as 3-4 days. When the polyamide solution containing lithium chloride was cast, the film was washed with water for several hours and then dried.

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# Acyclic Azoester Modification of 1,4- and 1,2-Polybutadienes. Structure and Properties

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ABSTRACT: This paper reveals salient structure-reactivity and structure-property relationships for the isopropyl azodicarboxylate (IAD) modification of high 1,4(*cis*)-, 1,4(*trans*)-, 1,4(mixed *cis,trans*)-, and 1,2-polybutadienes. It has been found that the 1,4 and 1,2 adducts differ in sequence distribution. The 1,2 product exhibits an essentially random distribution of functionality and single-phase morphology. In contrast, the modified 1,4 material evinces blocky character and multiphase morphology. It has been learned that both the forward ene reaction and the retroene process are more facile for the 1,4 backbone than for the 1,2 substrate. Consistent with an ene cycloaddition mechanism, the IAD modification of 1,4-polybutadiene involves no cis-trans isomerization of the unmodified olefin units; the IAD modification of 1,2-polybutadiene involves isomerization of vinyl units to internal double bonds. The IAD reactions are simple add-on processes. Yet, there is some evidence of free-radical leakage, especially in the case of the 1,2 substrate. The structures of the products of the IAD modification of 1,4- and 1,2-polybutadienes have been proven by $^{13}$C NMR, IR, UV, GPC, membrane osmometry, and TGA measurements. Supermolecular structures have been determined by DTA and dynamic thermomechanical measurements.

## Introduction

Substantial progress has been made toward an understanding of the ene reaction of acylic azoesters with monoolefins, e.g., isomeric butenes and pentenes. Yet most acylic, as well as cyclic, azo ene reactions on polymers have been performed on only 1,4 backbones, e.g., SBR and natural rubber.[3-12] Comparable modifications of 1,2 substrates have been virtually ignored. A notable exception is the recently reported reaction of 1,2-polybutadiene with one class of cyclic azoenophiles, the triazolinediones.[12] However, acyclic ene modifications of 1,2-polydienes have not been mentioned or studied. The relationship between cyclic and acyclic enophiles is also not well established. Moreover, salient questions of mechanism, structure, and sequence distribution for all such processes and products have remained unanswered.

This paper describes hitherto unrecognized structural and sequence information for the polymeric products of the reaction of an acyclic azoester, isopropyl azodicarboxylate (IAD), with high 1,4(*cis*)-, 1,4(*trans*)-, 1,4-(mixed *cis,trans*)-, and 1,2-polybutadienes. Also developed are backbone structure-reactivity and product structure-property relationships.

Table I
Characterization of Backbone Types

| polybutadiene type | microstructure | | | | |
|---|---|---|---|---|---|
| | % cis | % trans | % 1,2 | $10^{-5}M_n$[a] | [$\eta$] |
| high 1,4 (mixed cis,trans) | 34.7 | 54.0 | 11.2 | 1.07 | 2.06 |
| high 1,4 (cis) | 95.5 | 2.0 | 2.1 | 1.03 | 1.94 |
| high 1,4 (trans) | 11.5 | 84.2 | 3.3 | 0.82 | 1.32 |
| high 1,2 | 1.4 | 0.2 | 98.0 | 1.38 | 1.39 |

[a] By osmometry.

IAD was chosen for this work because of its commercial availability and easily managed liquid physical state. Also, unlike the triazolinedione modification of polydienes, the IAD process is homogeneous in hydrocarbons even up to high levels of modification. In the course of these studies,

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it was discovered that the IAD modification of 1,4 backbones tends to be more blocky than in the case of 1,2 backbones.

## Experimental Section

**Materials.** High 1,4(*cis,trans*)-polybutadiene was obtained from The Firestone Central Research Laboratory. High 1,4-(*cis*)-polybutadiene, Ameripol CB 220, was obtained from the B. F. Goodrich Co. High 1,4(*trans*)-polybutadiene was prepared according to modifications of known procedures.[13] The high-trans polymers so produced were semicrystalline and soluble in hydrocarbons. The high-vinyl (1,2) polybutadiene was prepared according to the method of Halasa,[14] which produces polymers with the highest known vinyl contents.

All polymers were used as received, i.e., containing antioxidant. The backbone polymers are characterized in Table I. Isopropyl azodicarboxylate (IAD) was obtained from the Muskegon Chemical Co. and was used without further purification. Toluene solvent was distilled and dried by passage through 3-Å molecular sieves.

**Equipment and Measurements.** IR spectra of polymers were obtained on a Beckman·IR-4 spectrophotometer. Microstructures for the starting unmodified polydienes were also determined by an infrared method.[15,16] However, microstructures for modified polymers could not be evaluated by IR spectroscopy because of the interference of isopropyl group absorptions (760–780 $cm^{-1}$) with the cis olefin bands of the polydienes. Instead, the microstructures for modified polymers were analyzed by $^{13}C$ NMR spectrometry.

Polymer $^{13}C$ NMR spectra were run on a JEOL PFT 100 spectrometer operating at 25.15 MHz for $^{13}C$ nuclei. Spectra were run on 5% (w/v) $CDCl_3$ solutions at 50 °C. Spin–lattice relaxation time, $T_1$, measurements revealed that the carbonyl carbon of the hydrazoester moiety has a $T_1$ of 4.6 s and the next longest $T_1$ is that of the methyl carbons, 0.87 s. A pulse width of 19.2 μs (70° tip angle) and a repetition time of 4.6 s were used. The spectral width was 5 kHz.

UV spectral analyses of the modified polymers were determined with a Beckman DK-2UV spectrophotometer.

Polymer $^1H$ NMR spectra were run on a JEOL FX60Q spectrometer at 60 MHz. The spectra were run on 5–20% (w/v) $CS_2$ solutions at room temperature.

**Membrane Osmometry.** Osmotic pressure measurements for number-average molecular weights ($\bar{M}_n$'s) were run at 37 °C with a Wescan Instruments, Inc., Model 231–200 membrane osmometer. Toluene was employed as the solvent.

**Gel Permeation Chromatography.** A Water Associates Model 200 gel permeation chromatograph (GPC) was used with both refractive index (RI) and ultraviolet (UV) detectors. The UV detector was set at 254 nm. Four 1.21 m × 0.95 cm Styragel columns of $10^3$-, $10^4$-, $10^5$-, and $10^6$-Å nominal pore ratings were employed. A flow rate of 1 mL/min was maintained, with tetrahydrofuran (THF) as the solvent at 24 °C. The instrument was calibrated with polystyrene standards, and the "universal" calibration was employed in conjunction with Mark–Houwink constants for polybutadiene in THF to perform the various molecular weight parameter calculations.

**Thermal Analyses.** Second-order transitions were determined by using a Du Pont Model 900 differential thermal analyzer (DTA) at a programmed heating rate of 20 °C/min. Sample weights of 15–25 mg were used with a nitrogen stream of 300 mL/min maintained over the sample.

