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Reaction of Butadiene with a Heterogeneous Ziegler–Natta Catalyst in Solid Polymers and Solutions

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ABSTRACT: In situ polymerization has proven to be a useful technique for obtaining polymer blends which cannot be prepared by other methods. We have synthesized blends of 1,4-polybutadiene in polystyrene and poly(1-butene) by polymerizing the monomer in a solid film of the host polymer with a $Et_2AlCl–Ti(OBu)_4$ catalyst. This constitutes an extension of the in situ technique to include heterogeneous catalysts in amorphous and semicrystalline matrices. In addition, we have conducted a detailed study of this catalyst and found that it can cyclotrimerize butadiene at low Al to Ti ratios. We showed that the catalyst particles produce only polymer and therefore conclude that cyclotrimerization occurs in solution or at the particle/solution interface. By investigating the product distribution with time, we found a steep decrease in the percent *cis*-polybutadiene, a small increase in percent *trans*-polybutadiene and a large increase in percent *ttt*-cyclododecatriene. Addition of *ttt*-cyclododecatriene to the catalyst solution prior to exposure to butadiene resulted in a relative decrease in the formation of *cis*-polybutadiene and a relative increase in the formation of *ttt*-cyclododecatriene. We thus determined that *cis*- and *trans*-polybutadiene must be synthesized at separate catalytic sites. This allows us to eliminate some of the mechanisms of polymerization that have been proposed for this commercially important class of catalysts.

Introduction

With the commercialization of materials such as high-impact polystyrene and Noryl [polystyrene–poly(2,6-dimethyl-1,4-phenylene oxide)], basic research in the field of polymer blends became quite prolific. Most of this research has dealt with the physics of miscibility while little has looked at the chemistry of preparing blends. In our laboratory we have chosen to concentrate in this area.

In situ polymerization has been proven to be useful for preparing several blends, including the following: poly(vinyl chloride) with solution-chlorinated polyethylene[1] or with poly(*n*-butyl acrylate);[2,3] polyacetylene in polyethylene[4] and poly(methyl methacrylate) in poly(methyl methacrylate).[5] Little of this research, however, investigated how the chemical reactions were affected by the use of a solid media as a solvent and only one[3] studied how phase separation was influenced by reaction conditions. These are the issues that we have tried to address in our work. Previously, we developed a technique for polymerizing butadiene in polystyrene with a homogeneous Ziegler–Natta catalyst.[6] On examining these blends we found that the domains were smaller than in mechanically mixed blends and their size distribution depended on how far below the glass transition the polystyrene matrix was during butadiene polymerization.[7] The stereoregularity of the polybutadiene was also influenced by this variable. One problem we had in these studies was that cross-linking of the 1,2-polybutadiene made the blends insoluble. To avoid this problem we decided to attempt to make mixed *cis,trans*-1,4-polybutadiene in polystyrene. The lack of stereoregularity is important to prevent crystallization, an added complication.

In choosing 1,4-polybutadiene we planned on addressing many questions. The glass transition temperature of this polymer and its solubility parameter are different from those of 1,2-polybutadiene. By examining the morphology of these two classes of blends, we hoped to determine how these variables influenced domain size when the in situ technique was employed. Second, we planned to run the polymerization in a semicrystalline polymer [poly(1-butene)] to determine how this affected morphology.

After examination of the literature, the catalyst $Et_2AlCl–Ti(OBu)_4$ was chosen for this phase of our study, regardless of the facts that it has not been extensively studied and that some of the literature on it is contradictory.[8,9] In its favor were the facts that it is a heterogeneous catalyst and would allow us to extend the in situ technique to this larger class of catalysts important in ethylene and propylene polymerization. A second factor is that it differs from our previous catalyst [$Et_3Al–Ti(OBu)_4$] by only one ligand and therefore might contribute to our understanding of why that catalyst behaved differently when the solvent was a solid polymer.[6] Ziegler–Natta catalysis is both the only way to achieve extremely stereoregular polymers and the only method for producing the technologically important polyolefins. Any understanding this study could yield would, therefore, be very valuable. This paper will deal with the preparation of these blends and the chemistry of this catalyst. The morphology of these blends will be discussed in a separate paper.

Experimental Section

Materials Purification. Toluene, cyclohexane, and pentane were distilled under vacuum off living polystyryl anion formed by initiating styrene with *n*-butyllithium. Poly(1-butene) (Aldrich—isotactic, low molecular weight) was outgassed on a vacuum line for 48 h prior to use. The *ttt*-cyclododecatriene was outgassed for 2 h. Polystyrene (PS) (Aldrich $\bar{M}_w = 209000$) was dissolved in toluene, precipitated in hexane, and dried in a vacuum oven at 70 °C.

