.60	270	24	4 <sup>e</sup>

<sup>a</sup>References 7a and 7d.

<sup>b</sup>Solvent, THF; temperature, 20°C.

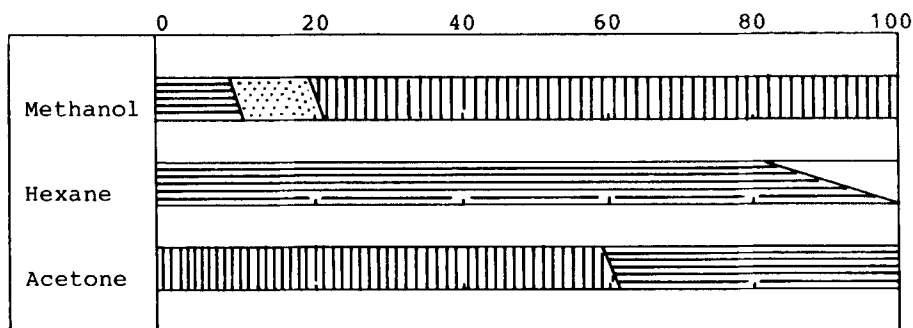
<sup>c</sup>Determined by GPC.

<sup>d</sup>Butyllithium was used as initiator.

<sup>e</sup> $\bar{M}_n$  GPC.

<sup>f</sup>Conversion of DVB determined by GC.

Extent of amination of soluble poly(DVB) in %






 : Soluble part ; 
  : Insoluble part at  $-50^{\circ}\text{C}$  ; 
  : Insoluble part at room temperature

FIG. 1. Change in solubility of poly(divinylbenzene) as a function of the extent of amination.

was allowed to react for several minutes at  $30^{\circ}\text{C}$ . After the reaction was quenched by methanol, the aminated polymer was poured into a nonsolvent. The solubility of the aminated poly(1,4-DVB) changed with its extent of amination (see Fig. 1). Referring to Fig. 1, methanol, acetone, or hexane was employed as the nonsolvent for purifying the aminated polymer. Polymer samples collected after precipitation were finally refined by freeze-drying with benzene or 1,4-dioxane.

#### Reactivity of Lithium Diethylamide toward Styrene Derivatives in THF

To a lithium diethylamide/diethylamine/THF solution prepared as stated above in a 100-mL round-bottomed flask, the styrene derivative was added ( $[\text{styrene}]_0 = [\text{>NH}]_0 = 0.25 \text{ mol/L}$ ;  $[\text{>NH}]_0/[\text{>NLi}]_0 = 10$ ). The mixture was allowed to react for several minutes at  $30^{\circ}\text{C}$ , and then a small amount of methanol was added to stop the reaction. The conversion of styrene derivatives was determined by gas chromatography by using the internal standard method.

### Lithiation of 4-Methylstyrene by Lithium Diisopropylamide [10]

To a stirred THF solution (19.0 mL) of diisopropylamine (10 mmol), a cyclohexane solution of butyllithium (2 mmol) was added in a round-bottomed flask (100 mL). After stirring for a few minutes, 4-methylstyrene (2 mmol) was added. The mixture was allowed to react for several minutes at 20°C, and then was analyzed directly by UV spectroscopy. Unreacted 4-methylstyrene was determined by gas chromatography after the reaction was stopped by adding carbon tetrachloride.

### Measurements

Number average molecular weight ( $\bar{M}_n$ ) and weight-average molecular weight ( $\bar{M}_w$ ) were determined, respectively, with a vapor-pressure osmometer (VPO, Corona 117 Molecular-Weight Apparatus) and gel permeation chromatography (GPC, Nihon Seimitsu Kagaku NSLC-200 Gel Permeation Chromatograph) by using a calibration curve of polystyrene standard samples and DVB oligomers.

$^1\text{H-NMR}$  spectra were taken with a JEOL GX-400 spectrometer at 50°C at 400 MHz using a 50 mm glass tube containing a solution of poly(1,4-DVB) sample in  $\text{CDCl}_3$  (10 g/dL).  $^{13}\text{C-NMR}$  spectrum was taken with a JEOL FX-100 spectrometer at 25.05 MHz with complete proton decoupling. A solution of poly(1,4-DVB) sample in  $\text{CDCl}_3$  (20 g/dL) was placed in a 5-mm glass tube which was sealed under purified nitrogen. The flip angle was 40°, and the pulse width was 6  $\mu\text{s}$ . For the measurement, 17 017 scans were accumulated with a pulse time of 3.0 s at 60°C. Tetramethylsilane (TMS) was used as internal reference in both measurements.

Extent of amination of poly(1,4-DVB) was determined by titrimetric analysis. The nitrogen content in the aminated polymer was analyzed by potentiometric titration in a nonaqueous solution by using a Toyo Model PT-5D pH-meter with a 0.1-mol/L acetic acid solution of perchloric acid as titrant.