Thermogravimetric analysis (TGA) was done with a Du Pont Model 950 TGA at a programmed 10 °C/min heating rate. A nitrogen stream of 50 mL/min was maintained over the sample. The sample size was approximately 12 mg.

**Elemental Analyses.** A Perkin-Elmer Model 240 elemental analyzer was employed for C, H, and N analyses. The instrument was calibrated with acetanilide (NBS standard material no. 141b). The reduction furnace temperature was 650–700 °C, and the combustion furnace was at 900–1000 °C.

**Mass Spectral Analyses.** Mass spectral analyses were run on an AEI MS12 mass spectrometer at 70 eV.

**Dynamic Mechanical Measurements.** Dynamic mechanical responses for IAD-modified polymers were obtained with a Rheovibron at constant frequency in the temperature range −90 to +150 °C. A computer program was used to convert the Rheovibron data into plots of tan δ, dynamic modulus, loss modulus, and storage modulus vs. temperature.

## Modification Process and Products

**Azoester Modification of 1,4- and 1,2-Polybutadienes.** The 1,4- or 1,2-polybutadiene was dissolved in toluene (13–16% by weight) overnight at 50 °C. To such solutions was added the desired weight of isopropyl azodicarboxylate (IAD). The 1,4 polymers were allowed to react for 22–27 h at 80 °C. The 1,2 polymers were allowed to react for 122 h at 80 °C. After cooling to room temperature, the reaction mixtures were coagulated in the presence of antioxidant, di-*tert*-butyl-*p*-cresol (DBPC). For polymer modification levels ≤50% (w/w), 2-propanol or methanol was used as the coagulating solvent. For polymer modification levels ≥50% (w/w), hexane or pentane was used.

**High-1,4 (Mixed Cis,Trans) Adduct.** Elemental analyses: Calcd (for 52.7% modification): C, 64.69; H, 8.75; N, 8.04. Found: C, 64.84; H, 8.73; N, 8.04. Prominent IR absorptions ($CS_2$ solution): 3320 (NH), 1720, 1760 (hydrazodicarboxylate carbonyls), 1590 (conjugated olefin?), 1110 (C–O, ester), 965 (*trans*-CH=CH), 911 ($CH{=}CH_2$), 760, 780 ($CH(CH_3)_2$), 740 (*cis*-CH=CH) $cm^{-1}$.

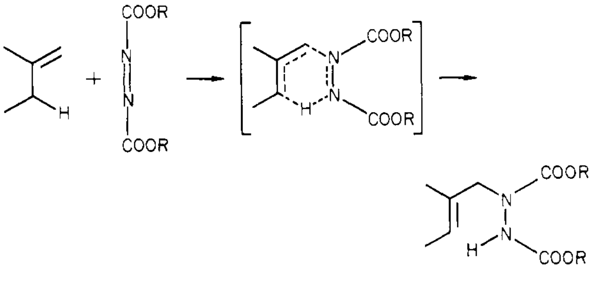
**High-1,4 Cis Adduct.** Elemental analyses: Calcd (for 53.0% modification): C, 66.93; H, 8.95; N, 7.34. Found: C, 66.72; H, 9.33; N, 7.54. Salient IR absorptions ($CS_2$ solution): 3320 (NH), 1725, 1765 (hydrazodicarboxylate carbonyls), 1565 (conjugated olefin?), 1105 (C–O, ester), 1655, 1408, 740 (*cis*-CH=CH), 760, 780 ($CH(CH_3)_2$) $cm^{-1}$; $^1H$ NMR δ 1.19, 1.30 (isopropyl $CH_3$), 4.9–5.2 (OCH, $CH_2N$); $^{13}C$ NMR, see Discussion section; UV, see Discussion section.

**High-1,4 Trans Adduct.** Elemental analyses: Calcd (for 10.1% modification): C, 84.86; H, 10.76; N, 1.40. Found: C, 84.49; H, 11.19; N, 1.20.

**High-1,2 Adduct.** Elemental analyses: Calcd (for 52.4% modification): C, 67.18; H, 8.89; N, 7.26. Found: C, 67.07; H, 9.29; N, 7.49. Important IR absorptions (film): 3320 (C–O, ester), 1675, 1345, 835 (>C=CH?), 1645, 1410, 909, 995, 672 ($CH{=}CH_2$), 760, 780 ($CH(CH_3)_2$) $cm^{-1}$; $^1H$ NMR δ 1.19, 1.29 (isopropyl $CH_3$), 4.06 ($CH_2N$), 4.73 (OCH); $^{13}C$ NMR, see Discussion section; UV, see Discussion section.

## Results and Discussion

**Background Model Compound Studies.** The reaction of an acyclic alkyl azodicarboxylate with a monoolefin is an example of an ene reaction, i.e., the cycloaddition of a compound with a double bond (enophile) with an olefin containing at least one allylic hydrogen (ene). This process is believed to occur in a concerted fashion via a cyclic transition state.[2] The product of the reaction is a hydrazoester-substituted olefin (eq 1).



(1)

By a comparison of the relative reactivity of various isomeric butenes and pentenes with ethyl azodicarboxylate, Thaler and Franzus[1] found that primary allylic hydrogens are abstracted in preference to secondary ones; secondary allylic hydrogens are abstracted in preference to tertiary ones. Thus, *trans*-2-pentene is significantly more reactive than 3-methyl-1-butene. These authors also found that trans olefins are more reactive than cis enes.

Moreover, Thaler and Franzus[1] noted that such monoolefins can form diadducts (II, depending upon the ratio of the olefin to the azoester and the relative reactivity of the starting olefin to the monoadducts. In fact, they found that it was difficult to isolate a monoadduct from 3-

Table II
Modification Efficiency[a]

| backbone | rxn time, h | rxn temp, °C | wt % IAD charged | wt % N incorp[b] | wt % IAD incorp | ME[c] |
|---|---|---|---|---|---|---|
| high (84.2%) trans | 24 | 80 | 60.0 | 7.75 | 56.0 | 93.3 |
| high (95.9%) cis | 24 | 80 | 60.0 | 7.54 | 54.4 | 90.7 |
| high (98.0%) vinyl | 122 | 80 | 60.0 | 7.49 | 54.1 | 90.1 |

[a] All reactions were charged at an IAD/polymer weight ratio of 1.5 and a solvent/polymer weight ratio of 6.25. [b] Based upon elemental analyses (±0.05%). [c] Modification efficiency = (wt % IAD incorporated)/(wt % IAD charged).

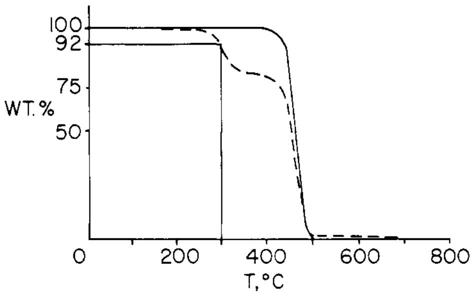


**Figure 1.** TGA thermograms for IAD-modified [25.4% (w/w), by elemental analysis] and unmodified 1,2-polybutadienes: (---) modified; (—) unmodified. Total weight loss by TGA, 22% (w/w); weight loss at 300 °C, 8%.

