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]

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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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Table I
Fischer Polymerization of Ethylene

max reactn temp, °C	time to reach max temp, min	consumed ethylene, mol	solid polyethylene yield, g	oil, g	% polyethylene in prod	T_m, °C	T_c, °C	IR, 1378 cm^{-1}	$\bar{M}_v$
155	100	28	176	660	21	129	110	linear	129000
80	35	30	512	191	73	128	110	linear	148000
65	25	10	109	48	74	129	110	linear	195000

known as Ziegler–Natta chemistry.

Catalytic polymerization of ethylene by Max Fischer, carried out in the early 1940s in the wartime German industry, remained relatively unnoticed.[3] Fischer, in a brief patent application containing a single experimental example, described that ethylene can be polymerized at temperatures of 130–180 °C and pressures of 30–80 atm by a catalyst comprised of $AlCl_3$, a "hydrogen chloride binding" metal (preferentially Al, but also Zn or Fe), and $TiCl_4$ to solid polyethylene. No characterization of the polyethylene was given, nor was any mechanism suggested.

$$CH_2{=}CH_2 \xrightarrow[\text{heptane}]{\text{Al} + AlCl_3 + TiCl_4} \text{solid polyethylene}$$

Although Fischer's polymerization of ethylene occasionally was mentioned in reviews, monographs,[4a-d] and the patent literature,[4e,f] its reproducibility was questioned and the nature of the polyethylene formed was not established.

No reinvestigation of the Fischer polymerization appeared in the scientific literature until a recent study by Martin et al.[5] They reported that the Fischer polymerization of ethylene gives, besides Friedel–Crafts-type oligomeric and cyclized liquid hydrocarbons (oils), only highly branched polyethylene with melting points between 100 and 120 °C. They consequently concluded that "the catalyst described by Fischer is of a different kind from that described by Ziegler". In view of Martin et al.'s publication[5] we would like to report our studies, which we feel will put the Fischer polymerization of ethylene in a different perspective and clearly establishes its significance as a forerunner of the Ziegler–Natta coordination polymerization.

Results and Discussion

At the beginning of our studies we asked ourselves the following questions: (a) Is the Fischer's polymerization reproducible and does it give solid polyethylene? (b) What is the structure of the polyethylene (branched or linear)? (c) Can such polyethylene be formed by a Friedel–Crafts-type reaction in a system containing significant amounts of $AlCl_3$ as well as $TiCl_4$? (d) If not, what is the nature of the Fischer polymerization?

Results of the experimental investigation of the Fischer polymerization gave the following results and answers to the questions raised. (a) The $AlCl_3$ + Al + $TiCl_4$ catalyzed polymerization of ethylene unequivocally gives solid polyethylene. Table I summarizes the results of three typical independent runs with identical reagent ratios varying only in time–temperature conditions. We have found no significant effect of the purity of the aluminum powder used on the reaction. More active (higher purity) aluminum generally resulted only in shorter initiation times of the reaction.

The single example given in Fischer's patent was rather vague on details of experimental conditions. The reaction was carried out in heptane solution. The reaction temperature was stated to have reached 155 °C. The patent itself claimed the temperature range of the polymerization process to be between 130 and 180 °C. It gave no indication of how rapidly this temperature was reached and how it was maintained (controlled, if at all). In our reinvestigation, the reaction was found to be highly exothermic and it was realized that good temperature control is essential. This was achieved by a water-cooled coil fitted within the pressure autoclave. Following closely the temperature of the reaction during the runs allowed control throughout the polymerization. Solid polyethylene was obtained besides Friedel–Crafts oils, in all polymerizations below 180 °C, including Fischer's specific example with a maximum of 155 °C. It was further observed that when the temperature was kept between 65 and 80 °C, the yield of solid polyethylene substantially increased. The polymerization proceeds even at room temperature, albeit much slower.[6] At 200 °C or above only oily products were formed.

In our studies it was also observed that the ethylene polymerization proceeds well under much lower, or even atmospheric, pressure of ethylene, allowing the use of laboratory glass equipment. A pressure of 5–10 atm is, however, preferred to maintain a suitable concentration of ethylene in the system for a good rate of polymerization.

It was found that the polymerization of propylene is also possible with the Fischer system. Since $AlCl_3$ more readily oligomerizes propylene than ethylene to low molecular weight Friedel–Crafts oils, it is convenient to start the reaction with ethylene and, once the polymerization starts, change the feed to propylene.

