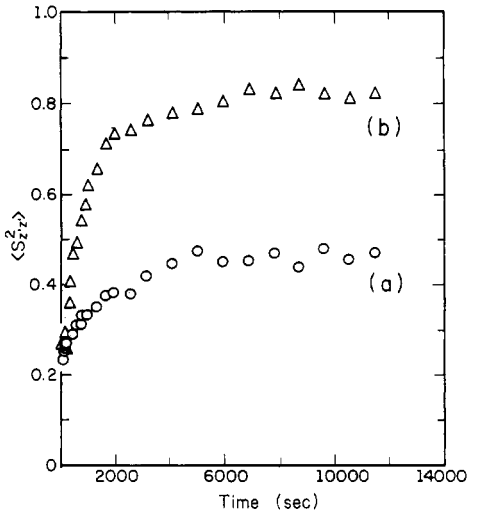


**Figure 4.** Kinetics curves plotted as the macroscopic order parameter $\langle S_{z'z'}^2 \rangle$ vs. time for samples oriented in (a) ungrooved and (b) grooved tube.

tinuing work in this area to elucidate some of these details. It is clear from the present study that surface interactions can have strong effects on the alignment of main-chain polymer liquid crystals when coupled with other force fields. The synergistic effect was manifested in this particular case by the enhancement of magnetic orientation rate.

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**Registry No.** (4,4′-$HO_2CC_6H_4O(CH_2)_5OC_6H_4CO_2H$)(4-$H_3CCO_2C_6H_4OCOCH_3$) (copolymer), 74774-52-0; (4,4′-$HO_2CC_6H_4O(CH_2)_5OC_6H_4CO_2H$)(4-$H_3CCO_2C_6H_4OCOCH_3$) (SRU), 74790-48-0.

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## In Situ Polymerization of Gaseous Monomers: Effect on Polymer Structure

Both the chemistry and physics of polymer blends have received considerable attention during the past 10 years. Much of this interest originated with the discovery that materials with improved mechanical properties can be obtained through blending [e.g., polystyrene/polybutadiene or polystyrene/poly(phenylene oxide)].[1] The extent to which these synergistic effects are realized is dependent on the miscibility or the degree to which phase separation occurs. Polymer miscibility is, however, limited by the fact that the entropy gained on mixing is very small. To minimize the phase separation that occurs in immiscible polymer pairs, interpenetrating networks (IPN) are synthesized. This is done by polymerizing the second monomer in a swollen cross-linked matrix of the first polymer. The cross-links serve to fix and limit the phase sizes. This field has been extensively examined for liquid monomers,[2] but very little has been done with gaseous monomers in a nonswollen, non-cross-linked matrix. It is this area of research that will be discussed here.

The goals of this work are threefold. First, the technique of polymerizing a gaseous monomer in a solid matrix could produce blends that cannot be obtained through other methods. This has been shown to be true with polyacetylene blends[3] and might be extended to other polymers such as poly(tetrafluoroethylene). Second, the technique has potential as a means of modifying polymer surfaces. A fundamental knowledge of the chemistry and physics of this technique is essential to its application. In the regime of chemistry, it is important to know whether the catalyst reactions are influenced by the use of a solid solvent. In the physics area, it is important to understand how the phase separation is influenced by polymerization conditions such as the difference between the polymerization temperature and the glass transition temperature of the matrix. Another issue to be addressed is whether this technique can be used to kinetically entrap chains in a nonequilibrium state and thereby provide a system with which to study the physics of phase separation.

Polybutadiene and polystyrene form an extensively studied incompatible polymer system. Since butadiene is a gas at room temperature, this system is a good choice for elucidating the important variables in solid-state in situ polymerization. This paper will deal with the synthesis of polybutadiene/polystyrene blends via in situ polymerization. An emphasis will be placed on the catalyst reactions and the structure of the polybutadiene. The morphology of these blends will be the subject of a future publication.