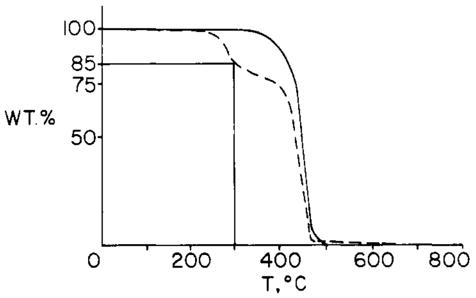
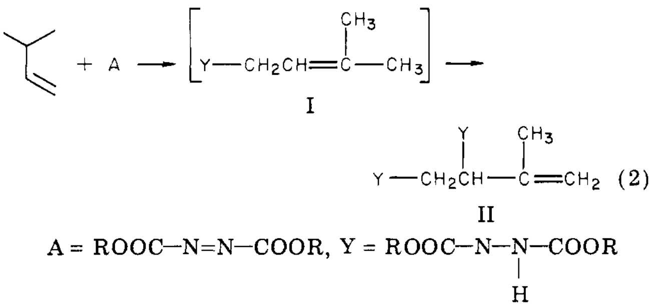


**Figure 2.** TGA thermograms for IAD-modified [21.2% (w/w), by elemental analysis] and unmodified 1,4-polybutadienes: (---) modified; (—) unmodified. Total weight loss by TGA, 22% (w/w); weight loss at 300 °C, 15% (w/w).

methyl-1-butene because its monoadduct (I) has six primary allylic hydrogens, while the starting olefin has only one inaccessible tertiary hydrogen (eq 2).



A = ROOC—N=N—COOR, Y = $\mathrm{ROOC{-}N{-}\underset{\displaystyle H}{\underset{|}{N}}{-}COOR}$

The presence of diadducts in the model compounds was of interest to us because it raised the possibility of blocky placement of the hydrazoester groups in the polymer systems.

**Polymer Backbone Structure and Reactivity.** Modification efficiency (ME), i.e., the ratio (IAD incorporated)/(IAD charged), is a good measure of the reactivity of IAD with the various polybutadiene backbones. ME is an empirical concept with a meaning similar to that of grafting efficiency (GE), used to characterize graft copolymerization. It can be seen in Table II that it takes about 5 times as long for the 1,2 backbones to reach a high modification level as does the trans or cis 1,4 substrates. Thus, the relative reactivity of the 1,4- and 1,2-polybutadienes with IAD seems to parallel the relative reactivity of the various isomeric monoolefins, as well as the qualitative order developed recently for the cyclic triazolinediones with 1,4 and 1,2 polymers.[12]

We have also studied the relative reactivities of the retroene IAD reactions with 1,4 and 1,2 backbones by use of thermogravimetric analysis (TGA). Figure 1 shows the TGA's for the base 1,2 polymer and an IAD-modified 1,2 polymer. Evidence for the retroene reaction is a TGA weight loss [22% (w/w)] corresponding to the amount of hydrazoester group present in the polymer [25.4% (w/w) by N analysis]. Similarly, a 1,4 backbone modified with 21.2% functionality released 22% of its weight upon heating (Figure 2).

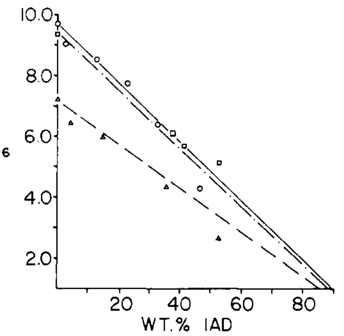


**Figure 3.** Plot of $M_n^{-1}$ vs. wt % IAD for the modification of high 1,4(mixed *cis,trans*)-, high 1,4(*cis*)-, and high 1,2-polybutadienes: (---) calculated for the high-1,2 polymer; (-•-) calculated for the high-1,4 (mixed cis,trans) polymer; (—) calculated for the high-1,4 (cis) polymer. Experimental values: (▲) high-1,2 polymer; (□) high-1,4 (mixed cis,trans) polymer; (○) high-1,4 (cis) polymer.

The mass spectra of the modified and unmodified polymers, as well as the mass spectrum of IAD, were run to further prove that the azo compound is the species eliminated from the IAD-modified polymers upon heating. The modified and unmodified polymers were heated ≥350 °C in the mass spectrometer. The spectra of the modified polymers and of IAD itself showed $m/e$ values of 204 (parent + 2) and 162 (loss of $CH(CH_3){=}CH_2$). The mass spectra of the unmodified polymers did not show such peaks.

It is interesting to note that the retroene reaction (weight loss) occurs at a lower temperature for the 1,4 adduct than for the 1,2-modified macromolecules. For example, the 1,4 backbone exhibits a 15% weight loss at 300 °C (Figure 2); the 1,2 backbone shows only a 8% weight loss at 300 °C (Figure 1). Thus, it would appear that the energy of activation of the retroene process, as well as the forward ene reaction, is lower for the 1,4 backbone than for the 1,2 base polymer.

**Osmometry/GPC Studies.** Evidence for polymer modification comes from $\bar{M}_n$(osmometry)/composition data. If the azoester modification of 1,4- and 1,2-polybutadienes is a simple "add-on" procedure, the molecular weight of the modified polymer should follow eq 3, where $M_n$(YPBD) is the molecular weight of the modified poly-

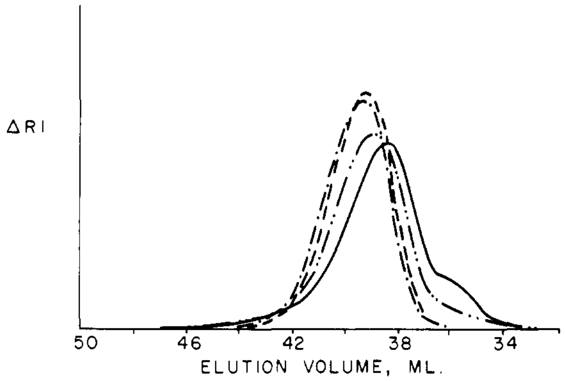


**Figure 4.** GPC traces for IAD-modified 1,2-polybutadienes: (---) base polymer; (-·-) polymer containing 4.2% (w/w) IAD; (-··) polymer containing 14.8% (w/w) IAD; (—) polymer containing 52.4% (w/w) IAD.

mer, $M_n$(PBD) is the molecular weight of the polybutadiene backbone, and $F$ is the weight fraction of IAD incorporated.

$$M_n(\mathrm{YPBD}) = \frac{1}{1-F} M_n(\mathrm{PBD}) \qquad (3)$$

A close correspondence between experimental and calculated $\bar{M}_n$'s is generally accepted as conclusive proof for modification or grafting, as well as for the absence of backbone scission or cross-linking.[17,18] Most of the previous workers[3,8,11,12] who studied the ene modifications of polymers have assumed that these reactions are free of backbone cross-linking or scission. Others[5] have questioned these beliefs. In all cases, direct proof, such as outlined above, was lacking.