(b) The solid polyethylene formed in the Fischer polymerization of ethylene shows after isolation and washing with aqueous HCl and ether (see Experimental Section) a melting point of 128–129 °C. After further purification, the polyethylene melts at 130–131 °C. The infrared spectra, on the basis of the absence of the characteristic methyl absorption at 1378 cm^{-1}, indicated minimal branching and were identical with that of authentic Ziegler polyethylene. Molecular weights obtained were between 124 00/ and 195 000. These data are typical of high-density, linear polyethylene. When the temperature is raised during the reaction above 180 °C, branching is observed with a corresponding decrease in molecular weight. Our experimental data are contrary to those of Martin et al.[5] who reported the formation of only highly branched polyethylene. The discrepancy, however, is easily rationalized if one considers the exothermicity of the reaction. It was found that the highly exothermic polymerization without close temperature control indeed gives the results quoted by Martin et al. (see Experimental Section). With proper temperature control, the Fischer polymerization was consistently found to give linear high-density polyethylene.

(c) On the basis of these observations one can clearly rule out a Friedel–Crafts-type carbocationic polymerization process in the Fischer polymerization reaction as this would give only highly branched polyethylene.[7] Since there are no radical initiators present in the system, and the reaction temperature and pressure are modest, one can also rule out any free radical type of polymerization.

(d) Having eliminated the possibility of cationic and free radical polymerization and having found that the Fischer polymerization gives high density linear polyethylene, we are left (with our present knowledge of coordination polymerization) with the only alternative that the polymerization proceeds via an in situ formed, Ziegler-type catalyst system.

How can a Ziegler-type catalyst be formed from ethylene with Al + $AlCl_3$ + $TiCl_4$? The related Al + $AlCl_3$ + ethylene system (without $TiCl_4$) was investigated by Hall and Nash as early as 1937.[8a-c] They discovered that the reaction of aluminum powder and anhydrous aluminum trichloride (1:3 by weight) with ethylene at 155 °C and 60 atm yields ethylaluminum dichloride and diethylaluminum chloride (i.e., ethylaluminum sesquichloride).

$$3CH_2{=}CH_2 + AlCl_3 + Al + 1.5H_2 \xrightarrow[60\ atm]{155\ °C} (C_2H_5)_2AlCl{\cdot}C_2H_5AlCl_2$$

The reaction is a complex process where Friedel–Crafts oligomerization and cyclization liberate sufficient hydrogen to allow formation of ethylaluminum halides. Ruthruff,[8d] indeed, was subsequently able to improve the Hall and Nash reaction by performing it under hydrogen pressure.

Martin has argued[5] that the stoichiometry used in Fischer's reaction was significantly different from that used by Hall and Nash (only $^1/_{10}$ the amount of Al metal was used). Consequently, even if the ethylaluminum sesquichloride would have formed, it would react with excess $AlCl_3$ to give ethylaluminum dichloride which is unsuitable to form a Ziegler catalyst with $TiCl_4$. Fischer in his patent, however, has remarked that the ratio of the metal to the halide can vary within a wide range, although only one specific metal to $AlCl_3$ ratio was used in his experimental example. Since the Fischer polymerization is carried out with a catalyst system formed in situ, any Et_2AlCl formed could not only react with excess $AlCl_3$ but also with the $TiCl_4$ present to give the active catalyst. Thus, overall bulk stoichiometry has little relevance. It is well recognized that even a very small amount of active catalyst can bring about effective polymerization. In the supernatant solvent layer of the polymerization reaction mixture no organoaluminum compounds could be detected by NMR spectroscopy. This is, however, understandable because of the low concentration (if any) of free organoaluminum compounds that would remain in solution in the presence of $TiCl_4$.

Besides ethylaluminum chlorides formed in the Hall and Nash type chemistry we have also found additional organoaluminum compounds in the system.

