Acknowledgment. Financial support from the National Science Foundation (Materials Research Group) and partial support from the Office of Naval Research is gratefully acknowledged.

Registry No. **1A**, 110458-67-8; **1B**, 110458-68-9; **1C**, 110458-71-4; (*S*)-$C_2H_5CH(CH_3)CH_2OTs$, 38261-81-3; TsCl, 98-59-9; (*S*)-$C_2H_5CH(CH_3)CH_2OH$, 1565-80-6; (*S*)-$C_2H_5CH(CH_3)CH_2C_6H_4$-*p*-CH_2CO_2H, 110458-62-3; HOC_6H_4-*p*-CH_2CO_2H, 156-38-7; (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-$CH_2CO_2C_2H_5$, 110458-63-4; (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-$CH(CO_2C_2H_5)_2$, 110458-64-5; $H_5C_2O_2CCO_2C_2H_5$, 95-92-1; (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-$CH(CH_2OH)_2$, 110458-65-6; $H_2C{=}CH(CH_2)_9OTs$, 51148-67-5; $H_2C{=}CH(CH_2)_9OH$, 112-43-6; $H_2C{=}CH(CH_2)_9OC_6H_4$-*p*-CHO, 110458-66-7; HOC_6H_4-*p*-CHO, 123-08-0; $H_2C{=}CH(CH_2)_9CH(CO_2C_2H_5)_2$, 52355-51-8; $C_2H_5O_2CCH_2CO_2C_2H_5$, 141-05-9; $H_2C{=}CH(CH_2)_9CH(CH_2OH)_2$, 108414-88-6; (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-CHO, 55535-61-0; (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-$BrBrC_6H_4$-*p*-OH, 106-41-2; $B(OC_4H_9)_3$, 688-74-4; H_3BO_3, 10043-35-3; (*S*)-$(HO)_2BC_6H_4$-*p*-$OCH_2CH(CH_3)C_2H_5$, 110458-70-3.

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Protection and Polymerization of Functional Monomers. 10. Synthesis of a Well-Defined Poly(4-vinylbenzaldehyde) by the Anionic Living Polymerization of *N*-[(4-Ethenylphenyl)methylene]cyclohexamine

Akira Hirao* and Seiichi Nakahama

Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12-1, Meguro-ku, Ohokayama, Tokyo 152, Japan. *Received February 17, 1987*

ABSTRACT: Anionic polymerization of *N*-[(4-ethenylphenyl)methylene]cyclohexamine (**1**), *N*-cyclohexylimine of 4-vinylbenzaldehyde, was investigated in THF at −78 °C with potassium naphthalenide, cumylpotassium, and oligo(α-methylstyryl)dialkali-metal salts. The polymerization of **1** proceeded without chain-transfer and termination reactions with each of the initiators to afford a stable living polymer. Yields of polymers were quantitative. The resulting polymers had predictable molecular weights and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.05–1.15). Under mild acidic conditions (0.5 N HCl in 1,4-dioxane–water), cleavage of the *N*-cyclohexylimino group was completely achieved to give a well-defined poly(4-vinylbenzaldehyde) which still retained a narrow molecular weight distribution. The Mark–Houwink equation for poly(**1**), $[\eta] = 4.3 \times 10^{-4} M^{0.58}$ (in THF at 40 °C), was correlated.

Introduction

Recently we have investigated the synthesis of linear functional polymers having uniformity of chain length as well as predictable molecular weight.[1] Our approach involves the anionic living polymerization of monomers with suitably protected functional groups, followed by the complete removal of the protecting groups from the resulting polymers to regenerate the original functional groups.

In the previous paper,[2] we successfully synthesized linear poly(4-vinylbenzaldehydes) with controlled molecular weights and with narrow molecular weight distributions by means of the anionic living polymeriation of 1,3-dimethyl-2-(4-vinylphenyl)imidazolidine and subsequent removal of the imidazolidine ring from the resulting polymer. A triblock copolymer of a new type, poly[α-methylstyrene)-*b*-(4-vinylbenzaldehyde)-*b*-(α-methylstyrene)] was also prepared by the above living polymerization. Although this provides an excellent method for preparing well-defined poly(4-vinylbenzaldehydes), the disadvantage of this method is the use of an expensive *N,N'*-dimethylethylenediamine, equivalent to monomer for the protection of aldehyde function. Therefore, we have been interested in exploring an alternative group to have the ability of masking the aldehyde function under the conditions of anionic polymerization.

