cooled, ground to a fine powder, extracted twice with boiling acetone and twice with boiling water, and dried overnight under vacuum at 120 °C. The reduced viscosity (in concentrated H_2SO_4) was 2.56 dL/g. A similar procedure was used to prepare the polymer from DHBP and 4,4′-difluorobenzophenone (Scheme Ib).

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Mechanism of Acetylene Polymerization by the Titanium Tetrabutoxide/Triethylaluminum Catalyst System

John A. Shelburne, III, and G. L. Baker*

Bell Communications Research, Red Bank, New Jersey 07701-7020.

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ABSTRACT: The dependence of the trans isomer content on acetylene polymerization conditions was examined for the titanium tetrabutoxide/triethylaluminum catalyst system. In toluene at 25 °C and at low ratios of Al/Ti, *trans*-polyacetylene was the exclusive product. As the temperature was lowered, the cis isomer became predominant. Increases in the Al/Ti ratio led to a decrease in the trans isomer content. When tetrahydrofuran was added to polymerizations, the trans isomer was obtained at all ratios of Al/Ti. No effects of catalyst concentration on the isomeric makeup of the polymer were observed. These results are interpreted in terms of the likely organometallic species responsible for the polymerization.

Introduction

Recent interest in the polymerization of acetylenes has been sparked by the observation that polyacetylene becomes highly conductive on oxidation or reduction.[1,2] Much work has addressed the question of whether the polymerization occurs by an insertion mechanism or alternatively by a metathesis route.[3] Nutation NMR techniques indicate that acetylene[4] and substituted acetylenes[5] polymerize via successive insertion reactions with titanium catalysts, while substituted acetylenes polymerize via a metathesis route using molybdenum-based catalysts.[5]

Polyacetylene serves as the prototype conducting polymer, and there has been much synthetic effort to ameliorate its intractability. Copolymers,[6–8] blends,[9,10] and graft and block copolymers[11–14] have been investigated as potentially tractable forms of polyacetylene, but each approach has had severe limitations. Improved conducting polymers might result from a better understanding of the organometallic species that catalyze the polymerization. In this way, desirable polymers may be prepared by ap-

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propriate manipulations of the catalyst chemistry.

Surprisingly, there have been few detailed mechanistic studies on the $Ti(OR)_4/AlR_3$ catalyst typically used to prepare polyacetylene. In part, this is due to the extreme intractability of the product and also to the poorly characterized catalyst. There has been previous work that gives hints about the nature of the catalytically active species. ESR studies[15,16] have correlated catalyst activity with the appearance of Ti(III) in the catalyst mixture, but an unambiguous identification of the active catalyst was not possible since a variety of ESR-active species are formed and only a small percentage of the titanium charged into a reactor ever becomes catalytically active. Dawes and Winkler[17] studied the catalyst and its ability to polymerize butadiene. Their observation of gas evolution during the catalyst formation was complemented by a later study[18] that examined the gas evolution both during the preparation of the catalyst and after hydrolysis. These studies suggest the likely initial steps leading to the catalyst. Other work[19,20] has focused on the kinetics of acetylene polymerization. This last approach is problematic due to the intractability of the product and the heterogeneous nature of the polymerization.

We have undertaken a systematic examination of the dependence of the polymerization behavior (specifically the isomeric makeup of the product) on changes in polymerization conditions to understand the mechanism of polymerization. Hopefully this would allow new, more tractable forms of polyacetylene to be synthesized by the proper manipulation of the reaction parameters.

Experimental Section

Acetylene was purified by passage through two dry ice/acetone cold traps and a column of Mn(0) supported on vermiculite. Solvents were dried and distilled from benzophenone ketyl dianion before use. Triethylaluminum (Aldrich) was used as received. Titanium tetra-*n*-butoxide was fractionally distilled under reduced pressure and stored under an inert atmosphere. Polyacetylene films suitable for infrared analysis were prepared by evaporating suspensions of the polymer onto silicon plates to give thin films. The method of Gibson et al.[21] was used in calculating the trans isomer content.

