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Preparation and Characterization of Some Derivatives of Poly(ethylenimine)

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ABSTRACT: Some acetylated and alkylated derivatives of poly(ethylenimine) have been prepared as macromolecular frameworks with potential catalytic properties. Proton nmr spectra of these derivatives have been examined and the resonances assigned. The nmr spectra together with other observations provide a means of establishing the sites of attachment of groups pendant on the polymer.

Poly(ethylenimine) (PEI) is a polymer synthesized by acid-catalyzed polymerization of ethylenimine (aziridine). The preparation and properties of PEI have been reviewed.[1-3] Under normal conditions for synthesis the polymer has a high degree of branching at the amine nitrogens. Previous reports from this laboratory have concentrated on a PEI with average molecular weight of about 50,000 and with a degree of branching such that about 25% of the amines are primary amines, 50% are secondary, and 25% are tertiary. Apolar derivatives of this polymer have been prepared by reaction of PEI with active esters of medium to long-chain carboxylic acids. The resulting macromolecules, which have 5–15% of the total amino groups modified to give amide-linked, apolar pendant groups, have been found to display particularly great ability to bind small molecules in aqueous solution.[4,5] In addition, these derivatives catalyze the release of nitrophenol from nitrophenyl esters in aqueous solution.[6,7] Related polymers which contain both apolar pendant groups and reactive nucleophiles such as imidazole are true catalysts for the hydrolysis of nitrophenyl esters.[8]

To better understand the mode of action of these catalysts we must know more about the structure of the polymer derivatives. The branching of PEI and the concommitant existence of three kinds of amines make the polymer intrinsically more complicated than linear polymers. Moreover, further complexity may appear when PEI is allowed to react with derivatizing agents, for reaction may occur at either the primary, secondary or, in some cases, even tertiary amine sites.

In our syntheses of binding and catalytic polymers, three principal derivatizing reactions have been used: acylation with an ester or anhydride, alkylation with an alkyl halide, reductive alkylation with a ketone and sodium borohydride. From studies with model systems one would expect acylation[9] and reductive alkylation[10] to proceed with some preferences toward the primary amines. Alkylation with alkyl halides might likewise occur preferentially at primary amines,[11a] or at comparable rates for primary and secondary amines.[11b] However, the model systems are not very closely related to the poly(ethylenimine) repeating units. Furthermore, one must consider the possibility that incorporation of the amines into a polymeric framework will change their relative reactivities in consequence of steric or electronic effects or by virtue of changes in the relative degrees of protonation of the nitrogens. Thus it is desirable to have direct, independent determinations of the courses of the reactions. Such scrutiny has been achieved with proton nuclear magnetic resonance studies of PEI derivatives coupled with considerations of the stoichiometry of reactions of known specificity.

Results and Discussion

Acylation and Reductive Alkylation of PEI. Specific details for the preparation of acetyl-PEI's are outlined in the Experimental Section. Table I summarizes some of the characteristics of six such derivatives, as well as the relative quantity of reagent used in the preparation. Included in Table I (final column) is the degree of acetylation inferred from the ratio of peak areas in the acetyl and the PEI backbone regions, respectively, in the nmr spectra. It is apparent that at moderate degrees of acetylation the reaction proceeds quantitatively to produce acetamide groups on the polymer. On the other hand, as expected, when the ratio of acylating agent to PEI becomes sufficiently high, the degree of substitution increases to a limiting value, presumably equal to the sum of the primary and secondary amino groups initially present. For convenience these acylated derivatives will be designated as Ac_XPEI, where X is the number of moles of acetyl covalently bound to 1 mol of PEI repeating unit, C_2H_5N.