As a part of a series of studies on protection and polymerization of functional monomers,[3] we wish to report

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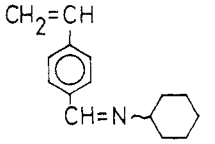
Table I
Anionic Polymerization of *N*-[(4-Ethenylphenyl)methylene]cyclohexamine (1) with Various Initiators in THF at -78 °C for 5–10 min[a]

run	1, mmol	initiator type	initiator mmol	α-methylstyrene, mmol	$\bar{M}_n$(calcd) × 10^{-4}	$\bar{M}_n$(obsd)[b] × 10^{-4}	$\bar{M}_w/\bar{M}_n$[c]
1	1.77	K-Nap[d]	0.0919		0.80	0.82	1.08
2	5.22	Na-Nap[e]	0.153	0.412	1.5_1	1.4_0	1.11
3	5.51	Li-Nap[f]	0.110	0.419	2.2_0	2.0_0	1.13
4	5.82	Na-Nap	0.111	0.419	2.3_2	2.2_0	1.10
5	7.10	K-Nap	0.089_6	0.440	3.5_0	3.1_0	1.15
6	3.90	K-Nap	0.035_4	0.522	5.0_0	5.9_0	1.13
7	8.25	cumyl K	0.028_6	0.340	6.3_0	6.6_6	1.06
8	8.74	cumyl K	0.014_9	0.368	$12._7$	$11._2$	1.05

[a] Yields of polymers were near quantitative in each case. [b] $\bar{M}_n$(obsd) were obtained by VPO. [c] $\bar{M}_w/\bar{M}_n$'s were calculated from their GPC peaks by using calibration curve from $\bar{M}_n$(VPO) and elution counts. [d] Potassium naphthalenide. [e] Sodium naphthalenide. [f] Lithium naphthalenide. [g] Cumylpotassium.

here the anionic living polymerization of *N*-[(4-ethenylphenyl)methylene]cyclohexamine (**1**) wherein the aldehyde group is protected as the *N*-cyclohexylimine.



(1)

Results and Discussion

To the best of our knowledge, there appears to be no example of anionic polymerization of styrenes containing *N*-substituted imines at the present time. When trying to prepare one, the carbon atom of the azomethine linkage would be attacked by anionic initiators before the polymerization. In fact, it has been reported in numerous literatures that various *N*-substituted imines are usually susceptible to nucleophilic attack by organolithium compounds often used as anionic initiators in the polymerization of styrene.[4]

In 1976 Ziegler and his co-workers demonstrated the interesting result that the *N*-cyclohexylimine of piperonal was observed to be stable to the conditions of lithiation with the use of *n*-butyllithium at −78 °C whereas the product of imine addition was obtained at 0 °C.[5,6] This may indicate that the addition of butyllithium to a carbon–nitrogen double bond can be suppressed by careful choice of reaction temperature and probably by the *N*-substituent of the imine.

On the basis of their result, we have synthesized the *N*-cyclohexylimine of 4-vinylbenzaldehyde as a new monomer, 1, and attempted the polymerization of 1 in the hope that the anionic initiator would attack not the imine group but the vinyl group selectively to initiate the polymerization.

Anionic Polymerization of 1. The anionic polymerization of 1 was carried out in tetrahydrofuran (THF) at −78 °C with various initiators. These initiators included potassium naphthalenide, [2-(1-methylethyl)phenyl]potassium (cumylpotassium), and oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium. Upon addition of 1 to the potassium naphthalenide in THF, an immediate color change from green to dark red occurred, whereas appreciable color change was not observed in the cases with either cumylpotassium or oligo(α-methylstyryl)dialkalimetal salts as initiators since they were similarly red colored. The color apparently remained unchanged at -78 °C for at least 1 h. It disappeared immediately by adding a few drops of methanol as expected. The polymer was then precipitated by pouring the reaction mixture into a large amount of water, giving a near quantitative yield in each case based on the form of poly(1). The polymers were then purified by reprecipitation twice by using a THF–hexane system. As shown in Figure 1, the infrared (IR) spectrum of the polymer showed a strong absorption at 1640 cm^{-1}, corresponding to the HC=N group. The ^{1}H-NMR spectrum showed the signals expected for poly(1) as shown in Figure 2. The characteristic singlet corresponding to the azomethin proton appeared at 8.17 ppm in the reasonable integral ratio to those of other signals. Thus, examination of the polymer by both IR and ^{1}H NMR spectroscopies revealed virtually the structure of poly(1), suggesting that the vinyl polymerization of 1 proceeded exclusively without side reactions. The *N*-cyclohexylimino groups on the polymer chain were stable and stayed intact during the course of the polymerization and the workup of the polymer treatment.

