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Evidence for Molecular Cr^{3+} Cross-Links in Cr^{3+}/Polyacrylamide Gels

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ABSTRACT: The gelation of buffered aqueous solutions of Cr^{3+} and polyacrylamide having a low degree of hydrolysis (0.7% and 10%) has been investigated over a wide range of pH. It has been found that gelation occurs between pH 2.3 and 6.7 and that the time of gelation increases dramatically at low pH. An inverse correlation between $Cr(OH)_3(H_2O)_3$ colloid formation (revealed by solution turbidity) and the pH range of gelation indicates that discrete, soluble (monomeric or oligomeric) rather than colloidal forms of Cr^{3+} are responsible for the cross-linking. The occurrence of gelation in the pH interval 6.0–6.7, where only a small amount of the Cr^{3+} would be soluble in a simple aqueous solution, has been attributed tentatively to Cr^{3+} complexation by the polymer. Cr^{3+} solubility experiments at pH 6.6 in solutions containing model, monomeric carboxylate compounds lend support for this hypothesis.

Aqueous polymer gels composed of high molecular weight, partially hydrolyzed polyacrylamide (or other synthetic or biopolymers) cross-linked by Cr^{3+} or Al^{3+} are of interest for use in augmenting the petroleum recovery from mature reservoirs.[1,2] So-called secondary oil recovery typically involves the continuous injection of water into a reservoir from a subset of the existing wells. The injected water physically displaces to the other wells a significant portion of the mobile oil with which it comes into contact. A major limitation to petroleum recovery by this method arises from the fact that most reservoirs are compositionally heterogenous and that the injected water floods preferentially the strata of highest permeability. A promising but still experimental reservoir treatment involves the occlusion of the higher permeability strata, after preliminary water flooding, with polymer gels which are formed within the reservoir from aqueous polymer/cross-linker solutions. Water injected subsequently is thereby diverted to lower permeability zones, and the mobile oil contained therein can be recovered. Among the various enhanced oil recovery techniques proposed and field-tested during the past 15 years, reservoir profile modification with aqueous polymer gels remains one of the few economically promising strategies in the present period of low-priced petroleum.

Several chemical impediments remain that prevent the full realization of the gel profile modification strategy. These include instability of the polymeric gels at high temperature, limited control over and understanding of the kinetics of gelation, and lack of satisfactory mathematical models which permit the controlled placement of the gels within the reservoir. A more detailed understanding of the structure and chemistry of the metal ion cross-links in these gels should aid in the rational design of aqueous gels having improved performance characteristics.

Both *colloidal* and *discrete molecular* cross-link structures have been suggested[3,4] for aqueous polymer gels cross-linked with Cr^{3+} (Figure 1). The distinction between the two types of cross-links is of great practical importance, since the development of accurate kinetic models of gelation and reliable predictions of gel stability under varying conditions depend on a knowledge of the structure and chemistry of the cross-link. In the present paper, we describe conceptually simple experiments on Cr^{3+}/polyacrylamide (PAAm) gels which provide clear evidence for a molecular Cr^{3+} cross-link structure.

Results and Discussion

The cross-linking chemistry of Cr^{3+}/PAAm gels depends on the complex aqueous solution chemistry of Cr^{3+}, which has been elucidated in remarkable detail over the past

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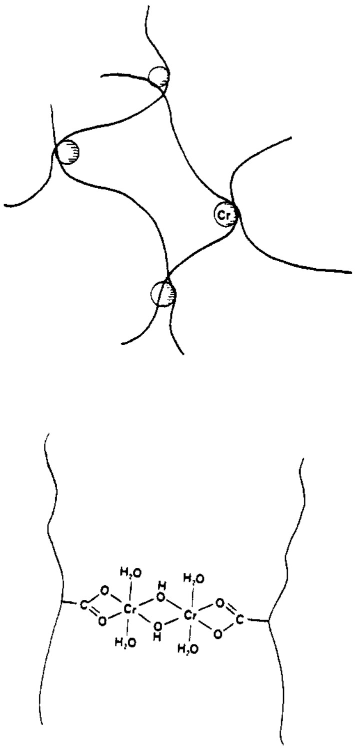

Figure 1. Representation of colloidal (upper) and discrete molecular (lower) Cr^{3+} cross-links. One possible form (dimeric in Cr^{3+}) has been represented for the latter.