Sodium 2,4,6-trinitrobenzenesulfonate has been demonstrated to be useful as a reagent for determination of amino groups.[12,13] This reagent is fairly reliable for assay of primary amines, such as α-amino groups of peptides and proteins and ϵ-amino groups of lysine residues in such compounds, since its reactivity toward secondary amines is much weaker. For example, diethylamine reacts 2500 times less rapidly than does n-butylamine.[14] Thus an

Table I
Acetyl-PEI Derivatives

No.	Reagent[a]	Amount (mol of Reagent/ mol of PEI)	TNBS Test (%)	Nmr
1	Ac_2O	0.27	5	29% acylation; some secondaries acylated
2	PnpAc	0.27		24% acylation; no secondaries acylated
3	PnpAc	0.26	2.5	
4	Ac_2O[b]	0.27	5	
5	Ac_2O	0.37	1	37% acylation; some secondaries acylated
6	Ac_2O	1.3	0	*Ca.* 70% acylation; many secondaries acylated

[a] Abbreviations used are: Ac_2O, acetic anhydride; PnpAc, *p*-nitrophenyl acetate; TNBS, sodium 2,4,6-trinitrobenzenesulfonate. [b] Reaction run at − 5 to 0°.

assay with trinitrobenzenesulfonate should measure the degree of acylation of primary amines on PEI.

When PEI-600, with amines completely unmodified, is assayed with trinitrobenzenesulfonate, and if the extinction coefficient of the picramide adduct is taken to be 12,000, the ratio of primary to total amines is found to be 0.25. Since the expected ratio is 0.25 (see ref 1, and evidence presented below), and since the picramide coefficient is well within the range of those used in this assay method,[12,13] we conclude that trinitrobenzenesulfonate reacts specifically with the primary amino groups on PEI, and that the extinction coefficient of the picramide formed is not altered by local environmental effects on the polymer.

Table I lists the amounts of free primary amine (relative to total amine nitrogen) found for the acetyl-PEI derivatives prepared. For a degree of acetylation of 0.7 as determined by nmr, zero residual primary amine was detected by the trinitrobenzenesulfonate test. For a degree of acetylation of 0.37, from nmr, a small amount, 1%, of primary amine appeared as picramide. This small positive value could be due to the slight reactivity of secondary amines with trinitrobenzenesulfonate or to the presence of small amount of residual free primary amine. In either event, it is clear that the primary amino groups of PEI are substantially more reactive toward the acetylating agents than are the secondary amino groups.

The trinitrobenzenesulfonate tests for the derivatives with degrees of acetylation near 0.25 indicate further that the primary amines are substantially more reactive than the secondaries. In these derivatives some residual primary amines always seem present. Three explanations of their presence can be envisioned: (1) locally high initial concentrations of acylating reagent caused a greater degree of acetylation in some macromolecules and a lower degree in others; (2) the ratio of primary to total amines is a little greater than 0.25; (3) the reactivity of secondaries is sufficiently great to be somewhat competitive under these conditions. The first possibility was essentially excluded by the observation that the product of the reaction at 0 to −5° was essentially the same as that prepared at room temperature. The second and third possibilities, however, cannot be separated on the basis of the data thus far discussed.

A more complete description of the polymer derivatives can be obtained from a more detailed explanation of the acetyl resonance(s) in the proton nmr spectra. These resonances for secondary and tertiary acetamides, which occur in the range 2.0–2.2 ppm downfield from tetramethylsilane, have substantially diffrent chemical shifts. For example, the separation in chemical shifts between the acetyl resonances of *N*-methylacetamide and *N,N*-dimethylacetamide is 0.11 ppm in chloroform-*d* and 0.15 ppm in methanol-d_4. There is a similar separation between the acetyl resonances of *N*-*n*-hexylacetamide and *N,N*-di-*n*-butylacetamide. (The secondary acetamide resonance appears upfield from that of the tertiary.)

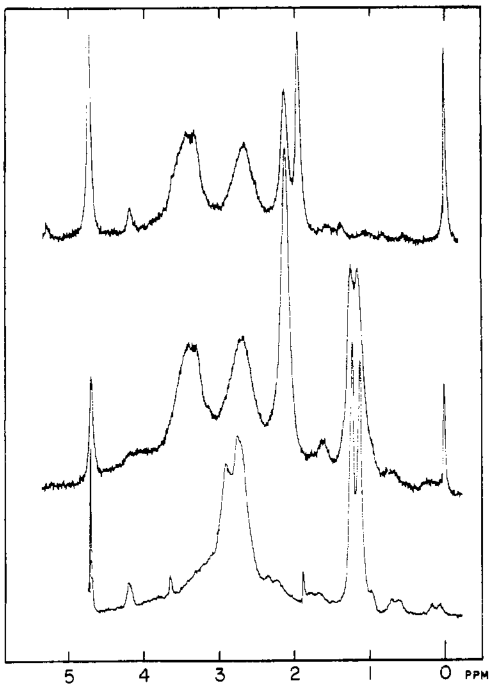

Figure 1. Proton nmr spectra of PEI derivatives in deuterium oxide: top, acetyl$_{0.75}$PEI with 2,2,3,3-tetradeuterio-3-(trimethylsilyl)propionate reference; middle, acetyl$_{0.50}$isopropyl$_{0.25}$PEI with same reference; bottom, isopropyl$_{0.25}$PEI.