Titanium tetrabutoxide [$Ti(OBu)_4$] (Aldrich) was distilled under vacuum. Triethylaluminum (Et_3Al, Aldrich), diethylaluminum chloride (Et_2AlCl, Aldrich, 1 M in hexane or 1.8 M in toluene), and titanium tetrachloride ($TiCl_4$, Aldrich) were used as received. Butadiene was collected at −78 °C after it passed through a column of potassium hydroxide pellets followed by a column of 4-Å sieves. It was then distilled under vacuum from dibutylmagnesium. Prior to polymerization a 2-L gas bulb was filled with butadiene to approximately 0.85 atm and frozen, pumped, and thawed three times.

Catalyst Preparation. The $Et_2AlCl–Ti(OBu)_4$ catalyst was prepared in a drybox by slowly adding 0.34 mL of $Ti(OBu)_4$ to 6.3 mL of Et_2AlCl (1 M in hexane). The catalyst was aged for $2^1/_2$ h at room temperature, during which time red particles precipitated. The $TiCl_4–Et_3Al$ catalyst was formed by very slowly adding 1.8 mL of Et_3Al (1 M in hexane) to 0.2 mL of $TiCl_4$ in 12.5 mL of pentane. This catalyst is also heterogeneous and was aged for 1 h.

Polymerizations. Solution polymerizations were run by adding 0.34 mL of Et_2AlCl catalyst or 0.25 mL of $TiCl_4$ catalyst to a reaction vessel that contained a stirring bar and 10 mL of solvent. For a few runs *ttt*-cyclododecatriene was added to the solution of catalyst in solvent. Solutions were briefly outgassed on the vacuum line at −78 °C. After warming, they were exposed to about 0.85 atm of butadiene gas while the solution was stirred

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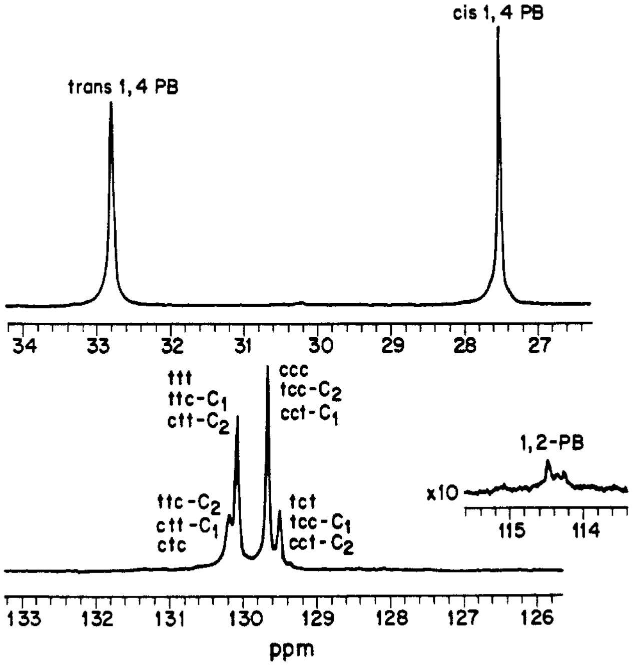


Figure 1. ^{13}C spectrum of precipitated polybutadiene synthesized in toluene solution with the $Et_2AlCl-Ti(OBu)_4$ catalyst.

slowly. With time, polymer grew around the catalyst particles and caused them to agglomerate and precipitate. To examine the catalyst more closely, we filtered it and washed the particles five times with a total of 5 mL of hexane. Then, the particles filtered from either 0.37 mL of catalyst solution or 0.37 mL of filtrate were added to 10 mL of toluene.

In situ polymerizations were run by casting a film of the matrix (3.0 g) with catalyst (0.37 mL) in a crystallization dish with a 10-cm diameter. Polystyrene films were cast from toluene. These manipulations were completed under argon in the drybox. As the solvent evaporated, the crystallization dish was rotated to disperse the catalyst particles. The poly(1-butene) films were made by dissolving 3 g of the polymer in cyclohexane at 50 °C. Once the polymer had dissolved, the solution was allowed to cool and then 0.37 mL of catalyst was added. Films were allowed to dry overnight in the drybox. The next morning they were outgassed for 2 h and then taken into the glovebox and weighed. Polymerizations were conducted on the vacuum line at 0.85 atm at ambient temperature.

Product Quantification. The polymerization products were identified by ^{13}C NMR spectroscopy at a frequency of 50.3 MHz by using a Varian XL-200 spectrometer. Sample preparation included sonication at −78 °C of both the in situ films dissolved in chloroform-*d* and the products of solution polymerizations with 10% chloroform-*d* added. The spectra were run at 45 °C with a 25-s delay between pulses and proton decoupling. The longest spin–lattice relaxation times (T_1) for the aliphatic and olefinic cyclododecatriene resonances were 4.9 and 7.7 s, respectively. The nuclear Overhauser enhancement (NOE) for resonances used for quantification ranged between 2.88 and 2.98. All spectra were referenced to hexamethyldisiloxane (HMDS).