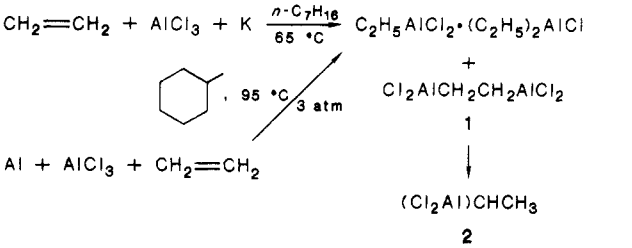
On restudying the product of the Hall and Nash reaction of ethylene with $AlCl_3$ + Al by ^1H, ^{13}C, and ^{27}Al NMR spectroscopy, we have observed that besides ethylaluminum chlorides, 1,1-bis(dichloroaluminio)ethane is also formed (present probably as its oligomers).

Kooyman et al.[9] and Eidt[10] respectively have reported that aluminum trichloride reacts with ethylene in the presence of reducing metals such as potassium or aluminum under relatively mild conditions (95 °C, 3 atm) to give 1,2-bis(dichloroaluminio)ethane (**1**). Kooyman et al.[9] isolated **1** as an ether complex. Neither authors offered, however, any structural (spectroscopic) proof for **1**. Martin and co-workers[6,11] were able to reproduce the above results and were able to identify small amounts of **1**. The major product obtained was, however, isomeric 1,1-bis(dichloroaluminio)ethane (**2**). We have carried out similar work with ethylene, aluminum, and aluminum trichloride in methylcyclohexane solution. In our studies we also found that in addition to ethylaluminum chloride (with ethylaluminum dichloride predominating) there is a small amount of initially detectable 1,2-bis(dichloroaluminio)ethane (**1**), besides geminal 1,1-bis(dichloroaluminio)ethane (**2**). after prolonged reaction times **1** is quantitatively isomerized to the more stable isomer **2**.

Table II
NMR Data on Bis(dichloroaluminininio)ethanes

compd	^1H NMR, δ^a	^{13}C NMR, δ^a	^{27}Al NMR, δ^b
1		5.2 (t)	35 (br)
2	−0.6 (quartet, J_{H-H} = 7 Hz)	−1.9 (d)	−23 (br)
	1.52 (d, J_{H-H} = 7 Hz)	10.0 (quartet)	

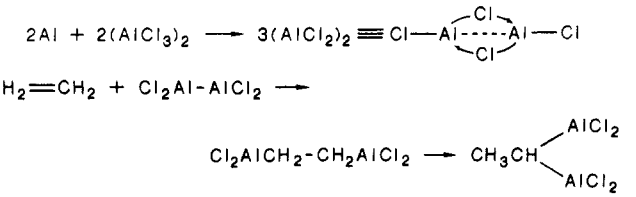
[a] In ppm from the tetramethylsilane signal. [b] In ppm from the $AlCl_3(CH_3CN)_6$ complex signal.



Compounds **1** and **2** upon deuteriolysis with D_2O gave 1,2- and 1,1-deuterioethane, respectively. They were further analyzed by ^1H, ^{13}C, and ^{27}Al NMR spectroscopy in THF-d_8 or heptane solution at −60 °C (see Table II).

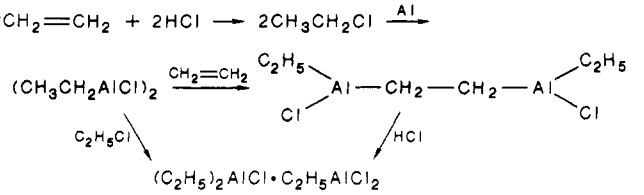
When $TiCl_4$ is added to a heptane solution of **2** an active Ziegler-type catalyst system is formed which polymerizes ethylene to linear high-density polyethylene. The Hall and Nash reaction mixtures upon addition of $TiCl_4$ gave similar results.

The formation of **1** and **2** from ethylene and $AlCl_3$ + Al is considered to involve intermediate formation of aluminum dichloride[12] which in its dimeric form adds to ethylene.



Other reducing metals besides K and Al, such as Na, Mg, and Zn, were found to act in a similar fashion. The metals mentioned by Fischer as "hydrogen chloride binding metals" thus only depict a class of metals which have good redox potentials. Mg powder was found to be particularly active. The $AlCl_3$ + Mg + $TiCl_4$ system gives high yields of linear high-density polyethylene even at atmospheric pressure of ethylene and ambient temperature.

Any HCl formed in the Fischer system would preferentially add to the large excess of ethylene present forming ethyl chloride. Ethyl chloride is well-known to react with aluminum in the presence of aluminum trichloride to give ethylaluminum sesquichloride.[13] In the presence of ethylene, 1,2-bis(ethylchloroaluminio)ethane formation can also occur as shown below. The reactions again are best understood as proceeding through divalent ethylaluminum chloride.