Polymerizations. All polymerizations were carried out on a high-vacuum manifold under an inert atmosphere. In a typical procedure, 0.5 mmol of purified acetylene was transferred from a storage bulb to a 50-mL flask equipped with inlets for the addition of gas and liquid reagents. The flask was warmed to 25 °C and the internal pressure of the flask was raised to 1 atm by the addition of argon. To the flask was added 3.6 mL of dry deoxygenated toluene. After the mixture was stirred for 10 min, 3.7 mL of a 0.134 M solution of titanium tetrabutoxide in toluene was added. The polymerization was initiated by adding 2.7 mL of a 1.88 M solution of triethylaluminum in toluene. After 30 min, the product was transferred under air-free conditions to a centrifuge tube. The polyacetylene product was exhaustively washed with dry deoxygenated hexane until the washings became colorless. The polymer was then washed twice with deoxygenated methanol, yielding a fine suspension that was transferred to a drybox for storage and later use. Polymerizations at temperatures less than 25 °C were terminated by the addition of 0.2 mL of methanol to destroy the catalyst before warming the reaction flask. When tetrahydrofuran was used as a competing ligand, it was introduced before the addition of the triethylaluminum, and the molar ratio of tetrahydrofuran to titanium tetrabutoxide was 3 in each case.

Results

The results of changes in reaction parameters were monitored by measuring the cis/trans isomeric content of the product. This procedure is attractive for two reasons. First, the intractability of polyacetylene and its slow rate of cis/trans isomerization at room temperature[22] suggests that the product observed after the polymerization represents the composition of the polyene as it was formed. Second, the cis/trans ratio can be routinely measured by IR[21] to an accuracy of about 5%.

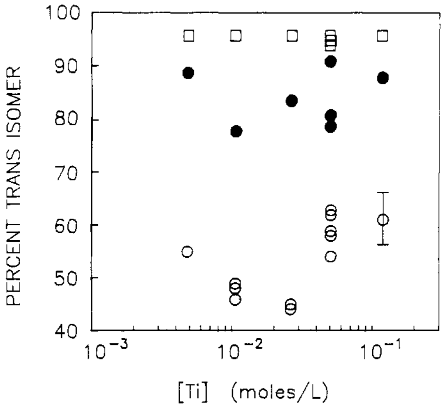


Figure 1. Dependence of the trans isomer content on catalyst concentration for acetylene polymerizations at 25 °C in toluene for Al/Ti = 1 (box), 2 (filled circle), and 4 (open circle).

We initially evaluated the effect of catalyst concentration on the trans isomer content of the polyacetylene product. In our previous work with polyacetylene block and graft copolymers,[23,24] we had suggested that a postsynthesis isomerization of polyacetylene might occur as a result of including a long, soluble block in the copolymer. Isomerization might also be expected for homopolyacetylene if the concentration of free chains is low enough to delay crystallization, thus allowing isomerization. If polyacetylene can isomerize in solution, then a decrease in the observed trans isomer content is expected as the catalyst concentration (and thus chain concentration) is increased.

We tested this prediction by obtaining data from a series of polymerizations in which the catalyst concentration was varied by more than 2.5 orders of magnitude (Figure 1). At the highest concentrations, gel formation made stirring difficult, and the polymerization became clearly heterogeneous. At the lowest concentrations, adventitous impurities consumed much of the triethylaluminum in the catalyst solution, resulting in higher levels of the trans isomer than expected. This was primarily a "wall effect" in that larger scale reactions, with a lower surface to volume ratio, gave lower trans contents. The results showed that the dependence on catalyst concentration was weak, with a tendency for an increase in trans content with concentration, opposite to that which was expected.

Note that as the Al/Ti ratio was varied from 4 to 2 to 1 the trans isomer content increased. This effect is more clearly depicted in Figure 2, where the results for polymerizations over a wide range of Al/Ti ratios are plotted. For analysis, the plot can be conveniently divided into three distinct regions. In region I, the trans content was high and the products tended to have a small particle size. In region III, the trans content was lower and slowly rose with increasing amounts of triethylaluminum. Region II, a transitional zone, bridges the high trans content of region I and the lower levels of region III. Our data unexpectedly suggested discontinuities at Al/Ti = 1 and 3. We have repeated these experiments several times, using different lots of triethylaluminum, titanium tetra-*n*-butoxide, and solvent, but the abrupt changes remained and appear to be real effects.