To obtain quantitative data, the NMR conditions were changed for the experiments that probed the interaction between the *cis*-1,4-polybutadiene (*cis*-PB) and the *ttt*-cyclododecatriene (*ttt*-CDT). Equimolar amounts of HMDS and *ttt*-CDT were added to 10 mL of toluene and catalyst before the 3-h polymerization. The spectra were collected with gated decoupling (no NOE) and a 60-s delay between pulses since the methyl T_1 of HMDS is 11.4 s. Thus, the original amount of *ttt*-CDT added was determined via this internal standard and subtracted from the total amount produced. The results reported are averaged values. The reproducibility was such that the mole fraction of a component varied by ±0.02 between identical runs.

Results and Discussion

Chemistry of $Et_2AlCl-Ti(OBu)_4$ Catalyst. In our first experiment, butadiene was polymerized in toluene with the $Et_2AlCl-Ti(OBu)_4$ catalyst, precipitated in methanol, and then examined by ^{13}C NMR. This spectrum (Figure 1) revealed that very little 1,2-polybutadiene had been synthesized. The aromatic region (129–131 ppm) indicates that the polymer is a mixture of *cis*- and *trans*-1,4-polybutadienes (*cis*-PB and *trans*-PB) with some triad defects visible. Having confirmed that the catalyst did produce the desired material in solution, we proceeded to make polystyrene–polybutadiene blends by the in situ technique. As polymerization proceeded it was noted that the blend was collapsing on itself. The blend, examined at the completion of polymerization, was very gummy, indicating significant plasticization of the polystyrene. DSC analysis showed that the polystyrene T_g had been lowered to 30 °C, in a blend that had consumed enough butadiene to be 30% PB by weight. ^{13}C NMR of the blend (Figure 2) had several new peaks that could not be attributed to polybutadiene or polystyrene.

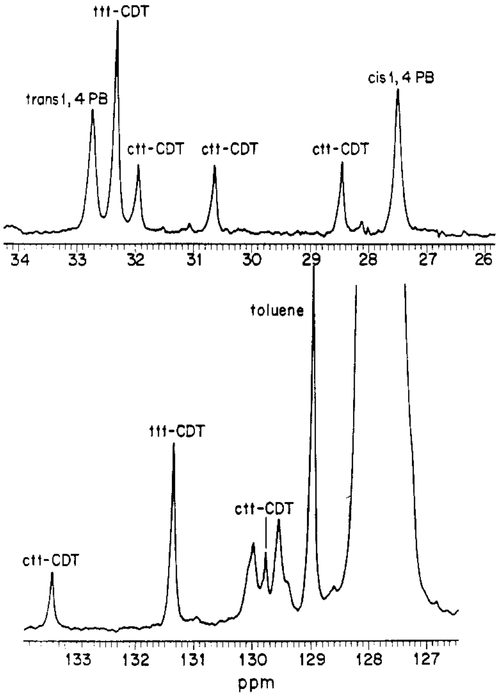
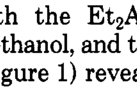
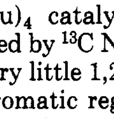
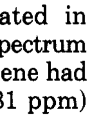


Figure 2. ^{13}C spectrum of a 16% polybutadiene–84% polystyrene blend prepared in situ with $Et_2AlCl-Ti(OBu)_4$.

A two-dimensional *J*-resolved NMR experiment determined that the new peaks were all methylene and methine carbons. This information combined with the number of peaks lead us to conclude that the compounds formed were *ttt*-cyclododecatriene and *ctt*-cyclododecatriene (*ctt*-CDT). Small amounts of octadiene (OD) were also observed. By running ^{13}C NMR of these compounds purchased from Aldrich, we were able to identify all the peaks in the spectra (Figure 2). A DSC scan of a polystyrene film with 10% cyclododecatrienes proved that they were responsible for plasticizing the polystyrene.


ttt-cyclododecatriene


ctt-cyclododecatriene


octadiene

A reevaluation of the spectra of solution-polymerized butadiene, run without first precipitating the polymer, showed that the cyclic trimers were also formed in solution in significant amounts. These results were surprising because a paper by Takahasi[8] stated that at 50 °C with Al/Ti ratios less than 12 this catalyst made only polymer