In conclusion the reinvestigation of the Max Fischer polymerization of ethylene under proper temperature control gave linear, high-density polyethylene similar to Ziegler polyethylene. Since no Friedel–Crafts or radical polymerization is involved, Fischer must have carried out the polymerization of ethylene with in situ formed ethylaluminum halides and $TiCl_4$. Although the studies of Hall and Nash preceded Fischer's work there was no mention of it in Fischer's patent, nor was the intermediacy of organoaluminum compounds suggested. Neither was the role of $TiCl_4$ discussed. Fischer, however, mentioned that it was advantageous to avoid oxygen from the system. This remark is hardly compatible with simple $AlCl_3$-catalyzed Friedel–Crafts-type chemistry, which is insensitive to air or oxygen[14] but is well recognized as essential for organoaluminum compounds.[13]

Without taking any credit away from Ziegler and Natta's pioneering work who first recognized the true nature and developed coordination polymerization, the Fischer polymerization of ethylene nevertheless should be considered as a direct forerunner of Ziegler–Natta coordination polymerization.

Experimental Section

General. Pressure reactions were conducted in a 2-L Parr Model 4531 pressure reactor, made of T316 stainless steel, equipped with turbine-type stirrer and water cooling coil. The autoclave was heated in an oven equipped with a solid-state potentiometric automatic temperature controller. Internal temperature was monitored with a thermocouple inserted into the thermowell of the reaction vessel. Normal heptane (Aldrich, 99%), anhydrous aluminum trichloride, aluminum powder (325 mesh), and titanium tetrachloride (Alfa Products, 99.9%) were used without further purification. Ethylene was obtained from Matheson (99.5%).

Typical Low-Pressure Polymerization of Ethylene with Al + $AlCl_3$ + $TiCl_4$. Into a 2-L stainless steel autoclave was added 500 mL of heptane, 1 g (0.037 mol) of aluminum powder, 30.6 g (0.23 mol) of aluminum trichloride, and 5.8 mL (10 g, 0.053 mol) titanium tetrachloride. The autoclave was closed and purged with ethylene, by being pressurized to ~10 atm of ethylene and mildly heated (~40 °C) to initiate the reaction. Subsequently, the temperature was maintained between 65 and 80 °C by alternate heating and cooling during the continued addition of ethylene. After a total of ~30 mol of ethylene had been added, the vessel was cooled to room temperature. After it was depressurized, the autoclave was opened and found to be packed with a wet granular polymer, which caked on the sides of the vessel, as well as being loosely packed around the stirrer and cooling coil. The product was successively washed with 10% aqueous HCl and with diethyl ether. Dried solid polyethylene 512 g, was obtained along with 191 g of oil (and additional heptane miscible oligomers). The IR spectrum was identical with that of a sample of authentic linear polyethylene. The absence of the characteristic IR methyl absorption at 1378 cm^{-1} indicates the absence of branching. Melting point (T_m, 129 °C) and crystallization temperatures (110 °C) were obtained on a Perkin-Elmer Model DSC-1B instrument with a heating–cooling rate of 10 °C/min. The viscosity molecular weight M_v was 148 000 (as determined by the ASTMD 1601-78 method using an Ubbelohde viscometer and decalin as solvent).

Polymerization reactions with maximum reaction temperatures of 65 and 155 °C were carried out similarly. Data are summarized in Table I.

Polymerization of Ethylene without Close Temperature Control. To the 21 autoclave was added 500 mL of heptane, 1 g (0.037 mol) of aluminum powder, 30.6 g (0.23 mol) of aluminum chloride, and 5.8 mL (10 g, 0.053 mol) of titanium tetrachloride. The autoclave was closed and purged in the usual manner. After the vessel was pressurized with ~40 atm of ethylene, the reaction became vigorously exothermic, the temperature rose and reached 230 °C before it leveled off and started to subside. After uptake of 32 mol of ethylene at ~120 °C, the autoclave was cooled to room temperature, depressurized, and opened and the contents quenched with 400 mL of 10% aqueous HCl. Both the organic and aqueous phases were filtered following the addition of 250 mL of methanol. The solid isolated was washed with diethyl ether and dried to yield only 1.3 g of polymer, mp 110–120 °C, IR, 1378 cm^{-1} (indicates extensive branching). The organic phase was separated and after removal of solvent (and lighter oligomers) by rotary evaporation gave 675 g of heavier oily product.