The acetyl region of the spectrum of acetyl-PEI 2 in Table I displays one resonance, consistent with the inference from the trinitrobenzenesulfonate test that all the acetamides are secondary. In contrast, the acetyl region from acetyl-PEI 5 displays one relatively intense, sharp resonance and a second weaker and broader one about 0.1 ppm to lower field.[15] The acetyl-PEI 6 shows a similar pattern (top spectrum in Figure 1) except that the lower field resonance is relatively stronger than for number 5.

The acetyl nmr of acetyl-PEI 1 (Table I) shows one strong resonance due to the secondary acetamide and a rather small second resonance at lower field and with about one-sixth the area. This observation clarifies the previously mentioned ambiguity with regard to interpretation of the results of the trinitrobenzenesulfonate test and its implication as to the sites of acetylation in acetyl-PEI 1 (and 4). The reaction with secondary amines is measureable even in the presence of a small excess of primaries. The proton nmr data indicate that in acetyl-PEI 1 about 24% of all amines have become acetylated primary amines. The trinitrobenzenesulfonate test for this derivative indicates 5% residual primary amine. The sum, 29% of all amines, should represent the ratio of primary to total amines in PEI. This is slightly higher than the figure, 25%, usually quoted.

The question of the amine composition of PEI has been further elucidated by studies of a reductively alkylated PEI and an acetylated modification of this polymer. Isopropyl-PEI was prepared by reductive alkylation using acetone and sodium borohydride, in a manner similar to that of Means and Feeney.[10] It was hoped that this reaction, which is highly specific for primary amines relative

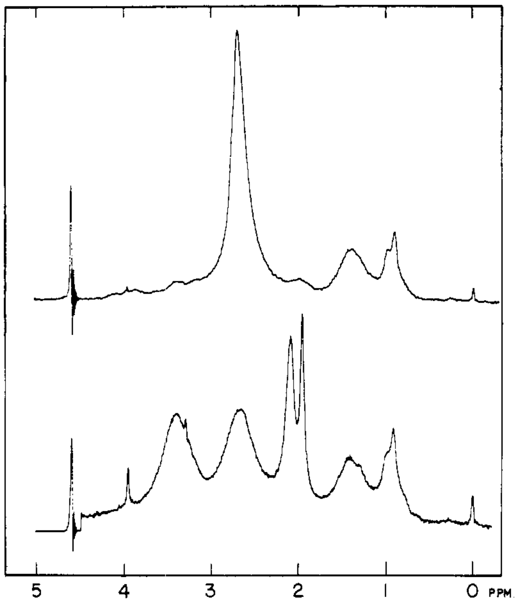

Figure 2. Proton nmr spectra of PEI derivatives in deuterium oxide: top, Butyl-PEI (This polymer had been preexchanged with deuterium oxide.); bottom, acetylbutyl-PEI.

to secondary, would also be exhaustive. Indeed the proton nmr spectrum (Figure 1, bottom) indicated 0.27 mol of isopropyl group/mol of PEI nitrogen. Within the limits of error, then, the ratio of primary to total amines is at least 0.27. Further, the absence of unreacted primary amines in this preparation was established by examination of the proton nmr (Figure 1, middle) of the acetylated isopropyl-PEI, which showed only one resonance in the acetyl region, that of a tertiary acetamide. Thus the isopropylation was exhaustive, and its extent implies that the ratio of primary to total amines is about 0.27. There are thus two lines of evidence which suggest that the ratio of primary to total amines is slightly greater than 0.25. While this small discrepancy will be kept in mind, we will, for convenience, refer to the derivatives just described as $IP_{0.25}PEI$ and $Ac_{0.5}IP_{0.25}PEI$.