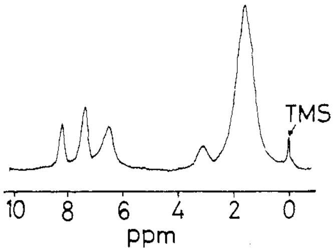


Figure 1. IR spectrum of poly(1).

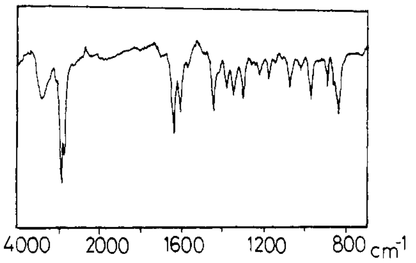


Figure 2. ^{1}H NMR spectrum of poly(1).

The molecular weights and the distribution parameters for this series of poly(1) are listed in Table I. As can be seen, there is a fair agreement between the predictable molecular weights based on monomer to initiator ratios and the measured values of molecular weight by vapor pressure osmometry (VPO). Analysis by gel permeation chromatography (GPC) reveals a unimodal molecular weight distribution of nearly monodispersity in the molecular weight range studied here. The $\bar{M}_w$ to $\bar{M}_n$ ratios were around 1.1 which were calculated from the GPC curves by using the calibration from $\bar{M}_n$ and elution count.[7] Representative GPC profiles are illustrated in Figure 3. Accordingly, these results clearly indicate that 1 undergoes

Table II
Values of Intrinsic Viscosity for Poly(1)

run	$[\eta]_{\mathrm{THF}}^{40\,°\mathrm{C}}$, dL/g	$\bar{M}_n$(VPO) × 10^{-4}
1	0.0754	0.80
2	0.102	1.4_0
3	0.120	2.0_0
5	0.166	3.1_0
6	0.240	5.9_0
7	0.255	6.6_6
8	0.344	$11._2$

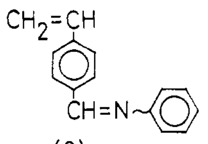
Table III
K and a Values of Mark–Houwink Equation[a]

polymer	$K \times 10^4$	a
poly(1)	4.3	0.58
polystyrene	1.2	0.72

[a] In THF at 40 °C. Mark–Houwink parameters of polystyrene in THF at 20–25 °C were published previously (see: Yau, Kirkland, Bly, Eds. *Modern SEC, Wiley*: New York, 1979; p 252).

anionic polymerization with each of the initiators and that the polymerization proceeds without chain transfer and termination reactions under the above conditions. Furthermore, rapid initiation may be evidenced by the fact that the polymers have narrow molecular weight distributions. The results also support that the cyclohexyl group satisfactorily protects the carbon–nitrogen double bond of imine from nucleophilic attack of both initiator and the propagating carbanion derived from 1 to eliminate the possibility of any chain-termination reactions.

We have also prepared *N*-[(4-ethenylphenyl)methylene]benzenamine (**2**), a structural analogue of 1, and



(2)

tried to the polymerization of **2** under identical conditions. However, no polymerization of **2** with either initiator occurred and the starting monomer **2** was nearly quantitatively recovered in every case. It is clear that *N*-phenyl substituent is not effective for the protection of the CH=N functionality toward the anionic initiators. Thus, the choice of N-substituent of imine is very important to achieve the anionic polymerization.

Mark–Houwink Equation of Poly(1). The poly(1) is a white solid in the molecular weight range prepared in this study. The solubility of this polymer appears to be similar to that of polystyrene. It is soluble in a wide variety of solvents such as benzene, toluene, diethyl ether, THF, 1,4-dioxane, methyl ethyl ketone, ethyl acetate, carbon tetrachloride, chloroform, dichloromethane, carbon disulfide, pyridine, and 1-butanol. It is insoluble in hexane, acetone, triethylamine, *N*,*N*-dimethylformamide, ethanol, methanol, and water. Poly(1) is stable in air and solution under neutral conditions but readily hydrolyzed even under weak acidic conditions which will be mentioned later. It can be cast from THF solution to give a colorless, transparent, and brittle film.