Purification of Chemicals. Butadiene (Matheson Research Grade 99.8%) was passed through two columns containing NaOH and 4A molecular sieves before collection in an evacuated flask. The monomer was then vacuum-distilled from dibutylmagnesium. For the polymerization reactions, a 2-L gas bulb was filled to 1 atm with the purified butadiene. A Ziegler–Natta catalyst consisting of

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6 mol of triethylaluminum ($AlEt_3$) to 1 mol of titanium tetrabutoxide [$Ti(OBu)_4$] was prepared in a Drilab and used to polymerize butadiene. The $Ti(OBu)_4$ (Aldrich) was distilled under vacuum, while the $AlEt_3$ (Alfa) was used as received. Toluene, the solvent for the catalyst, was distilled over $CaH_2$ under a dry, oxygen-free argon atmosphere. For a few polymerizations a 4 M $AlEt_3$ to 1 M vanadium(III) acetylacetonate [$V^{III}$(acac)] solution in toluene was utilized as the catalyst. The $V^{III}$(acac) was purchased from Aldrich and used without further purification.

Polystyrene (Aldrich, $\bar{M}_w$ = 209 000) was dissolved in toluene and precipitated in hexane. After filtration it was dried in a vacuum oven at 70 °C followed by outgassing on a vacuum line to $1 \times 10^{-4}$ atm. All polystyrene films containing catalyst were cast in a Drilab under argon.

Synthesis of Polybutadiene/Polystyrene Blends. Catalyst solutions were prepared by adding 1.35 mL of $Ti(OBu)_4$ to 15 mL of toluene in a Drilab. This was followed by a slow addition of 3.26 mL of $AlEt_3$. At this point the catalyst solution became warm and gas was evolved. The solution was aged for 30 min prior to use. In a few experiments the Ti:Al molar ratio was changed from 6:1 to 4:1. This was accomplished by adding less $AlEt_3$ in order to keep the Ti molarity constant. Vanadium catalysts were made in the same manner but consisted of 15 mL of toluene, 1.38 g of $V^{III}$(acac), and 2.2 mL of $AlEt_3$. With these quantities the V molarity is equal to the Ti molarity.

The second step in the synthesis involved casting a polystyrene film containing the appropriate catalyst. The catalyst solution (0.25 mL) was added to 1.5 g of polystyrene in toluene. A 0.2-mm-thick film was cast overnight in a crystallization dish in a Drilab. The next morning the film was outgassed on a vacuum line for at least 2 h. The catalyst-containing film was sampled in a Drilab for DSC analysis prior to exposure to butadiene.

Polymerizations were carried out on a submanifold of the vacuum line. A butadiene gas bulb, the reaction vessel, and a Hg manometer were attached to this submanifold. The film was outgassed, and then the submanifold was isolated from the main manifold. At this point the butadiene bulb was opened and polymerization began. The initial pressure was slightly less than 1 atm and decreased during the reaction. Room-temperature polymerizations required 3 days to obtain 30% polybutadiene. The temperature of polymerization was increased in some experiments by placing an oil bath around the reaction vessel. To terminate the polymerization butadiene was condensed into the gas bulb and the film was evacuated.

Characterization of the Blends. NMR spectra were recorded at 45 °C on a Varian XL 200 with a $^{13}C$ frequency of 50.3 MHz. The blends had to be sonicated at −78 °C to obtain spectra. The solvent used was $CDCl_3$. Spectra were proton decoupled and recorded with a full nuclear Overhauser enhancement (NOE). A control experiment proved that all the carbons used for quantification had the same NOE. Since the polystyrene peaks were not enhanced as fully as the polybutadiene peaks, the percent polybutadiene in the blends was not determined from the $^{13}C$ NMR. The time between pulses was 3.5 s.

Thermoanalysis was performed on a Perkin-Elmer DSC 4. The samples were scanned from −100 to +120 °C at a rate of 20 °C $min^{-1}$.

The Ti catalyst used was developed by Natta[4] and studied by Dawes.[5] These authors reported that one obtains a highly syndiotactic 1,2-polybutadiene with this catalyst. In agreement with Dawes, we found that at a 6:1 Al/Ti ratio the catalyst produces 4 times more polybutadiene than at a 4:1 ratio. We, therefore, did most of our work at a 6:1 ratio. The polystyrene films contained some residual toluene, which lowered the glass transition temperature to 70 °C. When a film containing dead catalyst was exposed to butadiene gas for 3 days, it gained only 2% of its weight in butadiene. No thickness increase was observed. This supports our statement that the polystyrene matrix is not swollen by the monomer.