The addition of coordinating solvents such as tetrahydrofuran had a dramatic effect on these results. Uniformly high trans contents were observed even at Al/Ti ratios as high as 10, with the molar ratio of THF/Ti only 3. Polymerizations using added THF were slower to ini-

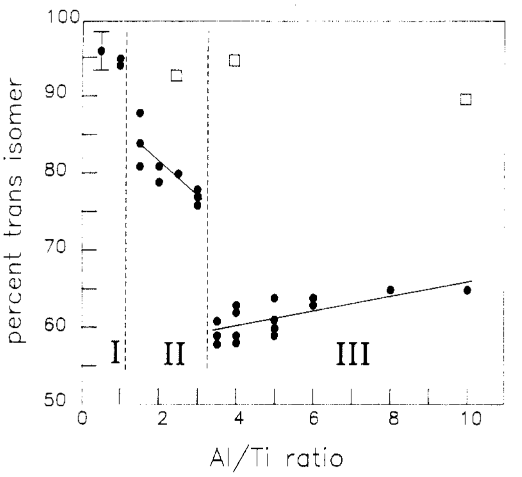


Figure 2. Dependence of the trans isomer content on the Al/Ti ratio for the polymerization of acetylene at 25 °C in toluene (circle). Titanium concentration, 0.05 M; monomer/Ti = 5. Reactions in which tetrahydrofuran was added (THF/Ti = 3 (box)) were carried out under the same conditions.

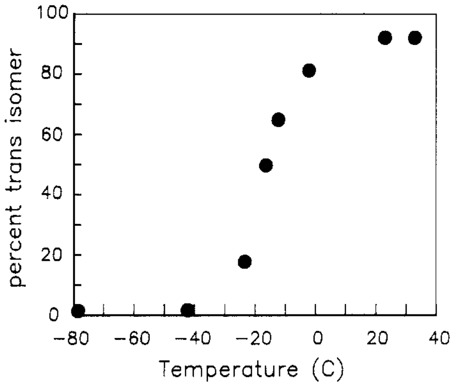


Figure 3. Dependence of the trans isomer content on temperature for the polymerization of acetylene in toluene. Titanium concentration, 0.05 M; monomer/Ti = 5; Al/Ti = 1.

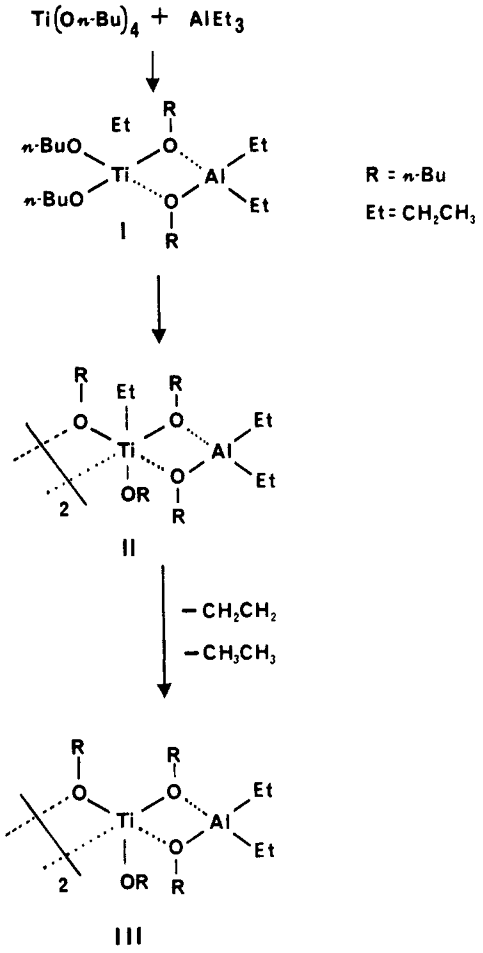
tiate than those without THF, and the polyacetylene product resembled that obtained in region I in both particle size and texture. Thus, the observed effect of impurities in the catalyst was to raise the trans isomer content, by either coordinating to titanium (similar to the case of tetrahydrofuran) or alternatively by reacting with triethylaluminum to lower the effective Al/Ti ratio and increase the trans isomer content.