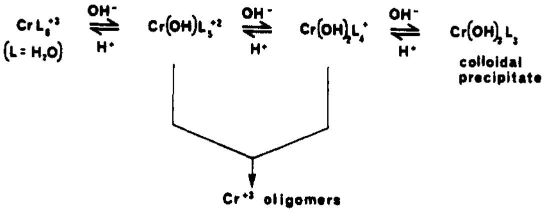

Figure 2. Aqueous solution chemistry of Cr^{3+} (see refs 5–8).

80 years.[5-8] The main features of this chemistry are illustrated in Figure 2. The predominant species at low pH is Cr(H$_2$O)$_6$$^{3+}$, but equilibria with monomeric Cr^{3+} mono-, di-, and trihydroxides are established rapidly at higher pH. The trihydroxide, Cr(OH)$_3$(H$_2$O)$_3$, is extremely insoluble in water (K_{sp} = $10^{-30.3}$)[5b] and precipitates at moderate pH. The soluble mono- and dihydroxides convert to dimeric and higher oligomeric species with rate constants that depend on temperature and pH[6] but are similar in magnitude to the rate of gelation of Cr^{3+}/PAAm solutions. It is apparent from this description that both molecular (monomeric or oligomeric) and colloidal (i.e., Cr(OH)$_3$(H$_2$O)$_3$) forms of Cr^{3+} may be available for cross-linking with PAAm over an interval of solution pH which depends on temperature and the Cr^{3+} concentration.

In order to evaluate the possible role of molecular and colloidal forms of Cr^{3+} in the cross-linking of polyacrylamide gels, we have carried out a systematic investigation of the gelation of Cr^{3+}/PAAm solutions (9.6×10^{-4} M (50 ppm) in Cr^{3+} and 8000 ppm in PAAm 0.7% hydrolyzed) as a function of pH. In preliminary experiments, Cr^{3+}/PAAm solutions were prepared having initial pH values from pH 2.0 to 10.1. The gelation results are summarized in Table I along with the estimated[5b] solubility of Cr^{3+} in water at each pH. Gels formed with widely varying rates in the pH range 3.0–7.0 at 25 °C. The presence of colloidal Cr^{3+} in the solutions at pH 7.0 and above was indicated by their turbidity.

The correlation of gelation with pH requires that the pH of the Cr^{3+}/PAAm solutions be stable over time. For many of the solutions reported in Table I, however, a drop in pH was found prior to gelation. For example, the pH of the solution with initial pH 7.0 had fallen to pH 6.5 4 h after preparation. The initial drop in pH can be rationalized in terms of Cr^{3+} oligomerization, which leads to the production of H$^+$ (Figure 2). After 60 days, the pH changes found (Table I) appear to indicate movement toward a common, presumably equilibrium, value between pH 8 and 9. The pH change is attributed tentatively to a small degree of polymer hydrolysis which leads to the formation of polymer carboxylate/ammonium ion pairs.

The pH instability of Cr^{3+}/PAAm solutions has been eliminated through the addition of buffering agents to the solutions (Table II). Buffers were selected with the criterion that they not interact significantly with Cr^{3+} in dilute aqueous solution; for this reason, traditional organic carboxylate buffers were avoided.[9] The general agreement of the results obtained for the buffered and nonbuffered solutions, and for solutions of comparable pH buffered by different compounds, confirms the inertness of the buffers used. As expected, the pH variation of the buffered gel solutions was much reduced: a variation of less than 0.15 pH unit over the first 43 days was confirmed for all solutions except that buffered with ethanolamine, which had fallen 0.2 pH unit in 30 days, and that buffered to pH 9.88 with 3-(cyclohexylamino)-1-propanesulfonic acid, which had fallen to pH 9.1 in the same period. At the time of gelation (315 days), the pH of the solution buffered to pH 3.18 had changed by only