The fourth-order spectroscopy of the ultraviolet spectrum (Hitachi 557 Spectrometer) at 296 nm [11] was employed for determination of unreacted vinyl groups with the aid of a calibration curve of 4-isopropylstyrene as a model of the monomeric unit of poly(1,4-DVB) (Fig. 2).

The thermal properties of poly(1,4-DVB) were determined by using a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA) (Mettler TA 3000-DSC 30 System) at a heating rate of 20°C/min from -100 to 200°C.

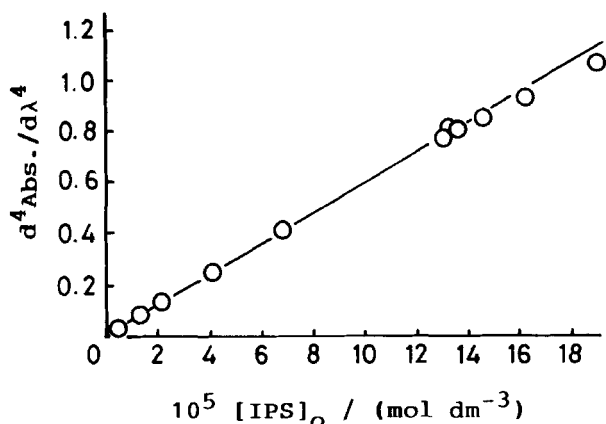


FIG. 2. Plots of intensity of the fourth-order derivative of UV absorption at 296 nm vs concentration of 4-isopropylstyrene in THF. Reproduced from Ref. 11 by courtesy of the publishers, Hüthig and Wepf, Verlag, Basel.

## RESULTS AND DISCUSSION

### 1. Anionic Polymerization of 1,4- or 1,3-Divinylbenzene (DVB) Initiated with Lithium Diisopropylamide (LDA)

Results of the anionic polymerizations of 1,4- or 1,3-DVB initiated with LDA and butyllithium (BuLi) are summarized in Table 1. When BuLi was used as initiator, nonsoluble gels were formed immediately after the addition of monomer to the initiator solution (Runs 1 and 2 in Table 1). In contrast to this, the DVB polymerization initiated with LDA proceeded homogeneously without any gel formation when the polymerization reaction was carried out in the presence of excess diisopropylamine (DPA) (for instance,  $[DPA]_0 / [LDA]_0 > 2$ ).

The polymers obtained by freeze-drying (see Experimental part) are white powders and soluble in many types of solvents such as THF, benzene, toluene, acetone, chloroform, and 1,4-dioxane. Figures 3 and 4 show the UV and  $^1\text{H-NMR}$  spectra of the polymer formed (Run 5 in Table 1). As shown in Fig. 3, the UV spectrum of poly(1,4-DVB) is similar to that of 4-isopropylstyrene (IPS), which suggests that the polymer obtained carries vinylphenyl groups in the repeating units.

As shown in the  $^1\text{H-NMR}$  spectrum of poly(DVB) (Fig. 4), protons at the



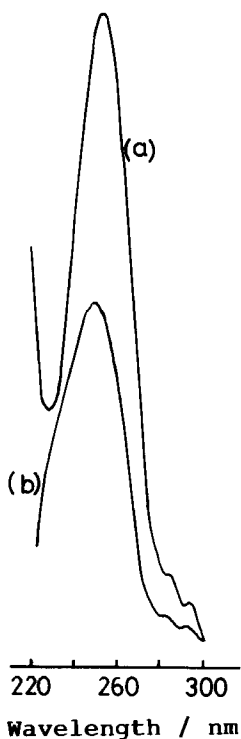


FIG. 3. UV spectra of poly(1,4 divinylbenzene) (a) and 4-isopropylstyrene (b).

$\beta$ -carbon of the vinyl groups in the side chain of poly(DVB) appearing around 5-6 ppm indicate also that one vinyl group of the DVB molecule had been polymerized selectively to form soluble poly(DVB).

Quantitative analysis of the vinyl groups in the polymer was carried out by means of the fourth-order derivative method of UV absorbance at 296 nm by use of the calibration curve of IPS as a model of the monomeric unit of poly-(DVB) (Fig. 2). As the result indicates, the pendent vinyl groups of poly(DVB) formed with LDA remain almost intact. In order to get further information about the number of vinyl groups along the poly(DVB) chain, 400 MHz  $^1\text{H}$ -NMR measurements were carried out. The results of the quantitative analysis of the pendent vinyl groups by use of signals in the phenyl and vinyl regions, are listed in Table 2, from which it was confirmed that a few percent of pen-