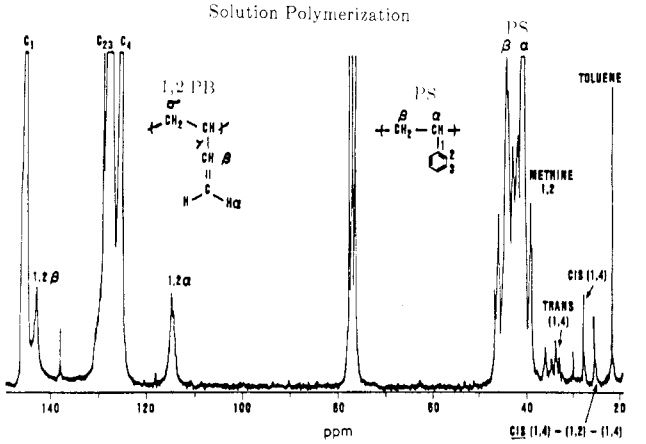


**Figure 1.** $^{13}C$ NMR spectrum of a mixture resulting from the polymerization of butadiene in a toluene solution of polystyrene at ambient temperature.

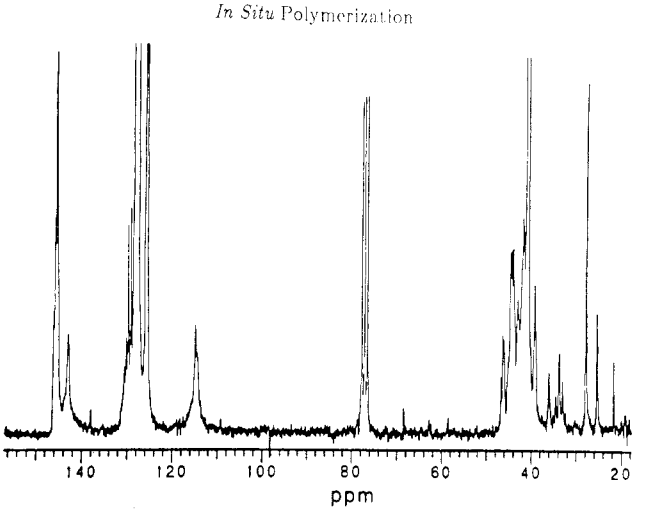


**Figure 2.** $^{13}C$ NMR spectrum of a blend of polybutadiene and polystyrene synthesized via the in situ technique at ambient temperature.

The polystyrene/catalyst films were a transparent brown initially and became hazy after 2 days of polymerization. This indicates that phase separation or the formation of a surface layer of polybutadiene had occurred. To ensure that polymerization was proceeding in the polystyrene, two experiments were performed. Samples were fractured and stained with $OsO_4$. The fracture surface was black across its thickness, indicating the presence of polybutadiene in the center of the film. Second, an NMR spectrum was recorded on a sample whose surface was scraped off. Polybutadiene was present in the spectrum, supporting the conclusion that polymerization occurred in the matrix. Transmission electron microscopy, which is presently being completed, will help in determining the distribution of polybutadiene in these blends.

$^{13}C$ NMR was used to characterize the polybutadiene. This was the method of choice because the 1,2 and 1,4 peaks are clearly separated.[6-8] Since the blends swell but are not soluble, it was necessary to sonicate them in $CDCl_3$ to obtain spectra. The insolubility of the blends is most

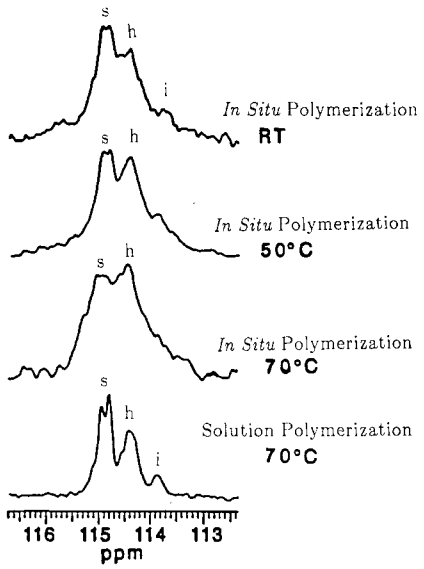


**Figure 3.**

**Table I**
**Polybutadiene Structure vs. Temperature**

| butadiene polymerized in solid PS | | butadiene polymerized in a toluene solution of PS | |
|---|---|---|---|
| temp, °C | % cis 1,4 | temp, °C | % cis 1,4 |
| 22 | 28 | 22 | 12 |
| 50 | 19 | 50 | 13 |
| 70 | 14 | 70 | 11 |

likely due to the fact that this Ti catalyst is known to cross-link polybutadiene.[4] By comparing IR and NMR spectra of sonicated polybutadiene, we were able to confirm that sonication was not influencing the conclusions.