Finally, we examined the effect of temperature (Figure 3) on the trans isomer content of polymerizations carried out at Al/Ti = 1. The polymer became cis rich as the polymerization temperature was lowered, eventually approaching 100% *cis*-polyacetylene, a result similar to that observed for acetylene polymerizations under Shirakawa conditions,[25] except that the changeover from all cis to all trans occurs over a much more limited temperature span.

Discussion

The results of these experiments can be interpreted within the context of previous work on titanium alkoxide/triethylaluminum catalysts. From these results, we have developed a scheme that we believe satisfactorily explains the unusual behavior of Figure 3 and allows us to make tentative identifications of the active catalysts. From previous work,[17,18] it is known that when triethylaluminum and titanium alkoxides are mixed, the initial event (Scheme I) is the transfer of an alkyl group from the aluminum to titanium. A complicating factor in defining the reaction scheme at this point and in later steps is the propensity for titanium alkoxides[26] and aluminum alkyls[27] to associate and form dimers and trimers in nonpolar solvents. Thus, the alkylated species may not be I as shown in Figure 4 but rather II. In any event, alkylation of the dimer or the monomeric titanium alkoxide eventually leads to the same product.

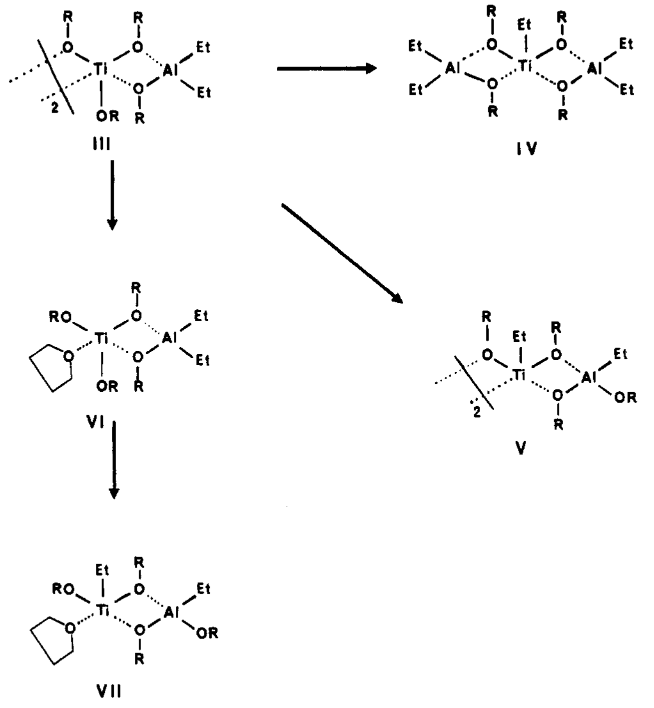
Scheme I



Titanium(IV) has been shown to be inactive toward the polymerization of acetylene,[28] and Ti(III) has been implicated as the oxidation state of the catalyst.[15,16,28] The route to a suitable Ti(III) species is also suggested by previous work. Dawes and Winkler[17] observed the evolution of 1 equiv of ethane from a similar catalyst mixture; ethylene was not observed and presumably remained coordinated to the metal center. It is important to note that at high ratios of Al/Ti, the evolution of less than 1 equiv of ethane (based on Ti) was observed. Later work by Dzhabiyev et al.[18] using a branched alkyl aluminum yielded the same results, except that the more bulky olefin could not effectively coordinate to titanium and was lost along with the alkane. These results suggest that the reductive elimination occurs from a binuclear complex. The evolution of equivalent amounts of alkene and alkane and the inhibiting effect of a large excess of trialkylaluminum[17,19] (which favors the formation of 2/1 aluminum/titanium complexes rather than the desired 2/2 complex) support this conclusion. The mechanistic pathway for this reduction is not clear.