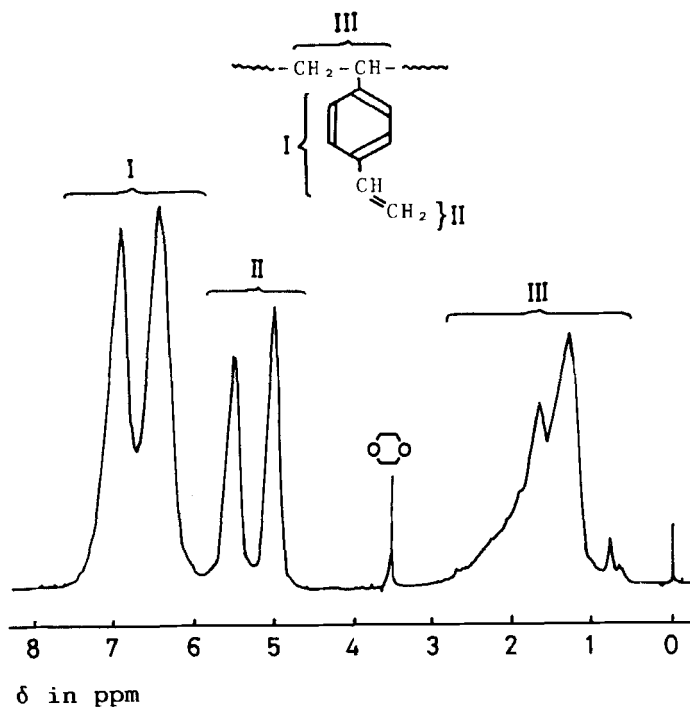


FIG. 4. <sup>1</sup>H-NMR spectrum of poly(1,4-divinylbenzene) (sample of Run 5 in Table 1). Temperature: 50°C. Solvent: CDCl<sub>3</sub>. Reproduced from Ref. 7d by courtesy of the publishers, Hüthig and Wepf, Verlag, Basel.

TABLE 2. Content of Pendent Vinyl Groups of Poly(DVB) [7d]

Molecular weight	Vinyl groups per 100 monomeric units
18 000	98.1
32 000	95.6

dent vinyl groups had disappeared in the poly(DVB) sample with a molecular weight above 20 000. Light-scattering, sedimentation equilibrium studies, and viscosity measurements in *trans*-decahydronaphthalene suggest that the soluble poly(1,4-DVB) possesses a branched structure, especially when the polymers have molecular weights above 20 000 [12].

## 2. The Initiation Reaction in LDA-Induced DVB Polymerization

It is seen from Fig. 4 that the NMR spectrum of the soluble poly(DVB) has methyl proton signals of the diisopropylamino group at 0.8–1.0 ppm. To get further information about the initiation reaction, quantitative analysis of amino groups in the poly(DVB) was carried out by nonaqueous titrimetry (see Experimental part). The molecular weight of a poly(DVB) sample (Run 6, Table 1) was estimated to be 3030, assuming that each polymer molecule possesses one diisopropylamino group. The result showed excellent agreement with the  $\bar{M}_n$  obtained by GPC (3000), which indicates that the initiation reaction takes place through the addition of LDA onto the DVB molecule.

## 3. The Propagation Reaction of DVB Polymerization

To obtain information on the stereochemistry of the propagation step, the tacticities of poly(1,4-DVB) were determined by analyzing its  $^{13}\text{C}$ -NMR spectrum (Run 5 in Table 1,  $\bar{M}_n$  20 000). In Fig. 5, Peaks 5 and 6 are assigned to the  $\alpha$ - and  $\beta$ -carbons of the vinyl groups, respectively. Signals of phenyl  $\text{C}^1$  carbons appearing around 143–147 ppm are separated into three regions that reflect the microstructure of the polymer.

The three regions in Fig. 5(b) are assigned, respectively, to the three triad placements, *mm*, *mr*, and *rr*. Placements *m* and *r* are *meso* and *racemo*, which express the mode of placement of monomeric units in a diad. This assignment was carried out in a way similar to that used for polystyrene or its *p*-substituted derivatives [13]. The fractions of population of triad tacticity *mm*, *mr*, or *rr*, determined from the ratio of areas of the corresponding three regions, are 0.13, 0.46, and 0.42, respectively. From the observed values for *mm*, *mr*, and *rr*, conditional probabilities,  $P_{m/r}$  and  $P_{r/m}$ , were calculated to be 0.63 and 0.35, respectively, where  $P_{m/r}$  is the probability that a monomer molecule adds in *r*-fashion to an *m*-chain end, and  $P_{r/m}$  is defined correspondingly. The sum (= 0.98) of  $P_{m/r}$  and  $P_{r/m}$  is very close to unity, which means that the stereochemical process of DVB polymerization is governed by Bernoullian statistics, that is, the penultimate unit has no influence upon