It should also be noted that quantitative area measurements of the nmr spectrum of the acetylated isopropyl-PEI give a total degree of acetylation of about 0.54 relative to total nitrogen. This is lower than the theoretical maximum of 0.75 if all secondary amines had been acylated. Since there is no reason to believe that the reactivity of the original, preexisting secondary amines would be reduced by alkylation of the primary amines, it seems reasonable to conclude that acetylation of isopropyl-PEI occurred principally on the preexisting secondary amines, and that the newly formed (isopropyl) secondary amines have lower reactivity. This is consistent with the observation of a substantial effect of α substitution in amines on their reactivity with methyl acetate.[9]

The isopropylation procedure is of potential value in the synthesis of imidazole-containing polymers with catalytic activity (*e.g.*, toward esters) since the relatively reactive residual primary amines can thereby be quantitatively eliminated without significant alteration of the nature of the polymer.

Many derivatives for binding or catalytic work and all derivatives for a study of polymer conformation[16] were prepared by acylation with the appropriate longer chain anhydride or nitrophenyl ester. The relative reactivity of these reagents toward primary and secondary amines should be much the same as that of the simplest member of each series, acetic anhydride and nitrophenyl acetate. Since the nmr and chemical studies have established the principal mode of linkage of the acetyl group to PEI, we assume that pendant larger acyl groups introduced with corresponding reagents are also attached principally in secondary amide linkage to the polymer.

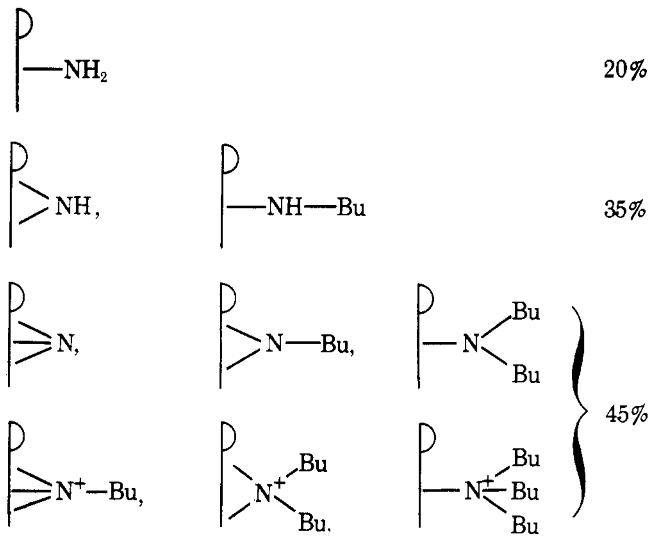

Figure 3. Species formed in the reaction of PEI with *n*-butyl iodide; Bu = *n*-butyl.

Alkylation of PEI with Alkyl Halides. The nmr spectroscopic methods described also provide a means for determination of the sites of alkylation of PEI with an alkyl iodide. For this purpose a butyl-PEI derivative was prepared by reaction of PEI with *n*-butyl iodide. The product contained 0.22 mol of butyl residue/mol of PEI repeating unit, as determined from the proton nmr spectrum (Figure 2). A portion of this derivative was further modified by reaction with excess acetic anhydride to yield an acetylbutyl-PEI. The proton nmr spectrum (Figure 2) of this derivative displayed two acetyl resonances, due to secondary and tertiary acetamides, with relative areas of about 1.0 and 1.75, respectively. The total degree of acetylation was about 0.54. Given these numbers, which are approximate due to the problems involved in estimating the areas of the partially overlapping peaks, one may infer that the original butyl-PEI had 20% primary amines, 35% secondary amines, and 45% tertiary and quaternary amines.[11a] This would imply that during the course of the alkylation of PEI only one-fifth of the primary amines reacted, whereas about two-fifths of the secondary amines reacted. This latter group would include some of the secondary amines initially present, as well as some of those formed in the course of the reaction, *i.e.*, by alkylation of primary amines. Figure 3 displays the amounts of all possible species formed in the reaction.

The different reactivities in acylation and reductive alkylation on the one hand and alkylation with alkyl halides on the other provides an interesting latitude in the placement of binding and reactive groups on PEI.