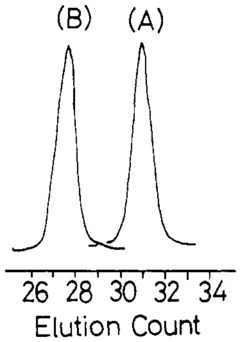


Figure 3. GPC curves for poly(**1s**): (A) $\bar{M}_n$ (obsd) = $3.1_0 \times 10^4$, $\bar{M}_w/\bar{M}_n$ = 1.15; (B) $\bar{M}_n$ (obsd) = $11._2 \times 10^4$, $\bar{M}_w/\bar{M}_n$ = 1.05.

The intrinsic viscosities of poly(1) samples were measured in THF at 40 °C shown in Table II and were correlated by the Mark–Houwink equation,[8,9] $[\eta] = KM^a$, since the polymers obtained had narrow molecular weight distributions. Good straight line plots of log $[\eta]$ versus log $[M]$ were obtained where M is $\bar{M}_n$ ranging from 0.80 to 11.2 × 10^4. The values of K and a are summarized in Table III. Both values of polystyrene are also listed for comparison. Since a molecular weight range for meaningful K and a is somewhat narrow, both values listed should be considered preliminary.

The value of "a" for polystyrene in THF is 0.72 showing that THF is a good solvent for polystyrene. In contrast, the value of "a" of 0.58 for poly(1) suggests that the polymer is relatively contracted in THF compared to polystyrene which is reasonably extended.

Since intrinsic viscosity and GPC measurements were run in THF at 40 °C, the values of viscosity and their volume counts of gel permeation chromatograms can be used to calculate molecular weight by the universal calibration technique.[10] The agreement of molecular weights determined in this way compared with absolute method by VPO is reasonably good as can be seen in Table IV. This proves that the universal calibration technique is also a good means to estimate the molecular weight of the polymer of 1.

Isolation of Poly(4-vinylbenzaldehyde). The complete deprotection is especially important in polymer synthesis using a protective group, since the separation of the protected and the deprotected forms in the same polymer chain is in principle impossible. Deprotection of the *N*-cyclohexylimino group from the poly(1) was carried out by the reaction of poly(1) with 0.5 N HCl in a 1,4-dioxane–water mixture (11/1, v/v) at 25 °C for 5–20 h. Polymer was then obtained by precipitation in water. The yield of isolated polymer amounted to nearly quantitative

Table IV
Molecular Weights for Poly(1)

run	$\bar{M}_n$(calcd)[a] × 10^{-4}	$\bar{M}_n$(obsd)[b] × 10^{-4}	$\bar{M}_n$[c] × 10^{-4}	$\bar{M}_w$[c] × 10^{-4}	$\bar{M}_w/\bar{M}_n$
1	0.82	0.80	0.72	0.79	1.10
2	1.5_1	1.4_0	1.4_5	1.6_2	1.12
3	2.2_0	2.2_0	1.6_8	1.9_3	1.15
5	3.5_0	3.1_0	2.8_5	3.3_5	1.18
6	5.0_0	5.9_0	5.4_3	6.0_3	1.11
7	6.3_0	6.6_6	5.9_6	6.1_7	1.03
8	$12._7$	$11._2$	9.5_5	$10._1$	1.06

[a] $\bar{M}_n$(calcd) were calculated from monomer to initiator ratio. [b] $\bar{M}_n$(obsd) were obtained by VPO. [c] $\bar{M}_n$ and $\bar{M}_w$ were calculated from the universal calibration method.

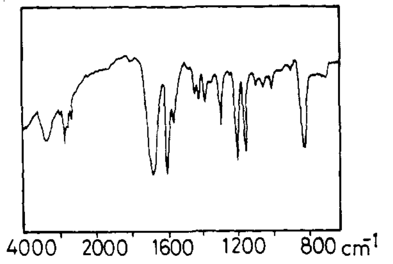


Figure 4. IR spectrum of poly(4-vinylbenzaldehyde).

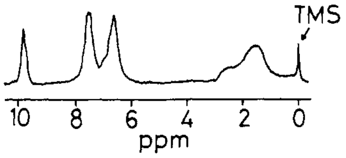


Figure 5. ^{1}H NMR spectrum of poly(4-vinylbenzaldehyde).

as poly(4-vinylbenzaldehyde).