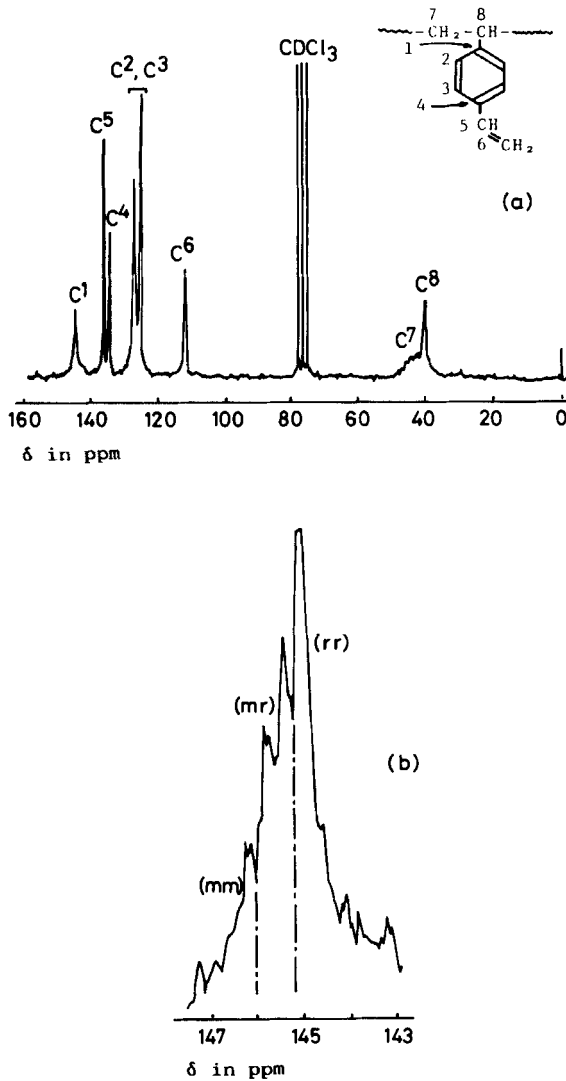


FIG. 5.  $^{13}\text{C}$ -NMR spectrum of poly(1,4-divinylbenzene) (a) and its expanded spectrum of phenyl  $\text{C}^1$  carbon (b). (The same sample as in Fig. 4 was used.) Reproduced from Ref. 7d by courtesy of the publishers, Hüthig and Wepf, Verlag, Basel.

TABLE 3. Dependence of Molecular Weight of Poly(DVB) on DPA Concentration<sup>a</sup>

Run	[DPA] <sub>0</sub> /[DVB] <sub>0</sub>	Time, min	Conversion, <sup>b</sup>	$10^{-3} \times \bar{M}_n^b$	$10^{-3} \times \bar{M}_w^b$	$\bar{M}_w/\bar{M}_n^b$	<i>p</i> <sup>b,c</sup>	$10^2/P$
1	5	1	38.4	16.5	31.8	1.93	126	0.79
2	10	2	30.9	8.04	15.0	1.86	61.1	1.64
3	15	3	19.3	5.26	9.59	1.82	39.7	2.52
4	20	4	13.1	3.99	5.94	1.49	29.9	3.34

<sup>a</sup>[1,4-DVB]<sub>0</sub> = 0.1 mol/L; [lithium diisopropylamide]<sub>0</sub> = 14.3 mmol/L; solvent, THF; temperature, 20°C.

<sup>b</sup>Determined from GPC results.

<sup>c</sup>Degree of polymerization.

the site of growth. From the observed value of 0.64 for  $P_r$ ,  $mm$ ,  $mr$ , and  $rr$  were calculated on the basis of Bernoullian statistics. The results (0.13, 0.45, and 0.41, for  $mm$ ,  $mr$ , and  $rr$ , respectively) agree well with the observed values.

#### 4. Chain Transfer Reaction in DVB Polymerization

The molecular weight of the polymer formed in the presence of DPA is dependent on the concentration of DPA; that is, higher molecular weights of poly(DVB) were obtained with lower concentrations of DPA, which indicates that the chain transfer reaction takes place between the growing chain end and DPA. To estimate the chain transfer coefficient of DPA, several DVB polymerizations were carried out by changing the ratio  $[DPA]_0/[DVB]_0$ , the results of which are summarized in Table 3. As seen in Fig. 6, the plot of  $[DPA]_0/[DVB]_0$  versus  $1/P$  is linear, and from its slope the chain transfer coefficient of DPA in LDA-induced DVB polymerization was estimated to be  $1.71 \times 10^{-3}$  at  $20^\circ\text{C}$ .

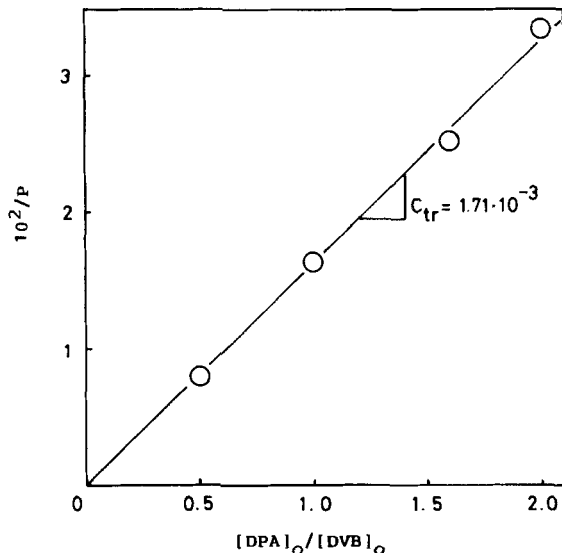


FIG. 6. Plots of  $[DPA]_0/[DVB]_0$  vs  $1/P$ . Reaction conditions as in Table 3.