Alkylation also offers a route for the simultaneous introduction into PEI of two potential nucleophiles. One interesting combination would be imidazole with carboxyl groups. Since a suitable small molecule, α-bromo-β-imidazolylpropionic acid, has been described recently in the literature,[17] we have used it to alkylate PEI. Unanticipated difficulties were encountered at first due to solubility problems. The alkylation reaction in ethanol as solvent generated an insoluble PEI derivative. This difficulty was circumvented when a strong base, such as potassium *tert*-butoxide, was present in the ethanolic reaction mixture. The water-soluble PEI derivative so obtained could not be dissolved, however, in a solvent compatible with the alkyl halide needed for the further introduction of binding

Table II
Proton Chemical Shifts in PEI Derivatives and in Model Compounds

Group	Compound	Chemical Shift (ppm)[a]
Isopropyl (CH_3)		
	N-isopropylethylenediamine	1.08
	Ac$_{0.50}$IP$_{0.25}$PEI	1.20
N-Methyl		
	N,*N*-Dimethylethylenediamine	2.15
N-Methylene, α to amine		
	PEI	2.65[b]
	IP$_{0.25}$PEI	2.70
		2.87
	Ac$_{0.75}$PEI	2.63
	Ac$_{0.50}$IP$_{0.25}$PEI	2.63
	N-Isopropylethylenediamine	2.67
		2.77
	N,*N*-Dimethylethylenediamine	2.33 2.58
N-Methylene, α to amide		
	Ac$_{0.75}$PEI	3.33
	Ac$_{0.50}$IP$_{0.25}$PEI	3.33
	Acetylated *N*-isopropylethylenediamine	3.35
	Acetylated diethylenetriamine	3.40
N-Acetyl		
	Ac$_{0.75}$PEI	1.93
		2.12
	Ac$_{0.50}$IP$_{0.25}$PEI	2.12

[a] In methanol-d_4, unless otherwise indicated, referenced to sodium 2,2,3,3-tetradeuterio-3-(trimethylsilyl)propionate or tetramethylsilane. [b] In deuterium oxide as solvent.

groups onto the polymer. Eventually the desired polymer was obtained by reversing the order of the alkylation reactions. The detailed procedure for synthesis is described in the Experimental Section. The resultant PEI derivative with binding and two potential nucleophilic groups is catalytically effective toward nitrophenyl esters and is capable of forming an acylimidazole intermediate that can be detected spectrophotometrically.[18] Although not yet detected synergistic effects of the carboxyl and imidazole groups should be manifested in some reactions.

Further Analysis of the Nmr Spectra. Chemical modification or protonation of the amino groups produces marked changes in the resonances due to the backbone of PEI. Examples of the effect of chemical modification are evident in Figures 1 and 2. Unmodified, nonprotonated PEI at high pD in D_2O displays one resonance (and a shoulder), with an apparent width at half-height of about 6 Hz (on a 60-MHz spectrometer), which broadens and moves downfield as acid is added. A downfield shift for CH_2 protons α to an amine nitrogen is expected when the nitrogen becomes protonated. If the various amines become protonated at different pH values, as is indeed observed,[3] then at intermediate pH values there will be a distribution of (time averaged) degrees of protonation and a resulting distribution of chemical shifts. This is equivalent to a broad resonance.

Isopropyl-PEI displays near 2.8 ppm (Figure 1) two closely spaced, overlapping resonances due to the backbone. In contrast acetyl-PEI with a high (0.75) degree of acetylation displays two broad, but well-resolved backbone resonances at about 2.6 and 3.3 ppm. These are due, respectively, to methylene protons α to (tertiary) amino groups and α to (secondary and tertiary) amide groups. Table II indicates chemical shifts of various classes of protons in several PEI derivatives and in model compounds. Where comparisons are possible there is good agreement between the shifts in model compounds and in the polymer derivatives. Thus the assignments in the latter are unequivocal.

Experimental Section

PEI. PEI-600, with average molecular weight about 50,000, was obtained from Dow Chemical Co. as a 33% aqueous solution (lot TA04039BCN). This material was dried by rotary evaporation followed by three successive operations consisting of solution of the polymer in absolute ethanol followed by rotary evaporation to dryness. The extremely viscous liquid that resulted was determined to be free of significant amounts of ethanol and water by examination of the nmr spectrum of a solution of the material in deuterium oxide. Portions of PEI were either weighed out individually or a stock solution of known concentration in ethanol was prepared and subsequently measured volumetrically.