The IR spectrum of the resulting polymer exhibited a strong band of 1690 cm^{-1} characteristic for a carbonyl group of aldehyde and the absorption of 1640 cm^{-1} corresponding to the carbon–nitrogen double bond disappeared as shown in Figure 4. The spectrum was virtually identical with that of poly(4-vinylbenzaldehyde) prepared by the method previously reported.[2] The ^{1}H NMR spectrum showed the signals expected for poly(4-vinylbenzaldehyde). The signal for the proton of the aldehyde was present at 9.90 ppm, whereas no trace of the signal corresponding to CH=N at 8.17 ppm could be detected at all as illustrated in Figure 5. It was found that the integral ratio of CHO to aromatic protons was 1:4 as expected. Thus, spectroscopic studies unequivocally reveal within their analytical limits that complete removal of the protecting group can be achieved. Furthermore, this is confirmed by elemental analysis of the resulting polymer which shows that the nitrogen was not detected at all. The measured values for carbon and hydrogen were in agreement with the calculated ones when the polymer was assumed to contain 0.456 mol of H_2O per monomer unit: Anal. Calcd for $C_9H_8O{\cdot}0.456H_2O$: C, 77.01; H, 6.40; N, 0.00. Found C, 77.02; H, 6.24; N, 0.00.

The poly(4-vinylbenzaldehyde) thus obtained is a white solid. It is soluble in THF, 1,4-dioxane, methyl ethyl ketone, chloroform, dichloromethane, and *N*,*N*-dimethylformamide but insoluble in hexane, benzene, toluene, carbon tetrachloride, diethyl ether, ethyl acetate, acetone, triethylamine, pyridine, carbon disulfide, 1-butanol, ethanol, methanol, and water.

The molecular weights of the polymers were determined by the universal calibration method. Table V summarizes the results of the molecular weights and their distributions of the series of poly(4-vinylbenzaldehydes) obtained here.

As can be seen, there is fair agreement between the values of $\bar{M}_n$ calculated and observed by the universal calibration method. This may suggest that main-chain degradation is not accompanied during the deprotection step. More reliable evidence for this was obtained by the analysis of GPC curves which showed that these polymers all had single peaks without any shoulders and had narrow molecular weight distributions. Thus, we have successfully obtained soluble, linear poly(4-vinylbenzaldehydes) of well-defined structures that have predictable molecular weights with near monodispersity. The key points of this method are the success of the anionic living polymerization of 1 and the complete removal of *N*-cyclohexyl group to generate the aldehyde group. Compared to our previous method where 1,3-dimethyl-2-(4-vinylphenyl)imidazolidine was used as a protected monomer, the evaluation of the resulting poly(4-vinylbenzaldehyde) may be essentially the same. The advantage of the present method is the use of much cheaper cyclohexylamine rather than *N*,*N*′-dimethylethylenediamine. Furthermore, in our sense, the stabilities of 1 and the poly(1) seem to be relatively better than those of 1,3-dimethyl-2-(4-vinylphenyl)imidazolidine and its polymer which are gradually cleaved even by the moisture in the air.

Table V
Molecular Weights for Poly(4-vinylbenzaldehyde)

$\bar{M}_n$(calcd) × 10^{-4} [a]	$\bar{M}_n$(obsd) × 10^{-4} [b]
0.51	0.54
0.93	0.76
1.3_6	1.2_9
2.1_7	2.5_6
3.1_0	2.8_0

[a] $\bar{M}_n$(calcd) were calculated from the monomer to initiator ratio. [b] $\bar{M}_n$(obsd) were obtained from the universal calibration method. The $\bar{M}_w/\bar{M}_n$ obtained by universal calibration method. The $\bar{M}_w/\bar{M}_n$ obtained by universal calibration were very close to those by the GPC curve using a polystyrene calibration curve and were in the range 1.10–1.18 in all cases.