## 5. Formation Mechanism of Soluble Polymers in LDA-Induced DVB Polymerization

DVB has widely been used as a crosslinking reagent in radical and anionic polymerizations because of its difunctionality. To solve the problem of why no gel formation takes place in LDA-initiated DVB polymerization, the following studies were carried out.

### 5.1 Reactivity of Pendent Vinyl Groups of Soluble Poly(DVB) toward Nucleophilic Reagents

Amination reactions of poly(1,4-DVB) by lithium diethylamide were carried out for comparison with those of some styrene derivatives.

The reaction between poly(DVB) and lithium diethylamide in THF proceeds homogeneously. As seen from the  $^{13}\text{C}$ -NMR spectra in Fig. 7, vinyl groups standing along the polymer chain are aminated easily by lithium diethylamide. Thus, partially aminated poly(DVB)s were obtained. Amination reactions of poly(DVB) by several alkylamines, such as isobutylamine,  $N,N'$ -diethylethylenediamine, and diethylenetriamine, catalyzed by lithium alkylamide, were also performed. It was confirmed that poly(DVB) possessing variety of alkylamino groups (primary, secondary, and tertiary amino groups) should be prepared easily without no gel formation.

In general, it is known in GPC analysis [10a, 14] that the elution of aminated polystyrene tends to occur later than that of nonaminated polystyrene owing to stronger adsorption through the amino groups. It is seen from Fig. 8 that the elution curves of the poly(DVB) samples after amination reaction peak later than that of the starting poly(DVB). Actually, 22.4%-aminated poly(DVB) was adsorbed completely. From this result it was concluded that the amination reaction takes place in a random fashion on the whole polymer molecule, leaving no nonaminated poly(DVB) molecules.

To estimate the reactivity of vinyl groups on the poly(DVB) chains, the conversion curve with time of vinyl groups of poly(DVB) in the reaction toward lithium diethylamide in THF was studied. The result is shown in Fig. 9, from which it is seen that the amination reaction of poly(DVB) proceeds smoothly up to 60%.

The second-order rate constant for the addition reaction of lithium diethylamide to the pendent vinyl groups of poly(DVB) is compared in Table 4 with those of low molecular weight styrene derivatives. Our previous studies of the reactivity of 1,4-DVB showed that the rate of the first step ( $k_1$ ) was 20 times as large as that of the second step ( $k_2$ ) in the addition reaction of lithium dialkylamide to double bonds of 1,4-DVB in cyclohexane at 50°C [15]. The

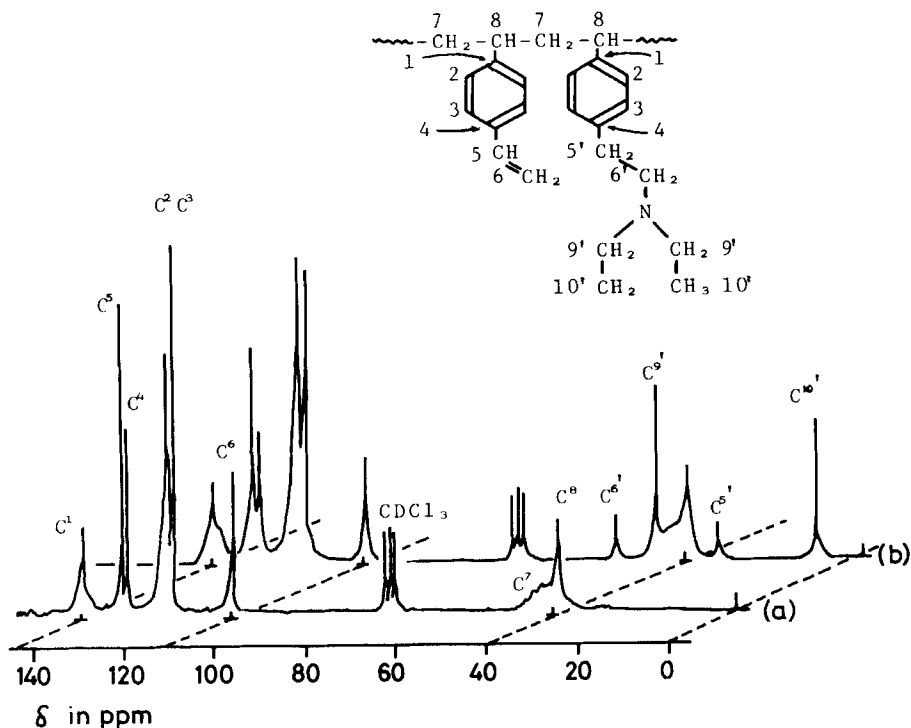


FIG. 7.  $^{13}\text{C}$ -NMR spectra of poly(1,4-divinylbenzene) (a) and poly(1,4-divinylbenzene) aminated with lithium diethylamide/diethylamine (b).