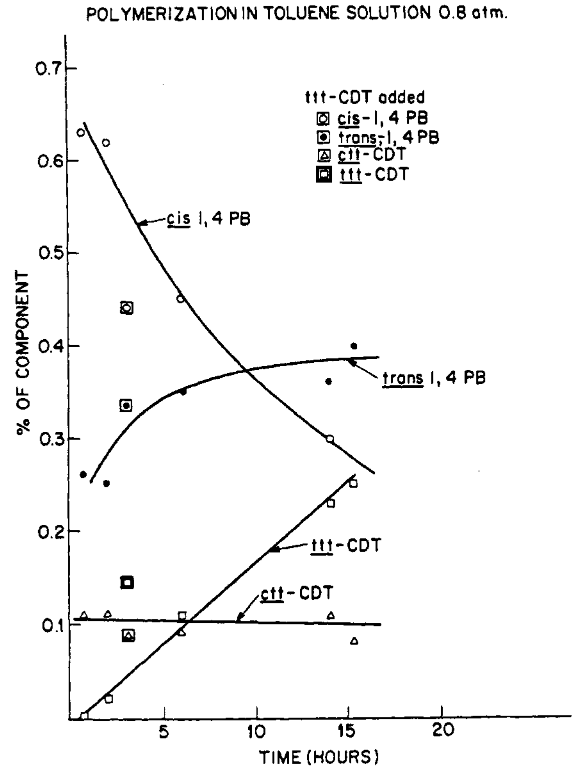


Figure 3. Variation in the amounts of *cis*- and *trans*-1,4-polybutadiene and *ctt*- and *ttt*-cyclododecatriene produced at differing times in toluene solution. Points enclosed in squares are for a polymerization in which *ttt*-CDT was added to the catalyst prior to the introduction of the monomer.

and at higher ratios it produced 81% *ctt*-cyclododecatriene with no *ttt*-cyclododecatriene. The ratio we employed in the majority of our experiments was 6.3/1, but polymerizations that we ran with ratios of 4/1 also produced both cyclododecatrienes. Carbonaro's research[9] (also at 50 °C) contradicted that of Takahasi in that he produced predominantly *ctt*-cyclododecatriene at Al/Ti ratios less than 10. By adding ligands such as pyridine he was able to shift the reaction to yield *ttt*-cyclododecatriene.

The patent literature on the synthesis of cyclododecatrienes adds more confusion than insight into these catalysts. Many transition-metal catalysts containing nickel and titanium have been patented for the synthesis of these compounds and several of the patents claim that $Ti(OBu)_4$ can be used with Et_2AlCl. Almost all examples, however, deal with $TiCl_4$ and Et_2AlCl or $Et_3Al_2Cl_3$. They also, in agreement with Takahasi,[8] give Al/Ti ratios generally greater than 10/1 and reaction temperatures between 50 and 70 °C. The exception on the Al/Ti ratio is work done by Wilke[10-12] that used 4.4 mol of Et_2AlCl to 1 mol of $TiCl_4$ at 40 °C. This system produced only *ctt*-cyclododecatriene. Examples with titanium alkoxide catalysts are found in patents by Mitsubishi Petrochemical Co.[3] [$Ti(OBu)_4$] and Du Pont[14] [$Ti(O\text{-}i\text{-}Pr)_4$]. Both systems used high temperatures (50 and 70 °C, respectively), Al/Ti ratios of 10/1, and added tributyl phosphine or alcohol as promoters. Under these conditions, Mitsubishi claims 100% yield of cyclododecatriene with tributylphosphine and Du Pont obtains 85% cyclododecatriene and 5% polymer with alcohol.

Although the literature was so contradictory, our interest in the physical properties of the blends, including the plasticization, led us to conduct a comprehensive investigation of this catalyst. To start, we used ^{13}C NMR to follow the catalyst reaction in toluene solution and in polystyrene with time (Figures 3 and 4). Note, however, that the in situ reactions are slower. It can take 5 days to get a 30% blend. For the in situ polymerizations the data are plotted against weight percent polybutadiene, not against time. This was done since, in the solid experiments, the weight percent polybutadiene was not a linear function of time. The reaction is diffusion limited and we made no attempt to control the sample thickness. Instead both the solution and in situ curves correspond to plots of product composition versus butadiene conversion. There is, therefore, no direct time comparison between curves. NMR spectra were taken of the solution reactions without precipitation of the polymer. The films were dissolved in deuterated chloroform and sonicated before collecting the data. Integration of the aliphatic region of the spectra (27–34 ppm) was used to quantify both the polymer and cyclododecatriene components. In this region of the spectra, resonances from cis or trans defect linkages in triad sequences (e.g., ctc) are not separate from ccc or ttt triads. But the aromatic peaks (where these resonances are separate) confirmed all the trends observed in the aliphatic region.