Figure 3 shows $\bar{M}_n^{-1}$ vs. wt % IAD plots for the modification of high 1,4(*cis,trans*)-, high 1,4(*cis*)-, and high 1,2-polybutadienes. The experimental molecular weights have been determined by osmometry. There is generally good agreement between experimental $\bar{M}_n$'s and calculated values over most of the range studied. This result is consistent with our observation that the modified polymers are soluble and not cross-linked.

However, close inspection of Figure 3 reveals some subtle but measurable other effects. For example, there is some discernible scatter in the molecular weight data above 40% (w/w) modifications. This result suggests that some small concomitant molecular weight changes are occurring during modification. Although there is nothing unusual in the GPC traces of modified 1,4 polymers, there are exceptional features in the traces of the 1,2 adducts. In fact, a high molecular weight shoulder develops in the case of the high-1,2 polymer after extensive modification (Figure 4). The $\bar{M}_n$(GPC) of this shoulder is approximately twice the molecular weight of the majority of the modified polymer chains. As a control experiment, the high-1,2 polymer was heated at 80 °C for 122 h in the absence of IAD. The polymer MWD, after heating (1.20), was not higher than that before heating (1.21).

We interpret these results by the involvement of two concurrent and competitive mechanisms, concerted and free radical. The major pathway for the reaction would lead to a simple "add-on" product via a cyclic transition state and the minor route would result in coupling via free-radical intermediates. The 1,2 backbone is expected to be more prone to stepwise radical reaction than the 1,4 backbone because the former is less reactive in the ene process and requires more severe conditions (e.g., longer times) to effect reaction. Furthermore, vinyl polymers are generally more prone to radical reactions than 1,4 polymers.

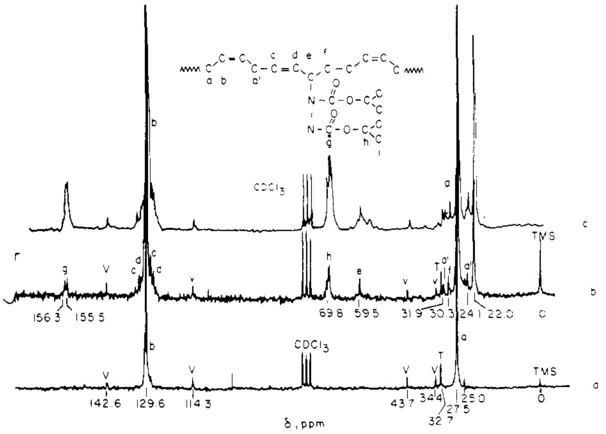


**Figure 5.** $^{13}C\{^1H\}$ FT NMR spectra at 25.15 MHz of a 95% 1,4(*cis*)-polybutadiene modified with the hydrazodicarboxylate group: (a) 0 mol %, 500 scans; (b) 7.9 mol %, 1000 scans; (c) 23.3 mol %, 20 000 scans. Spectra were obtained with a pulse width of 19.2 s (70° tip angle) and a repetition time of 2.5 s. The longest $T_1$ is 4.6 s. $CDCl_3$ is the solvent.

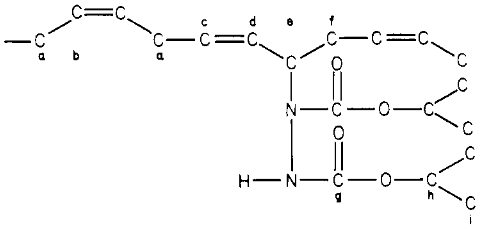
The indication of a small amount of radical products for the IAD modification (80 °C) of polydienes is particularly interesting because the reactions of ethyl azodicarboxylate with acyclic monoolefin model compounds at 80 °C show little, if any, free-radical character.[1] Nevertheless, free-radical intermediates have been implicated in the reaction of azoesters with cyclic olefins and sterically hindered alkylated dienes.[5,19]

**Infrared Spectral Studies.** Besides confirming the presence of the hydrazoester functionality in the modified polymers, infrared spectroscopy of modified 1,4 cis and 1,2 polymers has provided valuable clues concerning the modification process and products. For example, there is no apparent double-bond isomerization of the unmodified units after the modification of the high-1,4 cis polymer, as evidenced by the lack of change in the trans 1,4 absorption at 965 cm$^{-1}$.[20] There is also a hint of conjugation in the spectrum of the 1,4 cis adduct; there is a band at 1565 cm$^{-1}$ (lit., 1600 cm$^{-1}$).[20]

Important features of the IR spectra of the high-1,2 adducts are the diminution in the bands assigned to the vinyl unit (1645–1650, 1410, 909, 995, 672 cm$^{-1}$)[20] and the emergence of an absorption at 835 cm$^{-1}$. The latter band may be due, in part, to the presence of trisubstituted double bonds, >C=CH–, similar to those found in polyisoprene.[20] There is no indication of the presence of conjugation in the modified 1,2 polymers.

**$^{13}C$ NMR Studies.** $^{13}C$ NMR spectroscopy not only yields valuable structural information on hydrazodicarboxylate modified 1,4- and 1,2-polybutadienes but also provides information about the sequence distribution of this group. We have examined the $^{13}C$ NMR spectra of high-1,4 cis and high-1,2 adducts at low (7.9–9.2 mol %) and moderate (23.3–29.9 mol %) levels of modified repeat units. These spectra have been compared with those of the parent polymers.

**1,4(*cis*)-Polybutadiene Adduct.** The $^{13}C\{^1H\}$ spectra of the unmodified and two azoenophile-modified high 1,4(*cis*)-polybutadiene samples are shown in Figure 5. Shift positions in parts per million are referenced to $Me_4Si$. The base polymer (Figure 5a) is a high-1,4 cis polymer which has about 3% trans-1,4 units and 2% 1,2 units. The peaks of the 1,2 units are identified by "V" and those of the trans units by "T". The remaining peaks are designated by lower case letters and refer to structure III. The assignment of peaks was facilitated by using a gated decoupling technique which gives the nuclear Overhauser



III

enhancement (NOE) to the peak intensities but retains the couplings for identification purposes. The multiplet structures due to C–H couplings can thus be observed in the spectrum as if the protons were not being irradiated.