Acetyl-PEI Derivatives. These derivatives were prepared by treating a stirred solution of PEI (or its derivative) at a concentration of 2–4% in absolute ethanol with various amounts of nitrophenyl acetate or acetic anhydride, as indicated in Table I. When excess reagent was used it consisted of two to four times the amounts which were expected stoichiometrically to react with the polymer. The reactions were allowed to proceed at room temperature for at least 4 hr with nitrophenyl esters and 0.5 hr with acetic anhydride. The resulting polymers were purified by either of two methods. In one procedure the reaction mixture was fractionated on a Sephadex LH-20 column using ethanol as an eluent, and the resulting polymer-containing fractions were dialyzed against water and then lyophilized. In the other procedure the reaction mixture was dialyzed first against aqueous sodium chloride, then against water, and then was passed through a mixed-bed ion-exchange column, such as one packed with Bio-Rad AG 501-X8 resin. The resulting polymer solution was lyophilized.

Isopropyl-PEI. A 1.0-g (23 mmol of C_2H_5N) portion of PEI was dissolved in 100 ml of 10% acetone in water. The pH of the solution was adjusted to 9.0 using 1 *M* hydrochloric acid. The resulting stirred solution was cooled to about 5° in an ice bath and 0.4 g (42 mequiv) of sodium borohydride was added in several portions over a period of about 1 hr, during which time the pH of the solution was maintained at 9.0 ± 0.2 by addition of hydrochloric acid. After 1 additional hr at pH 9 the solution was made acidic and residual borohydride was allowed to decompose. The polymer was purified by the second method outlined for acetyl-PEI. The subsequent acetylation of a portion of this derivative was carried out in a manner similar to that described in the preceding paragraph.

Butyl-PEI. A 0.43-g (10 mmol of C_2H_5N) portion of PEI dissolved in 15 ml of absolute ethanol was treated with 0.40 ml (3.5 mmol) of 1-iodobutane. The resulting stirred solution was heated for about 5 hr at 50–60°. Thereafter modified PEI was isolated from one portion of the reaction mixture by methods previously outlined. The remaining portion was exhaustively acetylated and the polymer derivative then separated out.

Preparation of Lauryl-α-carboxy-β-imidazolylethyl-PEI. To a 0.86-g (20 mmol of C_2H_5N) portion of dry PEI dissolved in 20 ml of absolute ethanol 0.60 g (2.02 mmol) of 1-iodododecane was added. The container was evacuated, sealed, and then stirred, for 6 hr at 50–60° and overnight at room temperature.

After this time the reaction mixture was divided into two equal portions. One portion was subjected to gel filtration, dialysis, and lyophilization. It yielded a sample of lauryl-PEI with about 11% degree of substitution, as inferred from the proton nmr spectrum.

The other portion (10 mmol of C_2H_5N) was treated with 0.4 g (3.7 mmol) of potassium *tert*-butoxide, and stirred for about 20 min. Then 0.50 g (2.1 mmole) of α-bromo-β-imidazolylpropionic acid monohydrate was added. The flask was again evacuated and sealed, and the cloudy solution which resulted after stirring for 1 hr at room temperature was stirred further at 50° overnight. The solution was diluted with 10% of its volume of water, and subjected to gel filtration on Sephadex LH-20 using 90% ethanol as eluent. The resulting polymer-containing fractions were dialyzed three times against water and lyophilized to yield a lightweight white powder. The proton nmr spectrum of the polymer in D_2O containing a little CD_3CO_2D indicated 11% laurylation and 11% substitution with α-carboxy-β-imidazolylethyl units.

Analysis for Primary Amines. The amount of primary amine in the polymer derivatives was determined with sodium trinitrobenzenesulfonate. In each case a known weight (about 10 mg) of polymer derivative was dissolved in 100 ml of 0.1 *M* Veronal buffer (pH 8.5). This solution (1 ml) was mixed with 1 ml of a fresh solution of 30 mg of trinitrobenzenesulfonate in 50 ml of water. The resulting solution was incubated at 40° for 10 min and then diluted with 2 ml of glacial acetic acid. The absorbance of this mixture was measured at 340 nm. After correction for a blank, and on the basis of extinction coefficient of 12,000 for the picramide formed, we can calculate the amount of primary amine.