Table I
pH Dependence of Cr^{3+}/PAAm Gel Formation at 25 °C in Unbuffered Solutions[a]

initial pH	pH at 60 days	gel time, days	estimated soluble Cr^{3+},[b] %
2.0	2.5	*c*	100
4.0	6.2	9	100
5.1	6.9	1	100
6.1	7.4	<1	14
7.0	7.9	30[d]	0.5
8.1	8.2	*c*	0
10.1	9.1	*c*	0

[a] Gel composition: 8000 ppm PAAm, 50 ppm Cr^{3+} in distilled water. pH adjusted with aqueous HCl or NaOH solutions immediately upon mixing of reagents. [b] Percent soluble Cr^{3+} in water, estimated from data in ref 5b. [c] Free-flowing, ungelled solutions at conclusion of experiment (60 days). [d] Weak gel.

Table II
pH Dependence of Cr^{3+}/PAAm Gel Formation in Buffered Solutions[a]

pH	buffer	gel time, days		estimated soluble Cr^{3+},[b] %
		25 °C	60 °C	
2.31	3-chloropyridine	*c*	32	100
3.18	3-chloropyridine	315	18	100
4.13	*o*-toluidine	11	1	100
5.25	pyridine	1	1	100
6.11	pyridine	<1	<1	14
6.30	imidazole	<1	<1	6
6.60	imidazole	3	3	2
7.00	imidazole	*c*	*c*	0.5
8.30	ethanolamine	*c*	*c*	0
9.88	3-(cyclohexylamino)-1-propanesulfonic acid	*c*	*c*	0
10.38	3-(cyclohexylamino)-1-propanesulfonic acid	*c*	*c*	0

[a] 8000 ppm PAAm, 50 ppm Cr^{3+} in distilled water. For buffer concentration, see the Experimental Section. [b] As per Table I. [c] Free flowing, ungelled solutions at conclusion of experiment (226 days for samples at pH >7.0; 315 days for the sample at pH 2.31).

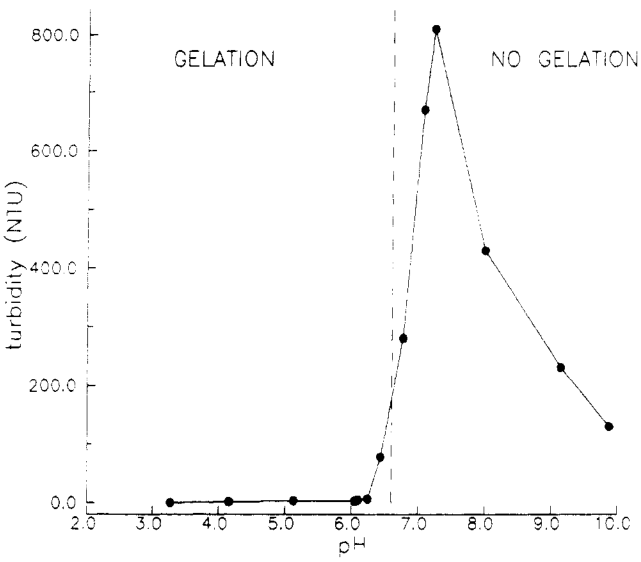

Figure 3. Turbidity (nephelometric turbidity units, NTU) of Cr^{3+}–PAAm gelation solutions as a function of pH. Regions of gelation and nongelling solution shown by dotted line.

0.1 pH unit.