A comparison of the unmodified with the modified polymers in Figures 5b (7.9 mol %) and 5c (23.3 mol %) shows that the relative amounts of the trans-1,4 and 1,2 units remain unchanged; i.e., the reaction introduces no isomerization of unmodified units. In Figure 5b, the two large peaks, a and b, are due to the unmodified cis-1,4 units. All of the peaks expected for the unreacted three isomers are observed. The lack of cis–trans isomerization of the unmodified units of the high-1,4 cis polymer is consistent with the involvement of a cycloaddition reaction. Yet, cis,trans forms of the modified units are likely because carbons c and d appear to show four peaks.

Peaks h and i are confirmed as the methine and methyl carbons of the isopropyl groups, respectively, by their chemical shift positions and by their gated decoupling multiplet structures. In the gated decoupling experiment, peak h is split into a doublet and peak i into a quartet. Similarly, the two g-carbon peaks remain singlets and peak e becomes a doublet upon coupling. Resonances g and h predominantly consist of equal-intensity doublets, reflecting the slightly different environments of the two carbonyl or the two methine carbons, respectively. In addition, they both display shoulders on the downfield (left) side which might be due to hindered rotation of the bulky groups about the nitrogens.

The resonance associated with carbon e is assigned to 59.5 ppm. This is considerably downfield from the 50-ppm position expected for a carbon $\alpha$ to an aliphatic substituted secondary carbon.[21] This difference in chemical shift is attributed to the deshielding effect of the hydrazoester group.

Of the assembly of peaks grouped around the large cis peak at 27.5 ppm, only three cannot be unambiguously assigned without further verification. However, most probable assignments can be made. Approximate chemical shifts can be calculated by using additivity parameters.[22,23]

The resonance assigned to carbon e in Figure 5b appears at first glance to be a singlet, which suggests that the modifier group is going on the chain randomly. However, a closer look shows a shoulder on either side, suggesting tacticity, H–H, H–T, or sequence distribution. In other words, the IAD substitution seems to be occurring on the same or consecutive polybutadiene repeat units or in blocks. This result is similar to diadduct formation in the model compounds (vide supra). Since only 7.9% of the butadiene units in this sample has been modified, the probability of two of them being next to each other in a random process is only about 0.6%. This would be too small to detect.

The polymer in Figure 5c has had 23.3% of its units modified. The blockiness is very apparent in the resonance of carbon e now. Tacticity, H–H, H–T, and/or sequence distribution peaks are observed. For a random placement of these modified units, the probability of having adjacent modifier groups is only about 5%. The fraction showing tacticity structure is clearly much greater. Therefore, we conclude that the modifier groups are attached to the polymer chain in a nonrandom, blocky manner.

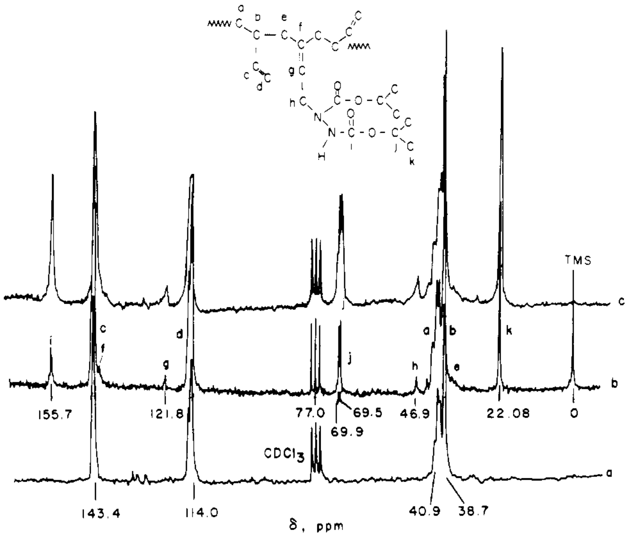
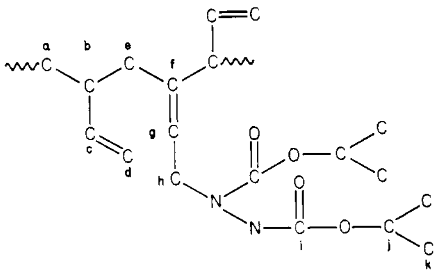


**Figure 6.** $^{13}C\{^1H\}$ FT NMR spectrum at 25.15 MHz of a 98% 1,2-polybutadiene modified with the hydrazodicarboxylate group: (a) 0 mol %, 1000 scans; (b) 9.2 mol %, 1000 scans; (c) 29.9 mol %, 20 000 scans. Instrument parameters were the same as in Figure 5.

Figure 6 shows the $^{13}C\{^1H\}$ NMR spectra of the base polymer and two levels of modification of a 98% 1,2-polybutadiene polymer. Figure 6a is the spectrum of the base polymer showing the large peaks of the 1,2 structure and the small peaks due to 1,4 units. Peak assignments are again given with lower case letters which refer to the carbons in structure IV. This is the most probable structure as deduced from the $^{13}C$ spectrum. Peak d displays the usual tacticity triad multiplet structure and peak a exhibits the tacticity tetrad multiplet structure of 1,2-polybutadiene.[24]



IV

Figure 6b is the spectrum of the polymer with 9.2% of its 1,2 units modified. Peaks i, j, and k are assigned, as in the cis polymer, to the carbonyl, the methine, and the methyl carbons, respectively, of the hydrazodicarboxylate group. Peaks i and j display essentially the same multiplet structure as in the high-cis polymer for the same reasons as stated above, although both peaks seem to indicate more freedom of motion of the modifier group than in the high-cis case.

By gated decoupling, it was revealed that peak f arises from a quaternary olefin carbon, peak g is due to a methine olefin carbon, and peak h is due to an aliphatic methylene carbon. The chemical shifts of peaks f and g are indicative of a substituted internal double bond, such as in 1,4-polyisoprene. The double bond is assigned to the position shown in the structure in Figure 6 because it is the most likely position from consideration of the reaction. Yet, the $^{13}C$ spectrum does not rule out the possibility that it might

Table III
Ultraviolet Spectral Features of Hydrazodicarboxylate Adducts

| backbone polydiene | wt % of IAD incorporated | $\lambda_{max}$[a] | $\epsilon_{max}$ |
|---|---|---|---|
| high 1,4 (cis) | 52.1 | 238 | 1400 |
| | | 276 | 74 |
| | | 287 | 51 |
| high 1,2 | 52.4 | 236 | 84 |

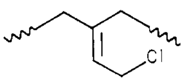
[a] In nanometers.

be located between carbons e and f. However, the use of additivity parameters[25] to calculate chemical shift tends to support the assigned structure.

Peak h was shown by gated decoupling to be a methylene carbon. Because of its low-field position, it is assigned to the carbon attached to the modifier group nitrogen as shown in the structure. If this structure is correct, peak h would have the possibility of being $\alpha$ to either a cis or a trans double bond. The component which is $\alpha$ to the cis bond would be buried under the large resonance at 40 ppm.