The Ti(III) product of this reduction can now initiate polymerization after alkylation (Scheme II). A second alkylation by additional triethylaluminum yields IV, with two diethylaluminum alkoxides coordinated to the titanium. This is the result most often encountered in acetylene polymerizations. Ordinarily they are carried out at

Scheme II



Al/Ti ratios of 3–4,[25] and increases in aluminum content beyond 3 have little effect on the product but do lead to a noticeable decrease in the rate of polymerization.[19] This rate decrease can be traced to an inhibition in the rate of the reductive elimination step that leads to IV. We believe species IV is responsible for the polymerization results found in region III of Figure 3.

The results of region 1 and the behavior observed when tetrahydrofuran was added to the polymerization suggest similar intermediates. When the concentration of triethylaluminum is low, the alkylation to generate the active catalyst must come from the aluminum species already coordinated to titanium. This is a slow step, since the ability of alkyl aluminums to alkylate titanium complexes decreases in the order trialkyl > dialkyl monoalkoxide > monoalkyl dialkoxide.[29] The resulting complex V remains dimeric and differs from IV not only in terms of its degree of aggregation but also because a monoalkyl aluminum is coordinated to the titanium and not a dialkyl. We propose that these differences are manifested by the production of trans-rich polyacetylene.

A similar effect can be proposed for the reactions in which tetrahydrofuran was added. The effect of the additional coordinating ligand (added at a 3:1 molar ratio based on titanium) would be to break the alkoxide bridges that hold the dimer together. Additionally, the ligand prevents the approach of a second triethylaluminum unit. Just as in reactions where the aluminum/titanium ratio was 1, the second alkylation must be the transfer of an alkyl group from the diethylaluminum alkoxide coordinate to the titanium. The resulting organometallic species (VII) is similar to V in that the aluminum alkyl bound to the titanium is a monoalkyl and not a dialkyl.

It is important to note that in standard polymerizations using the triethylaluminum/titanium-*n*-butoxide catalyst, the picture is much more complicated. Standard practice[25] is to combine the reagents and to allow them to age for about 30 min before the addition of the monomer. In that time, a variety of catalytic species may form. In our work, that problem has been avoided by preparing the catalyst in the presence of the monomer. Thus, the initially formed catalyst is intercepted by the monomer and the multiple equilibria of the titanium alkoxide system are avoided.

The unusual and unexpected breaks in the curve of Figure 2 can now be rationalized in terms of the relative rates of catalyst formation and polymerization. To observe such behavior, the alkylation of complex III by triethylaluminum must be fast relative to alkylation by coordinated diethylaluminum alkoxide. In addition, the rates of acetylene polymerization by V must be slow. These effects were observed (but not quantified); polymerizations at low Al/Ti or with added THF were slow to initiate and to reach completion while those at Al/Ti > 3 were much more rapid.

Always we presume that the polymerization proceeds by the coordination of acetylene to the alkylated complexes followed by the usual insertion sequence. From this work, we have no evidence for either a trans insertion mechanism or metathesis. When the polymerization temperature was lowered, the smooth change over to all *cis*-polyacetylene production is more indicative of a low activation energy (catalyzed) isomerization step rather than a change in polymerization mechanism. This isomerization, pronounced in the "trans-selective" catalyst, may well be associated with the aluminum portion of the catalyst. Coordination of the olefin to aluminum may be favored electronically or sterically in these catalysts, but, from our data, we cannot conclusively make such an assignment.

This information about the chemical species responsible for acetylene polymerization has allowed us to prepare *trans*-polyacetylene directly under mild conditions.[30] These products have identical crystal structures, morphologies, and electronic structures to standard preparations of *trans*-polyacetylene. Polyacetylene prepared in this way contains fewer paramagnetic defects than that prepared by either the Shirakawa[31] or Durham[32] routes. This material has proven useful as a model material[33] for understanding which properties of polyacetylene are intrinsic and which properties are the result of defects in the polymer.

Registry No. *trans*-Polyacetylene, 25768-71-2; tetrahydrofuran, 109-99-9; triethylaluminum, 97-93-8; titanium tetra-*n*-butoxide, 5593-70-4; acetylene, 74-86-2.