From the reliable data on buffered solutions several conclusions can be reached about the gelation of Cr^{3+}/PAAm solutions as a function of pH. First, the pH range for gelation of the Cr^{3+}/PAAm composition studied is from pH 2.3 to 6.7. The rate of gelation is also shown to be markedly sensitive to pH and temperature, particularly at low pH. These experiments also provide insight into the possible roles of colloidal and discrete molecular Cr^{+3} in gel cross-linking. Thus, it is found that gelation occurs when *no* colloidal Cr^{3+} is present (pH <5.5). This requires that a soluble (i.e., molecular) form of Cr^{3+} is capable of effectively cross-linking the polymer solution. Further, where the conversion of Cr^{3+} to the colloidal form is estimated to be total (above pH 7), no gelation occurs. This observation shows that colloidal Cr^{3+} is inactive in cross-linking PAAm in aqueous solution, at least above this pH.

Turbidity measurements, which can reveal the presence of colloidal Cr^{3+} in solutions and gels, were carried out on buffered polymer solutions before and after gelation and provide additional evidence in favor of molecular cross-linking forms of Cr^{3+}. The onset of the rise in turbidity of buffered Cr^{3+}/PAAm solutions was about pH 6.4, just below the upper pH limit for gelation (Figure 3). The solution turbidity reached a maximum above pH 7, where the conversion of Cr^{3+} to the colloidal form is estimated to be complete. The decrease in turbidity observed at even higher pH is attributed to the complex effects of particle size and aggregation on the total turbidity signal.

An equivocal point in the preceding analysis arises from the contrast between the small fraction of Cr^{3+} estimated to be soluble in water from pH 6.0 to 6.7 and the negligible-to-modest turbidity observed and occurrence of gelation in this pH interval. Turbidity measurements carried out on an aqueous solution of Cr^{3+} at the same concentration as employed in the gels and buffered over the range pH 4–9 gave a curve similar to that for the Cr^{3+}/PAAm solutions in Figure 3. This result indicates that the turbidimetric measurement has a low sensitivity to the dilute solution of colloidal Cr^{3+} particles formed below about pH 6.3. Dynamic light-scattering measurements of higher sensitivity, carried out with Cr^{3+} (9.6×10^{-4} M) in aqueous solution in the pH interval 5–11, confirmed that $Cr(OH)_3(H_2O)_3$ particles are formed within the time of mixing in aqueous solution at room temperature above pH 5.6. The particle diameter was estimated to be 1500 Å (polydispersity index 0.30) at pH 5.7. From pH 7–11, the particles formed were much larger (>5000 Å) and polydisperse, suggesting the formation of aggregates.[10]

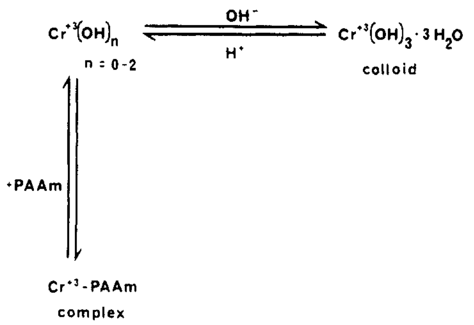

Figure 4. Reaction scheme by which complexation of Cr^{3+} with PAAm could displace equilibrium away from formation of insoluble Cr^{3+} colloid.

It is possible that complexation of Cr^{3+} with PAAm (e.g., cross-linking) in the polymer solutions could shift the onset of Cr^{3+} colloid formation to higher pH, by the mechanism illustrated in Figure 4. The possible influence of polymer complexation with Cr^{3+} on the pH range of $Cr(OH)_3(H_2O)_3$ formation could not be evaluated directly in light-scattering experiments because of the high background signal from the polymer. Turbidity measurements on a Cr^{3+}/PAAm solution prepared with a 10% hydrolyzed PAAm gave a turbidity versus pH curve shifted to higher pH by not more than 0.1 pH unit relative to that shown in Figure 3, even though the solution contained more than 10 times the concentration of reactive functional groups compared to the previous solutions (the two polymers were of identical molecular weight distribution). The upper pH limit of gelation for this polymer in buffered solution was between pH 6.6 and 7.0 (a structurally weak gel was formed at pH 7.0) at 60 °C, suggesting a small shift relative to the PAAm with lower functionalization. The observation that buffered Cr^{3+}/PAAm solutions gel slowly near the upper pH limit for gelation (Table II) could reflect the slow displacement of the equilibrium for Cr^{3+} colloid formation through reaction with the polymer. Taken together, these results provide some support for a shift in the pH for formation of colloidal $Cr(OH)_3(H_2O)_3$ owing to cross-linking with the polymer.