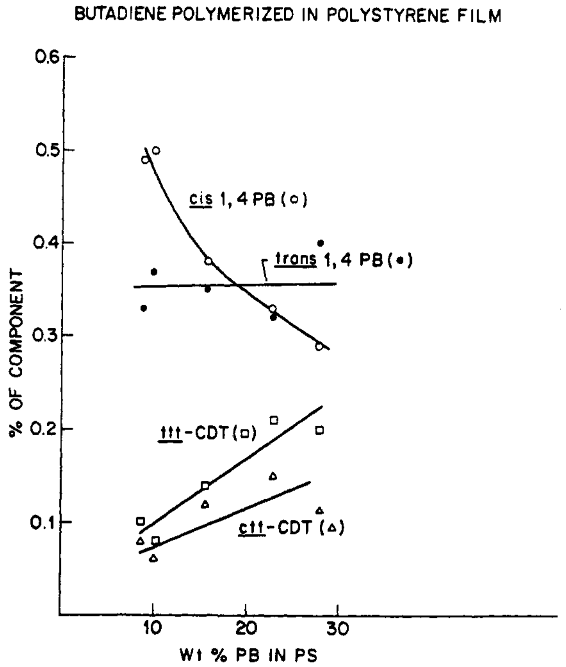


Figure 4. Changes in product distributions with time for the in situ polymerization of butadiene in polystyrene films.

The curves in Figures 3 and 4 are similar, indicating that conducting the reaction in the solid did not effect the major trends in percent product versus extent of butadiene reaction. In both data sets there is a significant loss in the relative amount of *cis*-polybutadiene and corresponding gain in the relative amount of *ttt*-cyclododecatriene with degree of reaction. The percent *trans*-polybutadiene is level in the in situ case, and in toluene solution it increases before leveling to the matrix value. This difference might, therefore, be eliminated if we had data points for blends of 1% or 2% polybutadiene. The main difference between the data sets is found in the relative amount of *ctt*-cyclododecatriene formed. It increases very slightly in the polystyrene matrix but is constant in solution polymerizations.

For further investigation of the catalyst chemistry we decided to restrict our work to solution polymerizations. The first obvious question to answer was whether the trends seen in Figure 3 could be attributed solely to catalyst aging. We therefore allowed a catalyst to age for 24 h in the drybox prior to exposing it to the monomer. The

Table I
Effect of Catalyst Aging

time of catal aging	mole fractn of component *trans*-PB	*cis*-PB	*ctt*-CDT	*ttt*-CDT
aged 2.5 h, 2-h poly.	0.25	0.62	0.11	0.02
aged 24 h, 2-h poly.	0.25	0.61	0.08	0.05

Table II
Polymerization with Catalyst Particles

sample	mole fractn of component *trans*-PB	*cis*-PB	*ctt*-CDT	*ttt*-CDT
particles only, 16-h poly.	0.28	0.69	0.03	none
complete catal, 15.5-h poly.	0.34	0.29	0.16	0.21

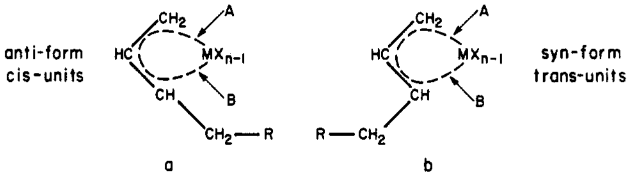
polymerization was ended after 2 h and the results are listed in Table I. After aging for 24 h the catalyst behaved identically to a catalyst aged for the standard $2^1/_2$ h. The trends observed in Figures 3 and 4 are, therefore, a result of the kinetics of the reactions or catalyst changes that occur on exposure to the monomer. They cannot be explained by catalyst aging.

The second issue of interest to us was whether the loss in *cis*-PB was connected to the gain in *ttt*-CDT. This relationship seemed important because both the patent literature and the organometallic literature on the use of titanium compounds with alkylaluminum chlorides claimed that these catalysts made *ctt*-CDT and *trans*-PB. Only in the presence of promoters was *ttt*-CDT obtained. To investigate the interaction, we added *ttt*-CDT in amounts similar to those produced in an 14 h polymerization to the catalyst prior to exposure to butadiene. The polymerization reaction was then conducted for 3 h. The original amount of *ttt*-CDT added was subtracted from the total amount of *ttt*-CDT found in solution after the polymerization, giving the amount of *ttt*-CDT produced during the polymerization. This amount was used to calculate the percent of each component synthesized. These results are plotted in Figure 3. The values on the graph are an average of two runs that differed at the most by ±0.02. The relative amounts of *trans*-PB and *ctt*-CDT are unchanged by the addition of *ttt*-CDT to the catalyst. But the relative amount of *cis*-PB decreases while the relative amount of *ttt*-CDT increases. This suggests that *ttt*-CDT either poisons the sites for cis polymerization (thereby allowing the amount of *ttt*-CDT to increase due to higher monomer concentration) or converts them to sites for formation of *ttt*-CDT. The decrease in the cis polymer was not as pronounced as in a 14-h run. This could be due to error in estimating the amount of *ttt*-CDT formed in a polymerization.