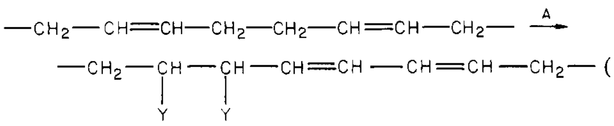
Figure 6c is the spectrum of a polymer having 29.9% of the 1,2 units modified. All of the peaks are broader than in Figure 6b, reflecting the reduced mobility of the polymer chains. However, there is no apparent evidence that the modifier group enters the chain in a blocky manner, as was the case for the high-cis polymer. If this were the case, several of the peaks, i.e., f, g, h, i, and j, would probably exhibit more complex resonance. Although these peaks are broader, they do not show additional structure.

We conclude from the $^{13}$C NMR data that the azodicarboxylate adds to the high 1,2-polybutadienes in a random manner; however, it adds to the high-1,4 cis polymer in a more blocky fashion. As expected for ene reactions, we find no isomerism of the unmodified units of 1,4-(*cis*)-polybutadiene upon modification, and the 1,2 backbone is isomerized from external to internal double bonds (structures III and IV). Incidently, there is analogy in the literature for the 1,2 product. Structures like V are known to be present in neoprene.[26]

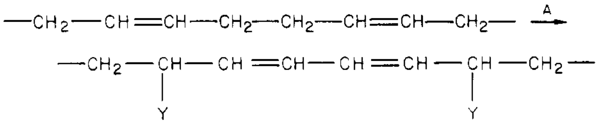


V

**UV Studies.** The $^{13}$C NMR data strongly indicate that the hydrazodicarboxylate adducts of 1,4-polybutadiene tend to be arranged in a blocky manner. Even more convincing evidence for the blockiness of the 1,4 adducts comes from UV data. Since the azodicarboxylate modification of olefins results in a shifting of olefin double bonds, it is reasonable to assume that a blocky modification of polydienes would result in the shifting of some double bonds into positions of conjugation, as illustrated in eq 4 and 5.



$$-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2}- \xrightarrow{A} -\mathrm{CH_2}-\underset{\mathrm{Y}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{Y}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2}- \quad (4)$$



$$-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2}- \xrightarrow{A} -\mathrm{CH_2}-\underset{\mathrm{Y}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH}-\underset{\mathrm{Y}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}- \quad (5)$$

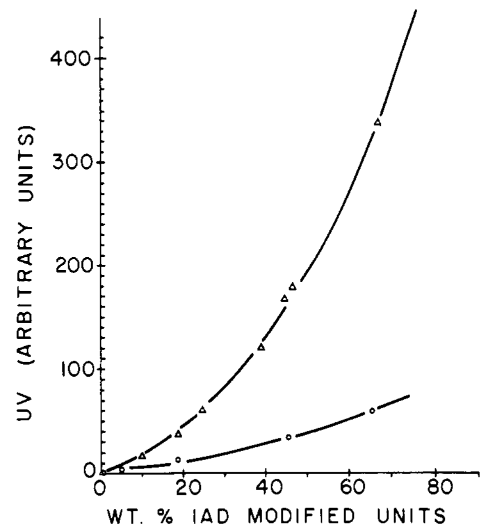


**Figure 7.** UV absorbance (arbitrary units) measured at 254 nm by a UV detector attached to a Waters 200 gel peremation chromatograph (GPC): (△) 1,4 cis; (○) 1,2.

Indeed, this expectation is borne out by our UV results (Table III). The 1,4-polydiene derivative exhibits not only more UV absorptions but also a $\lambda_{max}$ with a substantially higher $\epsilon_{max}$ than in the case of the 1,2 adduct. More significantly, the amount of UV activity (which could arise from the presence of the hydrazo moieties and/or conjugation) increases nonlinearly with increasing levels of hydrazo-modified repeat units in the 1,4 polymer. In contrast, the UV activity of the 1,2 adduct varies almost linearly with increasing levels of modification (Figure 7). These conditions are consistent with the development of conjugation and blockiness in the 1,4 backbone and little or none in the 1,2 backbone. Of course, once conjugation is present in the 1,4 polymer, Diels–Alder products, as well as ene multiple adducts, may also be part of the blocky structure.

As mentioned earlier, the infrared spectra of the 1,4 adducts also show hints of conjugated double-bond absorptions (vide supra). Thus, the present weight of $^{13}$C NMR, UV, and IR evidence favors a blocky arrangement for hydrazoester-substituted 1,4-polydienes and a more random placement of hydrazo units in the 1,2 polymer case.

Blocky modifications of 1,4-polydienes are rare but not without precedent. Cameron[27-30] reported that *p*-toluenesulfenyl chloride adds to 1,4-polydienes in a blocky or regioselective rather than a random fashion.

Since sequence distribution in the polymers is expected to be related to diadduct/monoadduct distribution in the model monoolefins, a comparison between polymer and model compounds is also appropriate here. Interestingly, 3-methyl-1-butene, the model for the 1,2 polymer, shows a greater tendency toward diadduct formation than 2-butene, the 1,4 model.[1] However, inspection of molecular models shows that the monoadduct of the 1,2 polymer backbone (IV) is much more sterically hindered than the monoadduct of the 1,2 model or the monoadduct of the 1,4 backbone (III). Consequently, di(multi)adducts or blocks should not form as easily with the 1,2 backbone as with the 1,2 model or the 1,4 polymer.

**$T_g$ Studies.** One would expect that increasing levels of IAD substitution would tend to raise polymer $T_g$'s because of the increase in inter- and intramolecular forces and chain stiffness. We see this result in the DTA's of the modified 1,4 and 1,2 polymers (Figures 8 and 9).

However, the thermal transitions for the modified 1,4 backbones are not nearly as sharp as those of the modified 1,2 backbones. In fact, the $T_g$'s for the 1,4 backbone broaden with increasing substitution until there is the apparent emergence of two polymer $T_g$'s. Two $T_g$'s are

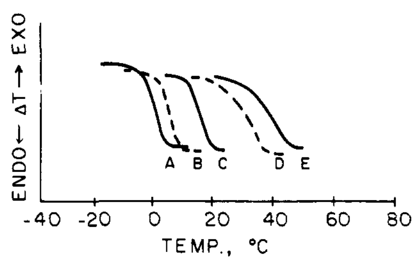


**Figure 8.** DTA traces of IAD-modified high-vinyl (1,2) polybutadiene. Mole percent IAD repeat units: (A) 0; (B) 4.2; (C) 9.2; (D) 15.0; (E) 29.9.

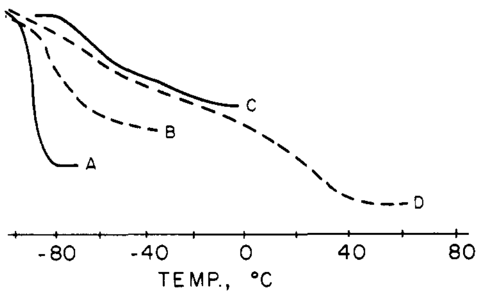


**Figure 9.** DTA traces of IAD-modified high 1,4(*cis,trans*)-polybutadiene. Mole percent IAD repeat units: (A) 0; (B) 4.8; (C) 14.6; (D) 37.0.

recorded for all 1,4 backbones, i.e., high-1,4 cis, high-1,4 trans, and high-1,4 (mixed cis,trans) (Table IV).