Additional insight into the possibility that polymer complexation with Cr^{3+} could lead to a shift in the pH for Cr^{3+} colloid formation has been gained from studies in which ligands which may model the thermodynamics of complexation between Cr^{3+} and the functional groups on polyacrylamide were employed. Aqueous solutions at pH 6.6 which contained preformed colloidal Cr^{3+} (50 ppm) were stirred at room temperature in the presence of 14 equiv of either acetate, succinate, or oxalate (the ligand concentration used was equal to the concentration of polymer-bound carboxylate groups for the gels prepared with a 10% hydrolyzed PAAm). Whereas the weakest ligand, acetate (pK_f for $Cr(acetate)_3$ = 9.6),[12] did not solubilize more than a few percent of the colloidal Cr^{3+}, the stronger ligands, succinate (pK_f for $Cr(succinate)_3$ formation = 13.5)[13] and oxalate (pK_f for $Cr(oxalate)_3$ formation = 15.4),[13] dissolved 60% and 80%, respectively, of the Cr^{3+} within 2 days. These results demonstrate that organic carboxylate ligands are capable of dissolving a significant amount of colloidal Cr^{3+} at pH 6.6 on the time scale of gelation.

Further comparison of the results for the model ligands with gel formation in the pH range 6–6.7 is uncertain because the Cr^{3+} coordinating strength of the polymer is unknown. Although acetate might seem to be an appropriate model for the reactive functional groups of partially hydrolyzed PAAm,[14] it is well-known that in some cases the binding capacity of polymeric complexing agents can be many times greater than those of the same, monomeric ligand.[15] If this is true also in the case of PAAm, then succinate or oxalate could be more appropriate models for the thermodynamics of compexation of PAAm with Cr^{3+}.

Two published studies on the cross-linking of aqueous Cr^{3+}/polymer solutions bear mention. Prud'homme[4] monitored the growth over time of the elastic modulus of a solution of Cr^{6+}, a reducing agent, and PAAm (25% hydrolyzed). The observed second-order dependence of the gelation rate on the Cr^{6+} concentration was interpreted in terms of rate-determining dimerization of Cr^{3+}. Shu[1a] has reported that solutions containing preformed Cr^{3+} oligomers cross-link Xanthan gum (a carboxylate functional biopolymer) much more rapidly than fresh solutions of monomeric Cr^{3+}, a result qualitatively consistent with a dimeric or oligomeric cross-linking form of Cr^{3+}.

A cross-linking mechanism with a rate-limiting Cr^{3+} dimerization or oligomerization step provides an attractive explanation for the pH dependence of gel time found in our experiments, since the rate of Cr^{3+} oligomerization is known to depend strongly on pH.[6] Additional experiments will be necessary to establish the validity of this mechanism.

Conclusions

Unambiguous evidence for the existence of discrete molecular Cr^{3+} cross-links in aqueous Cr^{3+}/PAAm gels has been obtained. In combination with results of other published studies, it is reasonable to speculate that the cross-linking species are Cr^{3+} oligomers. Experiments which may provide further insight into the chemistry (thermodynamic and kinetic stabilities) of the Cr^{3+}–polymer cross-link bonds are presently underway in our laboratory.

An important implication of the results described in this paper is that "molecular-level" strategies for the design of improved aqueous Cr^{3+}/PAAm gels for use in enhanced oil recovery are certainly warranted. Similarly, application of the knowledge of the inorganic coordination chemistry of Cr^{3+} to the study and modeling of the gelation process is appropriate.