ratio of the rate constants ( $k_1/k_2 = 47$ ) in THF is larger than that in cyclohexane (Table 4). Vinyl groups on polymer chains exhibited much lower reactivity than those of the low molecular weight styrene derivatives. In fact, the ratio of rate constants,  $k_{\text{DVB}}/k_{\text{poly(DVB)}}$ , is about 52 in THF. The observed low reactivity of the pendent double bonds toward nucleophilic attack may partly explain the reason for soluble polymer formation in LDA-initiated DVB polymerization.

## 5.2. Formation of 4-Vinylbenzylithium (VBL) in the Reaction between LDA and 4-Methylstyrene (MST)

Formation of soluble poly(DVB), however, could not be fully explained by just the difference in reactivities of vinyl groups toward nucleophiles. In



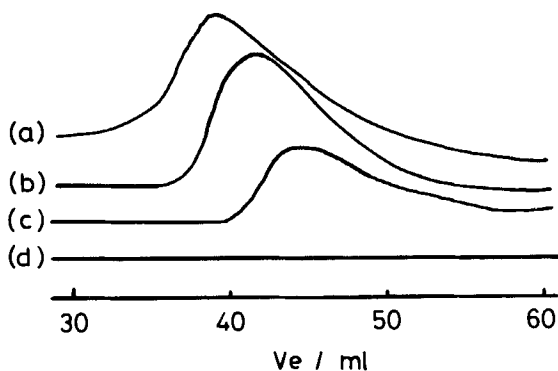


FIG. 8. GPC traces of aminated polymers prepared by the reaction of poly(DVB) with lithium diethylamide.  $[C=C]_0 = [NLi]_0 = 0.25$  mol/L;  $[>NH]_0/[>NLi]_0 = 10$ . Solvent: THF. Temperature:  $30^\circ\text{C}$ . Extent of amination: (a) 0.0%, (b) 8.5%, (c) 15.9%, (d) 22.4%.

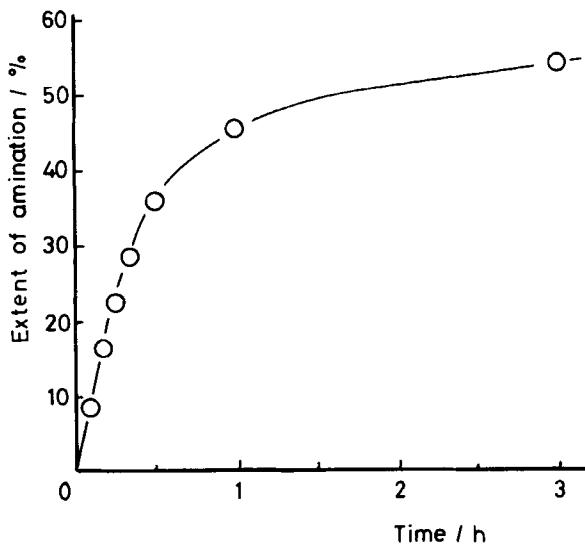


FIG. 9. Time course of the amination of poly(1,4-divinylbenzene) by lithium diethylamide in the presence of diethylamine. Operating conditions as in Fig. 8.

TABLE 4. Second-Order Rate Constants  $k_2$  of the Reaction between Lithium Diethylamide and Vinylbenzene Derivatives in the Presence of Diethylamine in THF<sup>a</sup>

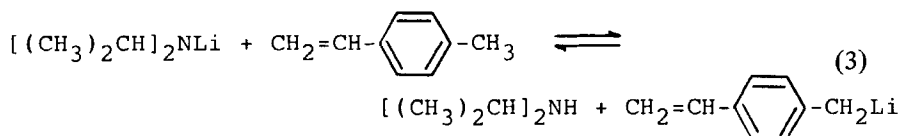
Vinyl compounds	$10^3 \cdot k_2$ in $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
1,4-Divinylbenzene	30.43 <sup>b</sup>
1,3-Divinylbenzene	8.95 <sup>b</sup>
Styrene	3.78 <sup>c</sup>
4-Diethylaminoethylstyrene	1.31
Poly(1,4-divinylbenzene)	1.19

<sup>a</sup>[Vinyl compounds]<sub>0</sub> = [Et<sub>2</sub>NLi]<sub>0</sub> = 0.25 mol/L; [Et<sub>2</sub>NLi]<sub>0</sub>/[Et<sub>2</sub>NH]<sub>0</sub> = 10; temperature, 30°C.

<sup>b</sup> $k_2/2$  values.