These DTA data are consistent with the presence of microphase separation and a blocky placement of modified repeat units in the case of the 1,4 backbones and a more random distribution of such units in the 1,2 backbones. Interestingly, two $T_g$'s were not observed for the triazolinedione modification of 1,4-polybutadiene or 1,4-polyisoprene. However, the DSC's for the triazolinedione-modified 1,4 homopolymers were not evaluated beyond the 8-10 mol % modification level.[12] We also fail to see two $T_g$'s at such low modification levels of IAD repeat units (Table IV).

Even more persuasive evidence for microphase separation and a blocky arrangement of the hydrazoester groups in the case of the 1,4 backbones and a more random placement in the 1,2 backbone comes from application of the Gordon-Taylor-Wood (GTW) treatment of glass transition temperatures.[31,32]

According to GTW, the glass transition temperature of a *random* copolymer should equal some weighted average of the individual glass transitions of the homopolymers, $T_{g_1}$ and $T_{g_2}$. The weighting factor is designed to include the weight concentrations, $C_1$ and $C_2$, and constants $A_1$ and $A_2$. For a binary random copolymer the relationship is shown in eq 6. Convenient forms of this equation are

$$A_1C_1(T_g - T_{g_1}) + A_2C_2(T_g - T_{g_2}) = 0 \qquad (6)$$

shown in eq 7 and 8, where $k$ is the slope of a $T_g$ vs.

$$T_g = k(T_{g_2} - T_g)C_2/(1 - C_2) + T_{g_1} \qquad (7)$$

$$T_g = (-1/k)(T_g - T_{g_1})(1 - C_2)/C_2 + T_{g_2} \qquad (8)$$

$(T_{g_2} - T_g)C_2/(1 - C_2)$ plot with $T_{g_1}$ as the intercept and $-1/k$ is the slope of a $T_g$ vs. $(T_g - T_{g_1})(1 - C_2)/C_2$ plot with $T_{g_2}$ as the intercept.

Since we did not know the $T_g$ of the 100%-modified polymer, we used the eq 8 form of GTW. Figure 10 shows the determination of $k$ to be 2.2 and the extrapolated $T_{g_1}$ for 100%-modified high-vinyl backbone to be 41 °C. It was possible, by using these values, to obtain a good fit between theory and experiment for the range of polymers studied (Figure 11). Therefore, the IAD modification of 1,2-polybutadienes must be essentially random.

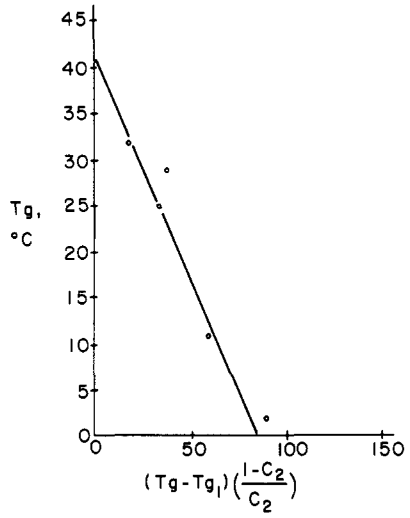


**Figure 10.** Plot of $T_g$ vs. $(T_g - T_{g_1})[(1 - C_2)/C_2]$ to determine the GTW $k$ value. $k = 2.2$.

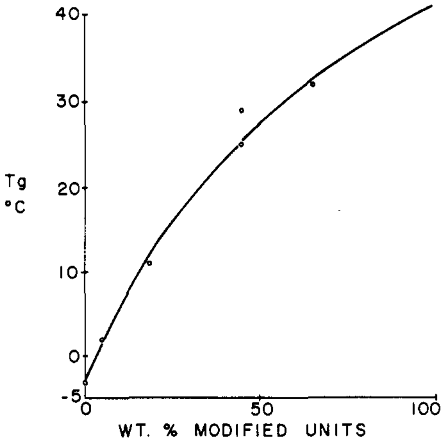


**Figure 11.** GTW plot of $T_g$ vs. wt % IAD-modified repeat units: (—) calculated GTW curve; (○) experimental points.

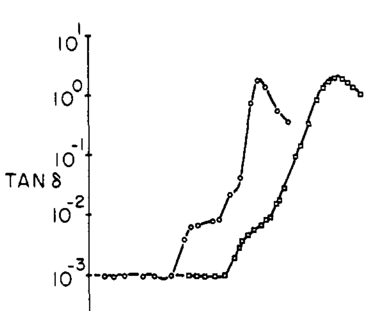


**Figure 12.** tan δ vs. temperature curves measured on the Rheovibron from -90 to +150 °C at 110 Hz for 1,2-polybutadiene (○) and 1,2-polybutadiene containing 30 mol % IAD-modified repeat units (□).

The situation is quite different for the 1,4 backbone, however. The IAD modification of the 1,4 backbone failed to correlate with GTW. In fact, a GTW-type $k$ value could not be determined. Thus, the modified 1,4 polymer must be nonrandom or blocky.

**Dynamic Thermomechanical Measurements.** Corroborative evidence for single-phase morphology in the case of IAD-modified 1,2 backbones and the development of multiphase morphology with the modified 1,4 backbones

Table IV
DTA Data

| mol % modified repeat unit | 1st $T_g$ onset, °C | 1st $T_g$ midpt, °C | 1st $T_g$ end pt, °C | $T_m$ | 2nd $T_g$ onset, °C | 2nd $T_g$ midpt, °C | 2nd $T_g$ end pt, °C |
|---|---|---|---|---|---|---|---|
| High-Vinyl Backbone | | | | | | | |
| 0.0 | −0.5 | 3 | +5 | | | | |
| 4.7 | 10 | 15.5 | 21 | | | | |
| 9.2 | 17 | 22 | 27 | | | none detectable | |
| 15.1 | 29 | 33 | 37 | | | | |
| 29.9 | 32 | 39 | 46 | | | | |
| High-1,4 (mixed cis,trans) Backbone | | | | | | | |
| 0.0 | −95 | 91.5 | −88 | | | | |
| 2.3 | −92 | −87.5 | −83 | | | | |
| 4.8 | −89 | −79 | −69 | | | | |
| 6.5 | −86 | −73.5 | −61 | | | | |
| 11.36 | −79 | −66.5 | −54 | | | 2nd $T_g$ developing | |
| 15.6 | −73 | −64 | −55 | | −26 | −17 | −8 |
| 36.9 | −81 | −75 | −69 | | 14 | 25.5 | 37 |
| High-1,4 (Cis) Backbone | | | | | | | |
| 0.0 | −108 | −103.5 | −99 | −11 | | | |
| 0.6 | −104 | −100 | −96 | −20 | | | |
| 3.2 | −103 | −96.5 | −90 | | | | |
| 7.9 | −100 | −87.5 | −75 | | | | |
| 12.8 | −96 | −87 | −78 | | −39 | −26.5 | −14 |
| 23.3 | −87 | −73 | −59 | | −7 | +5 | +17 |
| 29.2 | −85 | −72 | −59 | | −7 | +5 | +17 |
| High-1,4 (Trans) Backbone | | | | | | | |
| 0.0 | −88 | −84 | −80 | 32 | | | |
| 2.3 | −83 | −76.5 | −69 | 36 | | | |
| 7.5 | −78 | −71.5 | −65 | 10 | | | |
| 12.8 | −73 | −63 | −53 | | −35 | −24 | −13 |
| 17.42 | −71 | −62.5 | −54 | | −26 | −16.5 | −7 |