Nmr spectra were obtained on a Varian T-60 nmr spectrometer. To further confirm assignments, a few additional spectra were obtained on a 90-MHz Bruker nmr spectrometer.

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Behavior of the $R_2AlOAlR_2$ Catalyst in the Polymerization of Propylene Oxide[1]

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ABSTRACT: Polymerization of propylene oxide catalyzed by a type of $R_2AlOAlR_2$ (where R = CH_3, C_2H_5, and *i*-C_4H_9) compound derived from the reaction of R_2AlOLi with R_2AlCl gave three types of polymers; *i.e.*, a high molecular weight and highly isotactic polymer (M_v = 10^5-10^6), a low molecular weight and partially isotactic polymer (M_v = 600-1000), and an oligomer (~tetramer). Similar tri-dispersity was also observed in the polymers obtained with the corresponding AlR_3-H_2O (2:1) catalysts. The highest molecular weight and the most highly isotactic polymer was obtained with the $Me_2AlOAlMe_2$ catalyst. The isotacticity together with the molecular weight of the polymer varies with the nature of the alkyl groups in the catalyst: Me > *i*-Bu > Et. This decreasing order is not related to the bulkiness of the alkyl groups or to the polarizability of the Al-O-Al bond. In most experiments, a decrease in the isotacticity was coupled with a decrease in the molecular weight of the polymer. At low temperature, polymerization proceeded to form a high molecular weight and highly isotactic polymer, while the molecular weight and isotacticity were sharply decreased as temperature rose. One of the adverse factors for the stereoregular propagation reactions was the presence of AlR_3 or R_2AlCl which interacts with $R_2AlOAlR_2$ species. Since the polymerization at the final stage produces a polymer of a high stereospecificity (80%), one can conclude that the species $R_2AlOAlR_2$ gives mainly isotactic polymerization after the adverse species are consumed. A lower stereospecificity in the catalysis of AlR_3-H_2O (2:1) than in $R_2AlOAlR_2$ (R_2AlCl-R_2AlOLi) can be explained by the presence of a larger amount of AlR_3 and water unreacted in the catalyst preparation.

Bis(dialkylaluminum)oxide, $R_2AlOAlR_2$, is one of the key compounds for the study of the widely used catalyst systems derived from AlR_3 and water. We have discovered a new synthetic route to this series of compounds by reacting R_2AlOLi with R_2AlCl,[2a] and have shown that the $R_2AlOAlR_2$ compounds are actually formed.[2b] Also the catalytic behaviors of the systems Et_2AlOLi-Et_2AlCl (1:1) and $AlEt_3$-H_2O (2:1) are qualitatively identical for the polymerizations of acetaldehyde and epoxides.[3]

On reviewing the published works concerning the stereospecific polymerization of propylene oxide catalyzed by the AlR_3-water systems, one may find that two fundamental problems have remained unsolved. First, whether the species $R_2AlOAlR_2$ besides species $(-RAlO-)_n$ affords a stereoregular polymer or not, and second, whether the stereoregular polymer obtained by the AlR_3-water catalytic systems is a polymer with high tacticity or a polymer having short isotactic sequences combined with structural disorderings. These problems appear highly important to the mechanism of the stereoregulating action of the AlR_3-water catalyst.

In the present paper we will report on the polymers from the polymerization of propylene oxide catalyzed by $R_2AlOAlR_2$ compounds derived from R_2AlOLi-R_2AlCl and from AlR_3-water. (For convenience, we denote hereafter as $R_2AlOAlR_2$ and AlR_3-H_2O (2:1) catalysts, respectively.) We conclude that the species $R_2AlOAlR_2$ can, though not exclusively, propagate the polymerization to a highly isotactic configuration, and that AlR_3 and R_2AlCl species included in the catalysts cause at least a part in sterically irregular propagation to give chain-terminated products.

Results and Discussion

Fundamental Aspect of R_2AlOLi-R_2AlCl Binary Catalyst Systems. Three kinds of $R_2AlOAlR_2$ compounds, *i.e.*, $Me_2AlOAlMe_2$, $Et_2AlOAlEt_2$, and *i*-Bu_2AlOAl*i*-Bu_2 prepared from the corresponding R_2AlOLi and R_2AlCl compounds,[2b] were used as the polymerization catalysts.