Experimental Section

Materials. All studies were carried out with solutions of $CrCl_3 \cdot 6H_2O$ (Fluka purum p.a.) prepared with deionized water and stored until the blue color characteristic of the fully dissociated $Cr(H_2O)_6^{3+}$ ion appeared (typically within several days at room temperature). The stability of the stock $Cr(H_2O)_6^{3+}$ solutions (0.02–0.05 M, pH <3.0) toward oligomerization over the course of several months was confirmed by ion chromatography and ESR. The commercial sample of PAAm (Aldrich, catalog no. 18,127-7, MW 5–6 × 10^6) employed was shown by ^{13}C NMR and elemental analysis to contain ca. 0.7% carboxylate functional groups. Aqueous solutions of the polymer were prepared by pouring the solid into the vortex of the vigorously stirred solvent after which a very slow stirring rate was maintained for about 6 h. The solutions were left to stand overnight and then filtered gently through a 5-μM Millipore filter. The filtered polymer solutions were used to prepare gels within 2 days. A sample of PAAm 10% hydrolyzed was prepared from the commercial sample by controlled base hydrolysis according to a published procedure, except that a 1% rather than 4% concentration of PAAm was used in order to reduce the solution viscosity.[16] The degree of hydrolysis was determined from ^{13}C NMR measurements.

The ability of acetate, succinate, and oxalate to solubilize Cr^{3+} colloids at pH 6.5 was evaluated in the following way: the pH of a 50 ppm aqueous solution of Cr^{3+} was adjusted to pH 6.6, 14 equiv of the ligand was added in solid form, and the pH was readjusted if necessary. The solutions were stirred continuously at ambient temperature, and the pH was periodically adjusted. To determine the quantity of Cr^{3+} in soluble form, aliquots were removed and centrifuged for 20 min at 10 500 Hz, and the Cr^{3+} concentration in the supernatant solution was analyzed by flame emission spectroscopy (at 205.552 nm). The results were reliable to better than 1%.

Light-Scattering and Turbidity Measurements. Turbidity measurements were carried out on a Hach ratio turbidimenter Model 18900 on the 1.8-cm-diameter glass vials in which the gels were prepared. Dynamic light-scattering measurements were made on two different instruments. Qualitative determination of the onset of particle formation in Cr^{3+} solutions was carried out on a 64-channel Langley Ford Instruments photon correlation spectrometer with a 4-mW helium–neon laser light source. Detection geometry was fixed at 90° from the transmitted beam, and data were analyzed by the cumulant method. Solutions of Cr^{3+} near the final concentration were filtered (Millipore, 0.45 μm), the pH was adjusted with HCl or NaOH solutions, and the volume was brought to the final value. Initial light-scattering measurements were made within 2 min of sample preparation, the samples were analyzed periodically, and the pH was monitored over the course of 24 h. Determination of Cr^{3+} colloid particle size was made on a Brookhaven Instruments Model BI2030 spectrometer equipped with a 25-mW He–Ne laser, with scattering intensity detection (correlator with 78 data channels) between 15° and 160°; data analysis was by the cumulant method.

Preparation of Gels. Stock Cr^{3+} solutions were combined with solutions of PAAm (10 000 ppm by weight) in sample vials 10 cm long and 1.8 cm in diameter to give a solution within 80% of the final volume. The free-flowing solutions were mixed by shaking gently, and the pH was adjusted by addition of aqueous solutions of HCl (0.1 M) or NaOH (0.1 M). Solutions were brought to final volume (usually 10 mL) with the addition of water. Buffered gel solutions were prepared in a similar fashion, with the further addition of an appropriate amount of a stock buffer solution (0.2–0.4 M) of the desired pH; the pH was determined immediately after mixing and was monitored every few days. The final concentration of buffer in the gel solutions was 0.03 M except for 3-chloropyridine at pH 2.31 (0.06 M), pyridine at pH 6.11 (0.06 M), and ethanolamine at pH 8.30 (0.045 M). Gel solutions were maintained at 25 ± 1 °C in a circulating water bath and at 60 ± 1 °C in a forced-air oven.