<sup>c</sup>Reference 16.

the final stage of polymerization, more than 90% of DVB was converted to its polymer, so that the relative rate of the addition reaction of the pendent double bonds should become large enough to cause some gel formation in the reaction system. Since the reaction system is still homogeneous in the final stages of polymerization, we assumed that the stability of the carbanion at the growing chain end increased owing to its  $10\pi$ -conjugation system (vinylbenzyl anion), which probably was a much lowered reactivity toward the pendent double bonds. Using 4-methylstyrene (MST) as a model compound, we examined a possible activation of the methyl group by the *para*-vinyl group in MST, which may result in the formation of a  $10\pi$ -conjugated structure of the vinylbenzyl carbanion. In a reaction system containing LDA and MST prepared according to the Experimental section, it was shown by a series of UV measurements that a considerable amount of MST was converted to 4-vinylbenzyl lithium (VBL). In Fig. 10 an absorption band is clearly observed at 420 nm which is assignable to VBL, MST being metalated by LDA, as shown by



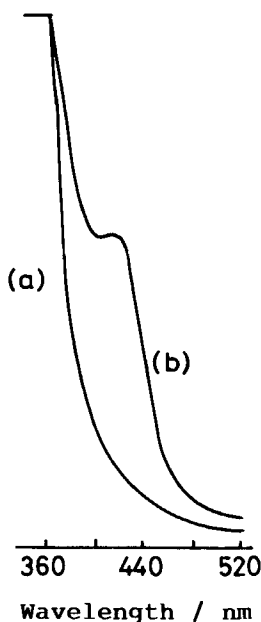


FIG. 10. UV spectra of lithium diisopropylamide (a) and 4-vinylbenzyl-lithium (b) in THF.  $[\text{LDA}]_0$ : 0.1 mol/L.  $[\text{DPA}]_0$ : 0.4 mol/L.  $[\text{MST}]_0$ : (a) 0 mol/L; (b) 20 mmol/L. Reproduced from Ref. 10a by courtesy of the publishers, Hüthig and Wepf, Verlag, Basel.

It was also confirmed by GPC measurements of the reaction product that neither polymerization nor oligomerization of MST has taken place, at least within a reaction time of 30 min, as shown in Fig. 11(a). A new peak was observed, however, at an elution volume of 116 mL when the reaction mixture was treated with chlorotrimethylsilane, as shown in Fig. 11(b). The product was assigned to trimethyl(4-vinylphenyl)silane by the use of mass spectroscopic analysis as well as NMR measurements. Contrary to the lithiation reaction of MST by LDA, toluene itself was not lithiated by LDA under the same reaction conditions as those for MST. These results show that the carbanion of 4-vinylbenzyl-lithium is stabilized enough, owing to the *para*-vinyl group, to exist more than 30 min without any side reaction, even when  $[\text{LDA}]_0/[\text{MST}]_0 = 1$ .

On the basis of the results discussed above, it is concluded that the reason for the formation of soluble poly(DVB) can be explained by the following

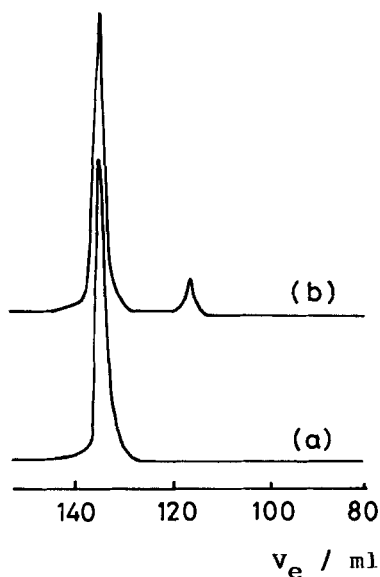


FIG. 11. GPC chromatograms of products formed in the reaction between 4-vinylbenzyl lithium and methanol (a) and chlorotrimethylsilane (b).  $[LDA]_0$ : 0.1 mol/L.  $[DPA]_0$ : 0.4 mol/L.  $[MST]_0$ : 0.1 mol/L. Column: 25 mm i.d. X 60 cm. Eluent:  $CHCl_3$  (2 mL/min). Detector: UV monitor (254 nm). Reproduced from Ref. 10a by courtesy of the publishers, Hüthig and Wepf, Verlag, Basel.

factors: (i) Relatively short lifetime of the growing carbanion owing to chain transfer by DPA; (ii) lower reactivity of the pendent vinyl groups of poly(DVB) compared with those of DVB monomer; and (iii) lowered reactivity of the growing carbanion which has a stabilized  $10\pi$ -conjugation.