Supporting evidence for this interaction between *ttt*-CDT and sites for *cis*-PB came from experiments where we looked at the behavior of the catalyst particles after filtration and washing. The results of the 16-h polymerization listed in Table II lead to several conclusions. First, the particles are active without the liquid phase. This is somewhat unusual and differs from what was observed by Moyer[15] in triisobutylaluminum and titanium tetrachloride. Second, the particles produce primarily polymer. Formation of cyclododecatrienes must occur in solution or at the interface of particles and solution. Third, the ratio of *cis*-PB to *trans*-PB is about the same as in a 2-h solution run. Since no *ttt*-CDT is present, the percent cis polymer has not been depressed as in a typical 16-h solution polymerization.

In general, the experiments with the filtrate were harder to interpret because particles formed in the filtrate with time. At present we are analyzing these particles to determine if they have the same composition as the filtered particles.

Scheme I



Mechanism of Polymerization. Several mechanisms have been postulated to explain stereochemical control of diene polymerization. Dolgoplosh[16] et al. proposed that for metals in the reduced state, such as titanium, the amount of syn versus anti π-alkenyl complex determines cis–trans ratios in polybutadiene (Scheme I). They further state that the monomer initially coordinates in the anti form leading to *cis*-PB. If addition of the next monomer is slower than isomerization to the thermodynamically more stable syn form, *trans*-PB is synthesized. According to this theory the role of electron donors is to change the stability of the anti form such that isomerization occurs. To form 1,2-polybutadiene the second monomer must coordinate from the B-side (Scheme I).

An alternative explanation for the stereoregulating ability of these catalysts is that polymerization occurs at different sites.[17] Minsker[18] et al. have done calculations on structures formed by adsorption by alkylaluminum halides or alkylaluminum compounds onto $TiCl_3$, $TiCl_4$, and VCl_3. In their model, the sites for cis polymerization coordinate the monomer through both double bonds. The trans polymer is produced at a different site that involves coordination through one double bond. This theory for polymerization on $TiCl_3$ is in accordance with results from Natta,[19] who found that β-$TiCl_3$ produced two separable polymers (1,4 cis and 1,4 trans). Natta interpreted the fact that the cis and trans polymers were separable as an indication that they came from different sites. Our data also support this theory.

When *ttt*-CDT is added to the catalyst, the percent of cis polymer formed decreases, the percent of ttt-CDT increases, and the percent of trans polymer is relatively constant. If *ttt*-CDT coordinated to a catalyst site and thereby caused increased isomerization, we should have seen an increase in *trans*-PB while the *cis*-PB decreased. This argument also applies to the kinetic data in Figure 3. There is little change in *trans*-PB after 5 h, yet the level of *cis*-PB is decreasing. Assuming isomerization is the operative mechanism, we would again have expected to see increases in the percent *trans*-PB. If both polymers were synthesized at the same site but through different coordination intermediates, then poisoning or loss of this site caused by *ttt*-CDT would have decreased the percent *trans*-PB along with *cis*-PB. In summary, our data strongly support the proposal for separate sites for the formation of *trans*-PB and *cis*-PB.

Cyclotrimerization. Preliminary elemental analysis has a considerable amount of scatter in the data but consistently indicates that the catalytically active particles contain some butoxy ligands. The catalyst particles are, therefore, different from those in Natta's $TiCl_3$ catalyst and from $TiCl_3$ particles formed when $EtAlCl_2$ is added to $Ti(OBu)_4$[20] since they contain ligands other than Cl. It is possible, however, that the surface of these particles might not have butoxy ligands. We plan to conduct further experiments to identify the species present in the particles and in solution. By conducting polymerizations with $TiCl_4$–Et_3Al, which does produce $TiCl_3$ particles, we found

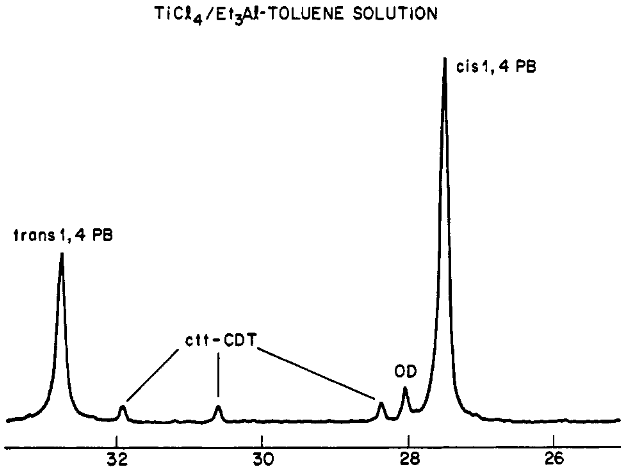
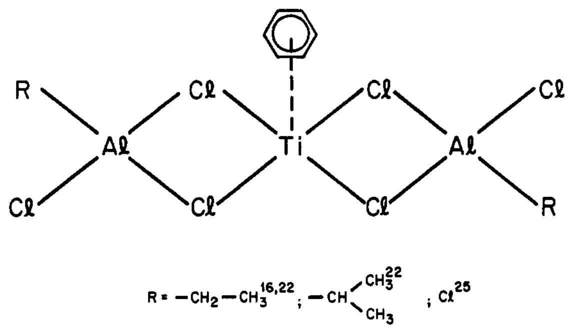