It was found that meaningful measurements of pH could not be made with a standard electrode once gelation had advanced beyond a very early stage. By using a microelectrode, however, it proved possible to monitor the pH of both solutions and gels at all times. The pH of gel solutions was determined at room temperature with a Metrohm Model EA 125 microelectrode. Excellent agreement of the pH of buffered gel solutions before and after gelation confirmed the validity of the pH measurements obtained on the gels.

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^{13}C NMR Analysis of Propene–Butene Copolymer. Steric Structure of Chain End Groups and Inhomogeneity of Isotactic Sites

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ABSTRACT: Propene and 1-butene have been copolymerized in the presence of the catalytic system $TiCl_3$/$Al(^{13}CH_2CH_3)_3$. The results of ^{13}C NMR analysis of chain end groups in isotactic fractions of different composition provide stereochemical evidences of the inhomogeneity of the isotactic sites.

In a recent paper,[1] we have reported the results of fractionation and of ^{13}C NMR analysis of a series of propene–butene copolymers. A broad compositional distribution in the fractions of copolymer samples obtained with a large range of feeding mixture compositions in the presence of $TiCl_3/Al(CH_2CH_3)_3$ as catalyst has been observed. This compositional distribution has also been found in the isotactic part of copolymers. Indeed, in each sample more than one essentially isotactic fraction characterized by decreasing 1-butene content, regardless of the feeding mixture composition adopted, has been isolated by fractionation. We interpreted the results in terms of the presence, on the catalyst surface, of different kinds of isotactic sites that show a partial selectivity toward the comonomers.

In an attempt to correlate the observed copolymer dispersity to structural characteristics of the isotactic sites, in this paper we have studied the configurational structure of ^{13}C-enriched chain end groups.

Experimental Section

Reagents. δ-$TiCl_3$ (HRA Stauffer) was purified by extraction with boiling toluene. $Al(^{13}CH_2CH_3)_3$ was prepared (starting from 90% ^{13}C-enriched $Ba^{13}CO_3$) by reaction of CH_3-$^{13}CH_2Li$ and $AlCl_3$.

Copolymerization. Copolymerization apparatus and reaction conditions have already been described.[1] To 100 cm^3 of toluene, containing 3 mmol of suspended $TiCl_3$ and saturated at 15 °C with the propene–butene mixture, were added 3 mmol of $Al(^{13}CH_2CH_3)_3$ (90% ^{13}C enriched). During the polymerization, a constant flow of gas mixture was maintained through the reaction medium by means of two computer-controlled mass flowmeters, coupled with flow control valves (MKS Intruments, Inc.). The rate of flow was ≈15 times higher than gas consumption. After 3 h the copolymerization was stopped with methanol and the copolymer was precipitated with acidified methanol, collected, and dried under vacuum (3.4 g).

Copolymer Fractionation. The propene–1-butene copolymer was fractionated in Kumagawa extractors with diethyl ether, *n*-hexane, *n*-heptane, and *n*-octane. Time of fractionation was 24 h.

^{13}C NMR Analysis. The ^{13}C NMR analysis of copolymer fractions was carried out at 125 °C on a AM-270 Bruker spectrometer operating at 67.89 MHz in the PFT mode. The copolymer samples were dissolved in 1,2,4-trichlorobenzene containing ≈1% of hexamethyldisiloxane (HMDS) and $C_2D_2Cl_4$ as internal standards. Copolymer composition and isotactic regularity were determined from ^{13}C NMR spectra, according to refs 2 and 3.

Molecular Weight Determination. Average molecular weights of propene–butene copolymer fractions were determined by GPC with a Waters 150-C apparatus at 135 °C using 1,2-dichlorobenzene as solvent.

Results

A propene–butene copolymer sample was prepared in the presence of δ-$TiCl_3$/$Al(^{13}CH_2CH_3)_3$ using a 3/1 propene/butene feeding mixture. The propene/butene ratio was chosen on the basis of the previously studied copolymers, in order to obtain a significant fractionation of the isotactic part. The copolymer was fractionated

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