Figure 1 is a spectrum of a room-temperature solution polymerization of butadiene in toluene with polystyrene present. The peak assignments have been appropriately labeled. In Figure 2 the spectrum of a blend from a room-temperature in situ polymerization of butadiene is displayed. Note tht the cis-1,4 peak (27.53 ppm) is significantly larger in Figure 2 than in Figure 1. In addition the peak corresponding to a 1,2 unit following a cis-1,4 sequence (25.15 ppm) is smaller in comparison to the cis peak. This means that the catalyst not only is making more *cis*-PB but also is making longer cis-1,4 sequences. To understand why the catalyst produced more *cis*-1,4-PB we conducted polymerizations at various temperatures. $^{13}C$ spectra were obtained for all of these samples. The areas under the 1,2-$\alpha$ peak (114.86 ppm) and the cis-1,4 peak (27.53 ppm) were integrated and the percent cis 1,4 calculated. The results from these experiments are reported in Table I.

When the polymerization occurs below the glass transition temperature of the matrix, the Ti catalyst produces more *cis*-1,4-polybutadiene. As the temperature increases, the catalyst produces polybutadiene with a cis-1,4 content that approaches the solution value. Careful evaluation of the spectra reveals that even at 73 °C there are differences between the butadiene polymerized in the polystyrene matrix and a toluene solution. Figure 3 contains an enlargement of the 1,2-$\alpha$ peak of blends synthesized at 22, 50, and 70 °C and a solution polymerization at 70 °C. Both the 22 °C blend and the 70 °C solution polymerization contain more syndiotactic polybutadiene than heterotactic. At 50 °C the syndiotactic and heterotactic triads are of approximately equal number. In the 70 °C blend there are more heterotactic triads than syndiotactic triads. The splittings in these peaks are due to pentad sequences.[9] The

**Table II**
**Structure of Butadiene Polymerized with a Vanadium Catalyst**

| butadiene polymerized in solid PS | | butadiene polymerized in a toluene solution of PS | |
|---|---|---|---|
| temp, °C | % cis 1,4 | temp, °C | % cis 1,4 |
| 22 | 12 | 22 | 17 |
| 70 | 20 | 70 | 19 |

isotactic content is very small in all the blends. In summary, the butadiene polymerized in situ at elevated temperatures is more random than its solution counterpart. The reason for this increased randomness in the matrix is as yet undetermined.

For Ti catalysts is has been proposed that *cis*-1,4-polybutadiene results from coordination of the monomer through both double bonds.[10] When the monomer coordinates through one double bond 1,2- or *trans*-1,4-polybutadiene is formed. Coordination through both double bonds can be influenced by many factors, including the ratio of cis to trans conformations of the monomer or the electron density around the Ti.[11,12] If the matrix has changed the cis:trans ratio of the monomer, it could explain our data and indicate that other catalyst systems might behave in a similar manner. To understand this we have also investigated an $AlEt_3/V^{III}(acac)$ catalyst.[13]

Table II contains results obtained with a vanadium(III) acetylacetonate catalyst. In contrast to the results for the Ti catalyst system, the blends synthesized at room temperature with the V catalyst are not rich in *cis*-1,4-polybutadiene. In fact there are more 1,2 units in the polybutadiene made by the in situ polymerization than by the solution polymerization. At elevated temperatures the vanadium catalyst also behaves as if it were in solution. It appears that the increased cis-1,4 content seen with the Ti catalyst at temperatures below the film $T_g$ is particular to the Ti catalyst. Additional studies of the Ti, V, and other catalysts are required to elucidate the mechanism behind these results. A fundamental understanding of how these catalysts work in a solid solvent should increase our knowledge of their solution behavior.

**Registry No.** $AlEt_3$, 97-93-8; $[Ti(OBu)_4]$, 5593-70-4; $[V^{III}(acac)]$, 13476-99-8; polybutadiene, 9003-17-2; polystyrene, 9003-53-6.

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