Figure 5. Aliphatic region of ^{13}C NMR spectrum of a butadiene polymerization in toluene with $Et_3Al-TiCl_4$.

Scheme II



that only *ctt*-CDT was synthesized (Figure 5). This agrees with most of the literature, which states that to obtain *ttt*-CDT from titanium systems, ligands such as triphenylphosphine must be added.[21,22] It also raises the question of whether the butoxy ligand can act as a promoter, accounting for the high yield of *ttt*-CDT. It is interesting to note that the polymer literature[15] on this $TiCl_4$ catalyst does not mention that cyclododecatrienes can be synthesized. It states that the yield of polymer is lower in toluene than in hexane, but gives no explanation for this observation. We believe this lower yield is because of formation of cyclododecatrienes.

Several organometallic chemists have studied the synthesis of cyclododecatrienes by compounds of the type found in Scheme II.[21-24] All of the authors suggest that Ti^{2+} is the active state for cyclotrimerization and that coordination of an aromatic ring is essential for this reaction. Dzierzgowski[21] et al. found that as the Ti–arene bond was destabilized in the sequence benzene, toluene, mesitylene, the formation of CDT increases.

Further examination of the $Ti(OBu)_4-Et_2AlCl$ catalyst exposed some behavior similar to that of the compounds in Scheme II and others that were different. A yet unanswered question is that of the oxidation state of titanium that is responsible for cyclotrimerization in our system. There exists a large amount of literature in polymer chemistry stating that $TiCl_4$ and $TiCl_3$ cannot be reduced to the 2+ state with Et_2AlCl even at ratios of 60 Al to 1 Ti.[25-27] Moyer[28] systematically replaced the chlorines in $TiCl_4$ with butoxy groups and found that $TiCl_2(OBu)_2$ was easier to reduce than $TiCl_4$, but $Ti(OBu)_4$ was significantly more difficult to reduce. This suggests that Ti^{2+} should not be present in our system. However, these studies also suggest that Ti^{2+} would not be present in most of the catalysts patented for cyclotrimerization. We hope to be able to determine that 2+ is the active state for cyclotrimerization by titrating our catalyst for the amount of Ti in each oxidation state.[29]

Table III
Effect of Aromatic vs Aliphatic Solvent

solvent, poly. time	mole fractn of component			
	trans-PB	*cis*-PB	*ctt*-CDT	*ttt*-CDT
toluene, 16 h	0.37	0.28	0.12	0.24
hexane, 16 h	0.34	0.56	0.06	0.04
toluene, 2 h	0.25	0.62	0.11	0.02

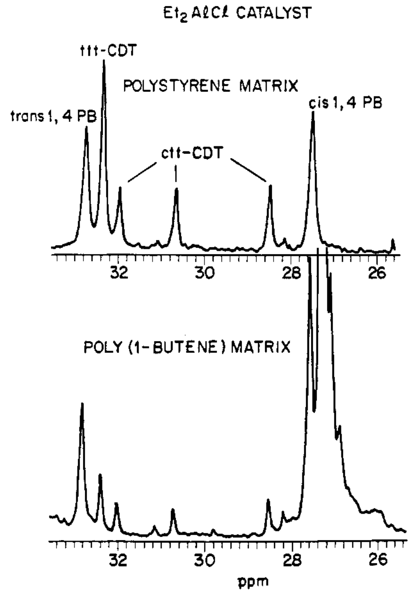


Figure 6. Comparison of the ^{13}C spectrum for blends of polybutadiene in polystyrene and isotactic poly(1-butene). The catalyst is $Et_2AlCl-Ti(OBu)_4$.

To determine if the coordination of an aromatic ring is important for cyclotrimerization, we conducted solution polymerizations in hexane and in situ polymerizations in poly(1-butene). As shown in Table III and Figure 6, considerably less cyclotrimerization occurs in aliphatic solvents. The blends in poly(1-butene) contain very small amounts of cyclic trimer. In all the experiments we conducted, the catalyst was prepared in hexane and then added to the solvent used for polymerization (i.e., toluene, polystyrene, poly(1-butene), or hexane). Since we know that cyclotrimerization is associated with the filtrate or the particle/solution interface, we can speculate that the aromatic ring of polystyrene or of the toluene solvent might promote solubilization of the catalyst, thereby enhancing cyclotrimerization, *ttt*-CDT should then be an even more effective ligand at solubilizing the catalyst and thereby promoting cyclotrimerization at the expense of polymerization, which is exactly what we found.