Experimental Section

Materials. 4-Chlorostyrene was kindly supplied from Hokko Chemical Industry Co., Ltd. It was distilled at 54 °C (5 mmHg) over calcium hydride. α-Methylstyrene was distilled over calcium hydride. After adding benzyl magnesium chloride in THF to α-methylstyrene, the mixture was degassed and then distilled together with THF on the vacuum line into the ampules fitted with break-seals. THF was refluxed over sodium wire for 5 h and distilled from its sodium naphthalenide solution. Naphthalene was purified by sublimation. Cumylpotassium was prepared by the reaction of cumyl methyl ether with sodium–potassium alloy in THF according to the method previously reported.[11] Metal naphthalenides were prepared by the reactions of a small amount of excess naphthalene with the corresponding metals in THF. Their concentrations were determined by colorimetric titration to colorless end point with standardized 1-octanol in a sealed reactor through break-seals under vacuum.[12] Oligo(α-methylstyryl)dilithium, -disodium, and -potassium were freshly prepared just prior to polymerization from the corresponding metal naphthalenides and 2–4 M quantity of α-methylstyrene at 30 °C for 1 min and then at −78 °C for 10 min.

4-Vinylbenzaldehyde was prepared from the reaction of 4-vinylphenyl magnesium chloride and *N*,*N*-dimethylformamide in THF according to the method previously reported.[13] The crude product was purified by fractional distillation at 62–63 °C (1 mmHg) (lit.[13] 92–93 °C (14 mmHg)). The purity was checked by gas chromatography and found to be always more than 99%.

***N*-[(4-Ethenylphenyl)methylene]cyclohexamine (1).** A solution of 4-vinylbenzaldehyde (9.30 g, 70 mmol), cyclohexylamine (7.62 g, 77 mmol), and *tert*-butylcatecohol (1 mg) in benzene (150 mL) was heated at reflux with azeotropic removal of water for 5 h. The solution was cooled and concentrated to give a yellow oil. Fractional distillation gave 12.4 g (58 mmol, 83%) of 1 as a colorless liquid: 60-MHz ^{1}H NMR (CCl_4) δ 8.23 (1 H, s, C*H*=N), 7.70, 7.38 (4 H, dd, *J* = 9 Hz, Ar), 6.73 (1 H, dd, vinyl C*H*), 5.74, 5.25 (2 H, dd, *J* = 18, 10 Hz, vinyl CH_2), 3.47–2.87 (1 H, m, =NC*H*), 2.33–1.00 (10 H, m, $=NC(CH_2)_5$); 100-MHz ^{13}C NMR ($CDCl_3$) δ 24.564, 25.497, 34.221 (cyclohexyl CH_2), 69.632 (=NCH), 114.408 (β-CH_2), 125.931 (Ar C3), 127.943 (Ar C2), 136.000 (Ar C4), 136.024 (α-CH), 139.028 (Ar C1), 157.493 (C=N).

In order to remove impurities in 1, phenyl magnesium chloride (5 mL, 0.25 M solution in THF) was added to 1 (6.0 g) at 0 °C under a nitrogen atmosphere and the mixture was stirred for 10 min. It was then degassed and distilled on the vacuum line into the ampules fitted with break-seals. Thus, distilled 1 was stored at −30 °C until ready to use for anionic polymerization.

***N*-[(4-Ethyenylphenyl)methylene]benzenamine (2).** The reaction mixture of 4-vinylbenzaldehyde (10.0 g, 76 mmol) and aniline (6.97 g, 76 mmol) was stirred at room temperature for 2

h. Recrystallization from 95% ethanol provided 12.42 g (60 mmol, 79%) of **2** as white needles: mp 69.4 °C; 60-MHz ^{1}H NMR (CCl_4) δ 8.47 (1 H, s, N=C*H*), 8.00–7.33 (9 H, m, Ar), 6.83 (1 H, dd, vinyl C*H*), 5.85, 5.19 (2 H, dd, J = 18, 10 Hz, vinyl CH_2).

It was dried over P_2O_5 for 48 h in the reactor with break-seals under vacuum ($\approx 10^{-6}$ mmHg) and was used for anionic polymerization.

Polymerization Procedures. All the polymerizations were carried out at −78 °C with shaking under high-vacuum conditions ($\approx 10^{-6}$ mmHg) in an all-glass apparatus equipped with break-seals. The polymerizations were carried out for 30 min and terminated with methanol. The polymers were precipitated by adding a large excess of water. They were redissolved in THF, precipitated into hexane an additional 3 times, and freeze-dried.