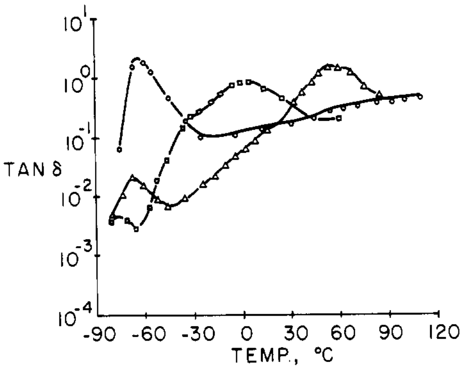


**Figure 13.** tan δ vs. temperature curves measured on the Rheovibron from −90 to +150 °C at 110 Hz for 1,4(*cis,trans*)-polybutadiene (○) and the 1,4-polybutadiene containing 15 mol % (□) and 37 mol % (△) IAD-modified repeat units.

comes from dynamic thermomechanical measurements. The temperature profile for the loss tangents of modified 1,2 and 1,4 backbones is shown in Figures 12 and 13. The modified 1,2 polymer shows a simple shift of tan δ after modification consistent with a simple increase in polymer $T_g$. Also, the breadths of the loss peaks for modified and unmodified 1,2 backbones are not appreciably different.

In contrast, the loss tangent for the modified 1,4 substrate shows a general broadening of the loss peak upon modification; this suggests an increasing number and type of relaxation processes in the branched polymers. Furthermore, at very high levels of modification of the 1,4 substrate, there is an apparent development of two tan δ peaks or two separate $T_g$'s.

## Conclusions

This paper reveals salient structure–reactivity and structure–property relationships for the isopropyl azodicarboxylate (IAD) modification of high 1,4(*cis*)-, 1,4-(*trans*)-, 1,4(mixed *cis,trans*)-, and 1,2-polybutadienes. For example, we have learned that both the forward ene reaction and the retroene process are more facile for the 1,4 backbone than for the 1,2 substrate. Consistent with an ene cycloaddition mechanism, the IAD reaction with 1,4-(*cis*)- polybutadiene involves no cis–trans isomerization of the unmodified units, and the IAD modification of 1,2-polybutadiene involves isomerization of vinyl units to internal double bonds. It has also been found that the IAD reactions on polydienes are essentially simple add-on processes. However, there is evidence for some free-radical leakage, especially in the case of the 1,2 substrates.

$^{13}$C NMR, IR, and UV spectral data indicate that 1,4 and 1,2 adducts differ in sequence distribution. Whereas the 1,2 products exhibit an essentially random distribution of functionality, the modified 1,4 polymers evince blocky character. A Gordon–Taylor–Wood (GTW) analysis of the glass transition temperatures of the modified polymers confirms the randomness of the 1,2 adduct and the blockiness of the 1,4 material. Moreover, supermolecular data by DTA and dynamic thermomechanical measurements indicate single-phase morphology for the modified 1,2-polybutadienes and multiphase morphology for the modified 1,4-polybutadienes.

We surmise that the hydrazoester monoadducts of the 1,4 backbone associate in nonpolar media with the incoming IAD molecules and encourage a blocky arrangement of substitutents along the 1,4 chain. In contrast, the monoadduct of the 1,2 substrate is so sterically hindered that blocky placement cannot be accommodated.

The unique structural and morphological features of the IAD-modified 1,4-polybutadienes result in important physical property advantages for these materials. They exhibit both high green (uncured) strength and tack (autoadhesion). These results will be reported elsewhere.[33]

**Acknowledgment.** We thank Professor G. B. Butler for sharing one of his manuscripts prior to its publication. Also, appreciation is extended to Professor H. J. Harwood for helpful discussions and to M. Hayes, C. Earle, and E. Galloway for experimental assistance. In addition, we thank The Firestone Tire & Rubber Co. for permission to publish this work.

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# Conformational Behavior of Poly(*N*-vinylimidazole). Potentiometric Titration, Viscosity, and Proton Nuclear Magnetic Resonance Studies

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ABSTRACT: The effect of protonation on the conformation of poly(*N*-vinylimidazole) was studied by potentiometry, viscometry, and $^1$H NMR spectroscopy. The polymer coil contracts during the initial stages of protonation but then expands upon further protonation. The conformational changes are discussed in terms of competition between an internal hydrogen bonding between protonated and nonprotonated rings and charge repulsion. The initial contraction requires that the hydrogen bonding involves non-nearest-neighbor imidazole rings.

The catalytic properties of imidazole-containing polymers have interested a number of workers.[1] Some of these polymers show unusual specificity to the substrate in their catalytic action and so have been considered as possible models for enzymes.[2] Several of these polymers also bind metals very strongly[3-5] and, in that sense, might be analogous to the metal-containing enzymes, where the imidazole group is found in the histidyl residue.

It is believed that the conformations of imidazole-containing polymers play an important role in their catalytic behavior.[6] The ability to form complexes with transition-metal ions also presumably depends on the ability of the polymer to assume a conformation which facilitates chelation. Nevertheless, relatively few details of the conformational behavior of poly(*N*-vinylimidazole) have been investigated.[7]

Information about the conformation of ionizable polymers in solution is often obtained from potentiometry and viscosity measurements.[8-11] Such methods are useful in drawing conclusions about whether the overall conformation of the polymer is extended or contracted, and changes in conformation induced by changes in pH, ionic strength, and temperature, for example, can often be detected. Details about the nature of the conformation or conformational transitions at a local level are much more difficult to obtain.

NMR spectroscopy has been a powerful tool for the determination of conformations of small molecules[12] and has the potential for giving information about the local conformation of polymers.[13] It was our hope that, by combining potentiometric titration, viscosity, and NMR techniques, we could obtain a more complete conformational description of poly(*N*-vinylimidazole) than with any single method. Even if the NMR chemical shift and coupling parameters could not be precisely interpreted in terms of the polymer conformation, the fact that they are

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