Conclusions

The experiments reported in this paper have revealed several important facts. First, we have demonstrated that in situ polymerization can be used in connection with heterogeneous catalysts and with crystalline matrices by the synthesis of new polybutadiene–poly(1-butene) blends. This extends the usefulness of the in situ technique and could lead to additional new polymeric systems. Second, we found that contrary to literature reports, $Ti(OBu)_4-Et_2AlCl$ is capable of cyclotrimerizing butadiene at low Al to Ti ratios. It also synthesizes both the ctt and ttt isomers, especially in aromatic solvents. The cyclic trimers are in turn responsible for plasticizing the blends. These studies illuminate why understanding the catalyst chemistry is important when in situ polymerization is being used to create blends with small domains. Any attempt to remove byproducts, which can affect the physical properties, would destroy the unique morphology that the technique provides.[7]

Since the polymer literature states that Et_2AlCl should not be able to reduce Ti to the 2+ oxidation state, but the organometallic literature proposes 2+ as the active state for cyclotrimerizing butadiene, this study has defined an area for future investigation that could be very valuable to both fields. Cyclododecatrienes are very versatile starting materials in synthetic chemistry and Ziegler–Natta catalysis is the most commercially important means of synthesizing polymers.

By following the product distribution of this reaction with time, we provided strong evidence for the proposal that *cis*-PB and *trans*-PB are produced at different catalytic sites. These results, combined with the experiments adding *ttt*-CDT to the catalyst prior to polymerization, suggest an interaction between *ttt*-CDT and the site for cis polymerization. Specifically, *ttt*-CDT either poisons the cis sites or converts them to sites for cyclotrimerization. Finally, we have shown that the catalyst particles are active toward diene polymerization to the exclusion of cyclotrimerization. We feel that our findings have led to a better understanding of these systems and, perhaps, might result in improved stereoregular diene catalysts.

Registry No. PB, 9003-17-2; *ttt*-CDT, 676-22-2; *ctt*-CDT, 706-31-0; OD, 29965-97-7; Et_2AlCl, 96-10-6; $Ti(OBu)_4$, 5593-70-4; butadiene, 106-99-0; poly(1-butene), 9003-28-5; polystyrene, 9003-53-6.

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Shear Modification of Low-Density Polyethylene: Its Origin and Its Effect on the Basic Rheological Functions of the Melt

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ABSTRACT: A low-density polyethylene has been subjected to repeated extrusion on a twin-screw extruder to investigate the effect of a mechanical treatment, commonly called shear modification, on the basic rheological functions of the melt. The dynamic quantities and the steady-state shear viscosity are hardly modified by the mechanical treatment, whereas the buildup of the extensional viscosity under a constant Hencky strain rate is slower after every extrusion running. The steady-state extensional viscosity drops by at least a factor 3 after five extrusions. This explains the decrease in die swell and increase in melt index often observed after shear modification. Heat and solution treatments nullify the effect of shear modification, which indicates that its origin is of a physical and not of a chemical nature. Solutions of the as-received polymer with concentrations of 1.5, 5, and 25 wt % were prepared. The polymer was then recollected by rapid quenching and evaporation of the solvent at ambient conditions. After 10^2 s in the molten state at 120 °C no effect of this solution treatment on the mechanical properties could be detected, whereas the effect of the mechanical treatment diminishes gradually to disappear completely after 10^4 s when the melt temperature is 200 °C. This indicates that a reduced interpenetration of the molecules is not the origin on a molecular basis of the effect of shear modification. The fact that the longest relaxation times of the melt are also of the order of 10^4 s at 200 °C is a strong indication that the physical change brought about by the mechanical treatment is a change in the conformation of the molecules. The fact that the flow behavior of strongly sheared long-chain branched material is similar to that of linear chain polymer melts supports the idea that an alignment of side chains along the chain backbone is effected by the mechanical treatment. This idea is further substantiated by the fact that the strain measure of the strongly sheared material approaches the strain measure predicted by the Doi–Edwards theory developed for linear chain polymer melts.

Introduction

It has been known for a long time that a technique called "shear modification", "shear working", or "shear refining" causes a reversible modification of the rheological properties of melts of thermoplastics consisting of long-chain branched molecules.[1-15] There is also a number of reports on shear modification of linear polymers.[17-20] Whereas agreement exists on the susceptibility of long-chain branched materials to shear modification, the situation is less clear for linear molecules. The origin of the effect is

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