## 6. Thermal Properties of Poly(1,4-DVB)

The thermal properties of poly(1,4-DVB) were measured by differential scanning calorimetry (DSC) and thermogravimetry (TGA) at a heating rate of  $20^\circ\text{C}/\text{min}$  from  $-100$  to  $200^\circ\text{C}$ , the results of which are shown in Fig. 12. In the DSC measurements, poly(1,4-DVB) showed a slightly endothermic peak corresponding to the glass-transition temperature ( $T_g$ ) around  $90^\circ\text{C}$ , and a strong exothermic peak in the temperature range above  $T_g$ . The TGA mea-

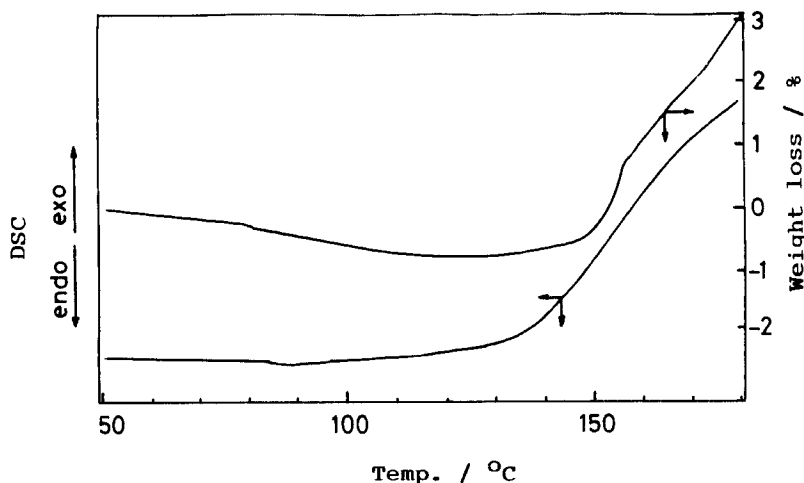


FIG. 12. DSC (a) and TGA (b) thermograms of poly(1,4-divinylbenzene).

surement showed that the weight of the polymer increased with the exothermal peak to attain 103%-weight at 200°C. Figure 13, which shows the infrared spectra of the poly(DVB) sample before and after DSC measurement, indicates that the poly(DVB) sample after DSC measurement has strong carbonyl absorption around 1700  $\text{cm}^{-1}$  and hydroxyl absorption around 3500  $\text{cm}^{-1}$ . The poly(DVB) sample after DSC measurement was not soluble in any of the solvents. Poly(DVB) was probably converted to a hydrophilic gel possessing hydroxyl and carboxyl groups by oxidation along with crosslinking at temperatures above  $T_g$  in air. Further investigations of the thermal properties of poly(DVB) will be published elsewhere.

### CONCLUSIONS

The anionic polymerization of divinylbenzene (DVB) with lithium diisopropylamide (LDA) was confirmed to consist of the following three elementary reactions: (i) Initiation, which takes place through addition of LDA to the DVB molecule; (ii) propagation, the stereochemistry of which is governed by Bernoullian statistics in terms of the diad placement; and (iii) chain transfer, by diisopropylamine.

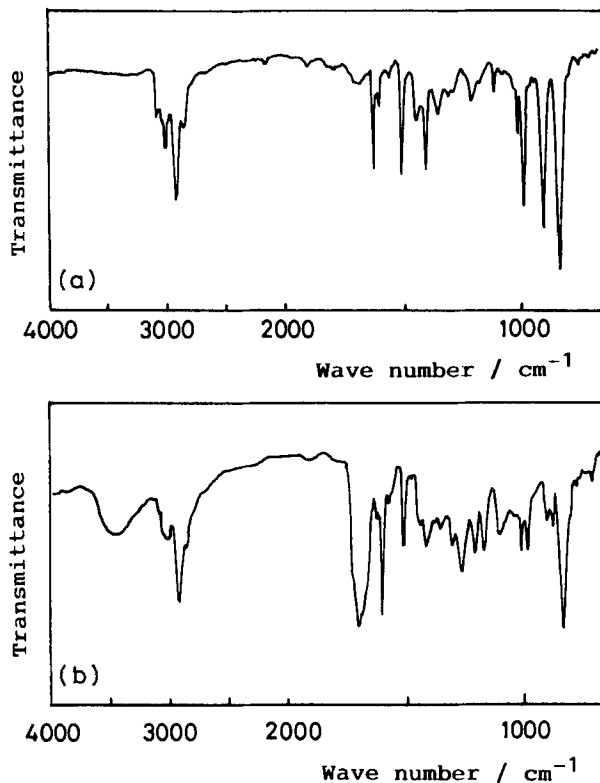


FIG. 13. IR spectra of poly(1,4-divinylbenzene) before (a) and after (b) DSC measurement.

Formation of soluble poly(DVB) is explained in terms of the following three reasons: (i) Relatively short lifetime of the growing carbanion owing to the chain transfer by diisopropylamine; (ii) lower reactivity of the pendent vinyl groups of the soluble poly(DVB) compared with those of DVB monomer; and (iii) lowered reactivity of the growing carbanion which has a stabilized  $10\pi$ -conjugation.

The thermal properties of poly(DVB) suggest that the poly(DVB) sample (or film) is converted to a hydrophilic gel possessing hydroxyl and carboxyl groups.

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