Deprotection. Poly(**1**) (0.300 g) was dissolved in 1,4-dioxane (11 mL) containing 6 N HCl (1 mL). The slightly cloudy mixture was stirred for 5 h at room temperature and poured into an excess of water. The polymer was recovered by filtration, washed with water and then hexane, redissolved in THF, and precipitated into hexane an additional 2 times. Then it was freeze-dried from its 1,4-dioxane solution. The yield of polymer was near quantitative (0.121 g, 98%). The polymer was identified as poly(4-vinylbenzaldehyde) by its IR and ^{1}H NMR spectra as shown in Figure 4 and 5, respectively. ^{1}H NMR ($CDCl_3$) (60 MHz) δ 9.92 (1 H, s, C*H*O), 8.25–6.28 (4 H, m, Ar), 2.60–1.08 (2 H, m, CH_2 and 1 H, m, CH); IR C=O at 1690 cm^{-1}. Anal. Calcd for $(C_9H_8O\ 0.456\ H_2O)_n$: C, 77.01; H, 6.40; N, 0.00. Found: C, 77.02; H, 6.24; N, 0.00.

Measurements. IR spectra were run with a Jasco IR-G spectrophotometer. ^{1}H NMR spectra (60 MHz) were recorded with a JEOL JNM-PMX 60 instrument. ^{13}C NMR spectra (100 MHz) were recorded with JEOL GX-400 instrument in $CDCl_3$. Gel permeation chromatograms were obtained with Toyo Soda HLC-802 instrument with UV or refractive index detection. THF was carrier solvent at a flow rate of 1.4 mL min^{-1} and a temperature of 40 °C. Vapor pressure osmometry (VPO) measurements for number-average molecular weight determination were made with a Corona 117 instrument. Under very precise temperature control with thermocouples with high sensitivity, a molecular weight up to 2×10^5 could be determined within analytical error of ±10%. Intrinsic viscosities were obtained for all polymers in THF at 40 °C by using Ubbelohde-type viscometers.

Registry No. **1**, 110718-25-7; **1** (homopolymer), 110718-26-8; **2**, 67735-81-3; K-Nap, 4216-48-2; Na-Nap, 3481-12-7; Li-Nap, 7308-67-0; cumyl potassium, 3003-91-6; 4-H_2C=$CH_2C_6H_4CHO$, 1791-26-0; $C_6H_5NH_2$, 62-53-3; cyclohexylamine, 108-91-8; oligo(α-methylstyryl)dilithium, 57486-16-5; oligo(α-methylstyryl)disodium, 37244-89-6; oligo(α-methylstyryl)dipotassium, 52219-57-5.

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The Low Pressure Fischer Polymerization of Ethylene with Al + $AlCl_3$ + $TiCl_4$ Revisited[1a]

George A. Olah,*† Mark Bruce,† Francoise Clouet,†,1b S. Morteza F. Farnia,† Omar Farooq,† G. K. Surya Prakash,† John Welch,† and Jack L. Koenig*‡

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089, and Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106. *Received July 15, 1986*

ABSTRACT: Fischer in 1943 described the $AlCl_3$ + Al + $TiCl_4$ catalyzed polymerization of ethylene to solid polyethylene at temperatures of 130–180 °C and pressures of 30–80 atm. No characterization of the polyethylene formed was given nor any mechanism suggested for the reaction. Recently, Martin et al. reinvestigated the Fischer polymerization and reported that the polyethylene obtained in admixture with Friedel–Crafts-type hydrocarbon oils is highly branched. In contrast, our reinvestigation of the Fischer polymerization of ethylene showed that if the temperature of the reaction mixture is kept in the range suggested by Fischer (130–180 °C) or below, besides Friedel–Crafts-type oils, linear high-density polyethylene similar to Ziegler polyethylene is obtained. Without proper temperature control, however, the exothermic reaction can lead to the results reported by Martin et al. Study of the mechanism of the Fischer polymerization indicates that the system is well suited for the in situ formation of ethylaluminum chlorides via the Hall and Nash reaction, as well as isomeric bis(dichloroaluminio)ethanes which, with $TiCl_4$, form the active Ziegler–Natta-type coordination polymerization catalysts.

Introduction

Karl Ziegler and his associates' discovery of the low-pressure polymerization of ethylene with Et_3Al + $TiCl_4$ to high-density linear polyethylene is well recognized as one of the major chemistry achievements of our time.[2] The work with subsequent studies by Natta and co-workers[2] on the related stereoregular polymerization of propylene culminated in 1963 by awarding the Nobel prize in chemistry to Ziegler and Natta for their development of a new and most significant branch of polymer chemistry now

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† University of Southern California.
‡ Case Western Reserve University.

0024-9297/87/2220-2972$01.50/0