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Photoinitiated Polymerization of Styrene in Microemulsions

Ping-Lin Kuo and Nicholas J. Turro*

Chemistry Department, Columbia University, New York, New York 10027

Chi-Ming Tseng, Mohamed S. El-Aasser,* and John W. Vanderhoff

Departments of Chemical Engineering and Chemistry and Emulsion Polymers Institute, Lehigh University, Bethlehem, Pennsylvania 18015. *Received July 7, 1986*

ABSTRACT: Photoinitiated polymerization of styrene in oil/water microemulsions has been successfully performed by using dibenzyl ketone (DBK) as initiator. The system remains transparent during the whole polymerization process. The molecular weights of polymers produced are in the order of 10^5, and the polydispersity indexes (PDI) are in the range 1.6–2.2. The particle sizes of the latexes produced are in the range 30–60 nm, with polydispersity indexes 1.05–1.08. The degree of polymerization (D_p) and the rate of polymerization (R_p) were studied as a function of initiator concentration ([DBK]) and light intensity (L). It is found that $D_p \propto [\mathrm{DBK}]^{-0.4}L^{-0.2}$; $R_p \propto [\mathrm{DBK}]^{0.2}L^{0.2}$. The mechanism of polymerization in microemulsions is discussed on the basis of polymerization rate and particle size.

Introduction

Emulsion polymerization has been a widely used industrial process for water-insoluble and sparsely soluble monomers.[1] Conventional emulsion polymerization is sometimes referred to as "macroemulsion" polymerization[2] because of the large size of monomer droplets (hundreds of microns) in the system compared to those in a "microemulsion" system (tens of nanometers). Between these two extremes, there is another type of emulsion that has been termed as "miniemulsion".[2,3]

Polymerizations in microemulsion systems have gained some attention in the past few years. Atik and Thomas[4] reported microemulsion polymerization of styrene with azobis(isobutyronitrile) (AINB) as an initiator and γ-irradiation as an initiating source. Jayakrishnan and Shah[5] studied polymerizations of styrene and methyl methacrylate microemulsions using oil-soluble initiators AIBN and benzoyl peroxide. Tang[6] reported the microemulsion polymerization of styrene using both water-soluble ($K_2S_2O_8$) and oil-soluble (AIBN) initiators. All of these are oil/water (o/w) systems. Candau[7] carried out w/o microemulsion polymerization of acrylamide using AIBN and $K_2S_2O_8$.

In a conventional emulsion polymerization, the reaction system can be represented by the simplified scheme shown in Figure 1a. During polymerization, monomer is located in the following four locations: (1) monomer droplets, (2) inactive micelles containing monomer, (3) active micelles that become monomer-swollen polymer particles where polymerization occurs, and (4) solute monomer in aqueous phase. The o/w microemulsion reported in this paper can be presented by the simplified scheme shown in Figure 1b. Three characteristics of o/w microemulsion polymerization are different from those of conventional emulsion polymerization: (1) No monomer droplets and no inactive micelles exist. (2) All of the initiator exists in the microemulsion droplets; thus polymerization occurs only in the monomer reservoir encapsulated in the particle. (3) The system is optically transparent.

Because of the transparency of microemulsion systems, light provides an interesting method to initiate polymerization not only because the polymerization rate can be made to be fast but also because the polymerization rate and the molecular weight of the polymer can be easily varied by controlling the light intensity and the time of irradiation. Photoinduced polymerization in conventional emulsion polymerization with dibenzyl ketone (DBK) as an initiator has been reported.[8] In the present work, the effects of the light intensity and initiator concentration on polymerization were studied in terms of molecular weight of polymer, polymerization rate, and percent conversion.

Experimental Section

Materials. Styrene (Aldrich) was washed with 10% sodium hydroxide 3 times and dried over anhydrous sodium sulfate after repeated washing with water. Further purification was carried out by distillation at 35 °C under aspirator pressure, and the purified sample was stored at 0 °C under nitrogen. Sodium dodecyl sulfate (SDS, Bio-Rad Laboratories) was recrystallized once from water and then once from ethanol. Pentanol (Aldrich) was purified by drying over potassium carbonate and by distilling at 45–46 °C under aspirator pressure. Dibenzyl ketone (DBK, Aldrich) was purified by three crystallizations from ether. Water was triple-distilled from $KMnO_4$/NaOH and purged with argon.

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