Polymerization of Ethylene with Mg + $AlCl_3$ + $TiCl_4$ at Ambient Temperature and Atmospheric Pressure. Into a 100-mL three-necked round-bottom flask equipped with a high-speed mechanical stirrer, reflux condenser, gas condenser, gas inlet, and thermometer was added 25 mL of heptane, 1 g (0.041 mol) of magnesium powder (325 mesh), 3.20 g (0.024 mol) of aluminum chloride, and 1.08 g (0.0057 mol) of titanium tetrachloride. Into this suspension with stirring was slowly introduced ethylene (C.P. Matheson) over a period of 3 h. The temperature of the reaction mixture was held constant near 35 °C to prevent the loss of the heptane solvent. The sides of the flask, the stirrer, and thermometer were covered with a white to brown granular solid. The solid was washed from the flask with 10% aqueous HCl and diethyl ether. Suction filtration of both the organic and aqueous phases yielded, after drying under reduced pressure, 6.8 g of white solid polyethylene, mp 130 °C. The IR spectrum showed no absorbance in the 1378-cm^{-1} region, indicating linear polyethylene. Related experiments with K, Na, and Zn were carried out in a similar fashion.

Preparation of 1,1-Bis(dihaloaluminio)ethane 2. Into an autoclave equipped with a mechanical stirrer was charged aluminum (1.0 g, 37 mmol), aluminum trichloride (2.1 g, 0.16 mmol), and methylcyclohexane (25 mL) under an argon atmosphere. The autoclave was then pressurized with 2.5 atm of ethylene and the mixture stirred for 12 h at 90–95 °C. After the reaction, the dark red reaction mixture was transferred into a flask and filtered under argon. The filtrate was treated with 25 mL of *n*-pentane to precipitate **2** as a beige solid. **2** was filtered (the filtrate contains ethylaluminum chlorides), washed several times with *n*-pentane to remove any residual ethylaluminum chlorides, and dried under vacuum at 50 °C to yield 2 g of 1,1-bis(dichloroaluminio)ethane (**2**).

^1H, ^{13}C, and ^{27}Al NMR spectra were obtained on a Varian Associates Model FT-80 spectrometer equipped with broad-band variable-temperature probe. IR spectra were obtained on Perkin-Elmer 257 spectrophotometer.

Registry No. $AlCl_3$, 7446-70-0; Al, 7429-90-5; $TiCl_4$, 7550-45-0; $H_2C{=}CH_2$, 74-85-1; Mg, 7439-95-4; $(Cl_2Al)_2CHCH_3$, 95465-40-0; polyethylene, 9002-88-4.

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(1) (a) Based on a lecture presented at the "Polymer Synthesis Symposium" honoring Professor M. Schwarz, University of Southern California, Los Angeles, CA, Nov 22, 1985. (b) Visiting scientist from the CNRS, Macromolecular Research Center, Strasbourg, France.

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Chain Transfer in Group-Transfer Polymerization

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ABSTRACT: When group-transfer polymerization (GTP) is carried out in the presence of carbon acids with pK_a values (in DMSO) in the range of 18-25, chain transfer can occur with lowering of the number average molecular weight and, usually, with an increase in polydispersity. Among the most effective chain-transfer agents are methyl α-phenylpropionate, methyl α-phenylacetate, and α-phenylpropionitrile. Chain-transfer constants in the range 0.4-1 were obtained for these compounds. Among the GTP catalysts that catalyze the chain-transfer process are bifluoride, acetate, *m*-chlorobenzoate, and bibenzoate. By the use of hydroxyl-labeled silyl ketene acetal initiator and α-phenylpropionitrile, the amount of polymer formed by direct initiation and by chain transfer can be measured by using HPLC to separate the resulting PMMA-OH from PMMA formed by chain transfer. Similarly, a labeled chain-transfer agent, 2-(trimethylsiloxy)ethyl α-phenylacetate, was used to permit direct measurement of PMMA formed by chain transfer. Other chain-transfer agents for GTP are indene, fluorene, and γ-thiobutyrolactone. Consistent with chain transfer by indene, 1-(trimethylsilyl)indene was shown to be an initiator for GTP of MMA.

Introduction

Chain-transfer processes in free radical and in ionic polymerizations have been thoroughly documented.[1a-d] Chain-transfer agents are often added to polymerizations to reduce the molecular weight or to introduce terminal functional groups. On the other hand, unwanted chain transfer to monomer occurs in some systems (notably in cationic polymerizations) placing an upper limit on the molecular weight which can be obtained. We have found several classes of compounds that are effective chain-transfer agents[1e] in the recently reported group-transfer polymerization of acrylic monomers using organosilicon initiators[2,3] and suitable catalysts.[4] The more effective of these chain-transfer agents can be used to replace nearly all of the organosilicon initiator (e.g., 1 in Scheme I) required for a given $\bar{M}_n$. This paper details these studies.

Experimental Section

Materials and Methods. Phenylacetonitrile, α-phenylpropionitrile, methyl phenylacetate, indene, and methyl (4-methoxyphenyl)acetate were purchased from Aldrich Chemical Co. and distilled in a 12-in. spinning-band column prior to use. γ-Thiobutyrolactone and fluorene were used as purchased from Aldrich Chemical Co. 2-(β-naphthyl)propionitrile was provided by Dr. R. J. McKinney.[5] Methyl α-phenylpropionate was prepared by the reaction of α-phenylpropionic acid with thionyl chloride followed by treatment with methanol and triethylamine and distillation in a spinning-band column. Solvents, 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene, 1-(2-(trimethylsiloxy)-ethoxy)-1-(trimethylsiloxy)-2-methyl-1-propene, and tris(dimethylamino)sulfonium bifluoride ($TASHF_2$), were prepared and purified as described earlier.[3] The general procedures for performing group-transfer polymerizations of MMA were the same as described earlier.[3] Tetrabutylammonium acetate was used as purchased from Fluka Chemical Corp. Tetrabutylammonium *m*-chlorobenzoate and tetrabutylammonium bibenzoate were prepared as described earlier.[4] Molecular weights and polydispersities ($D = \bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) using a Waters Associates 590 pump with elution over four consecutive columns containing microstyrogel 10 000, 1000, 500, and 100 Å with 401 refractive index detection. The standard was PMMA. Proton NMR spectra were recorded on an IBM NR80 NMR spectrometer. Proton NMR analysis of reaction mixtures for extent of conversion was performed with a Varian EM390 spectrometer at 90 MHz. High-performance liquid chromatographic analysis of mixtures of PMMA and PMMA with a terminal hydroxyl group (PMMA-OH) was performed by using a Du Pont Instruments chromatographic pump with a Lichrosorb Si 60 (5 μm) packed (E. Merck) column 4.0 × 250 mm with a Waters Associates differential refractometer Model R401 using ethyl acetate solvent as described by Andrews and Vatvars.[6] The retention volume for PMMA was 2.7 mL, and the retention volume for PMMA-OH was 3.8 mL at a flow rate of 1 mL/min.

General Procedure for Polymerization of MMA with Alternating Feeds of Monomer and Chain-Transfer Agent. Chain-Transfer with α-Phenylpropionitrile. To a stirred solution of 0.4 mL (2 mmol) of 1 and 10 μL of tetrabutylammonium *m*-chlorobenzoate (0.46 M in THF) in 30 mL of THF was added dropwise at a rate such that the reaction temperature did not exceed 44 °C (with the occasional aid of an ice bath) 10 mL of a solution of MMA (100 mL of 5 M solution in THF). Then 2 mL of a solution of α-phenylpropionitrile (18 mL of 1 M solution in THF) was added rapidly with development of a yellow color. In a similar manner, the remaining solutions were added by alternating nine more additions of MMA solution with eight more additions of α-phenylpropionitrile solution. After the reaction temperature had cooled to room temperature, 1 mL of methanol was added to quench the reaction, and a small sample was removed for analysis. NMR showed a trace of residual monomer. The polymer was isolated in nearly quantitative yield by precipitation with 1:1 aqueous methanol in a blender followed by drying at 80 °C (0.1 Torr). Gel permeation chromatography (GPC) showed that the PMMA had $\bar{M}_n = 2550$, $\bar{M}_w = 5550$, and $\bar{M}_w/\bar{M}_n = 2.18$.

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