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Chemical Reactions on Polymers. II. Modification of Diene Polymers with Triazolinediones via the Ene Reaction

Koon-Wah Leong[a]; George B. Butler[a]
[a] Department of Chemistry and Center for Macromolecular Science, University of Florida, Gainesville, Florida

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Chemical Reactions on Polymers. II. Modification of Diene Polymers with Triazolinediones via the Ene Reaction

KOON-WAH LEONG and GEORGE B. BUTLER

Department of Chemistry
and Center for Macromolecular Science
University of Florida
Gainesville, Florida 32611

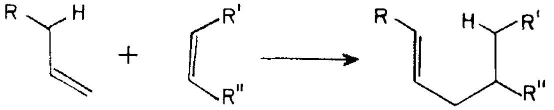
ABSTRACT

A wide variety of polymers and copolymers of 1,3-dienes have been modified at low temperatures via the ene reaction with 4-substituted 1,2,4-triazoline-3,5-diones. The resulting modified polymers were characterized via infrared spectroscopy, nuclear magnetic resonance, intrinsic viscosity, gel-permeation chromatography, differential scanning calorimetry, solubility tests, and tensile measurements. Physical properties measurements support the postulate that the highly polar pendant urazole groups contribute intermolecular and intramolecular hydrogen-bonding interactions and thus impart to the modified polymers thermoplastic elastomer properties. Changes in the solubility character, thermal behavior, and tensile properties of the modified polymers are in accord with this postulate. Since the association between molecules is physical in nature, the modified polymers remain soluble in appropriate solvents. They also show dramatic decreases in molecular size; for example, the average molecular size of polymers at 1% modification is about one tenth that of the unmodified polymer due to intramolecular interactions, a size reduction of the same order of magnitude as that of chemically crosslinked polymers. Poly-1,2-butadiene, when modified to the

extent of 5%, gave values for elongation to break, Young's modulus, and tensile strength twice those for the parent polymer, while tensile recoveries were > 90%.

INTRODUCTION

Ene reactions have been known in the organic literature for some time [1]. Basically, the ene reaction involves an olefin having active allylic hydrogens and an enophile which is relatively electron deficient [Eq. (1)].



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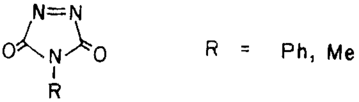
During the reaction, a bond is formed between the enophile and the olefin, which is accompanied by abstraction of an allylic hydrogen by the enophile from the olefin. The mechanism can be stepwise, involving a 1,4-polar intermediate or can be concerted in a double suprafacial or antarafacial manner. We wish to discuss some of our investigations on the modification of diene polymers via the ene reaction.

The enophiles we have been using are 4-substituted 1,2,4-triazoline-3,5-diones (I). The substituents for this study were phenyl and methyl



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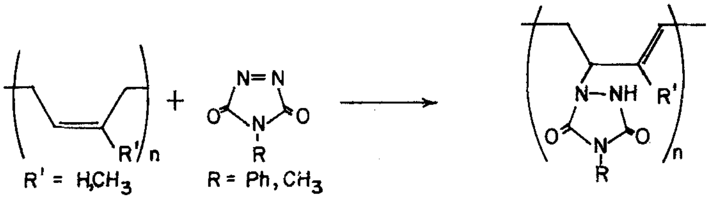
groups, and for convenience we designate the former as PhTD and the latter as MeTD. Both triazolinediones are known to be very reactive dienophiles as well as enophiles. PhTD has been known to have 10^4 times the reactivity of conventional olefins in its thermal reaction with allylic systems. The syntheses of triazolinediones are very simple and were first reported by Thiele [2] in 1894. All triazolinediones have a characteristic red color which disappears after the completion of the ene reaction.

The polymeric olefins we chose for our study are block copolymers of styrene-butadiene (SBS) and styrene-isoprene (SI), random copolymers of styrene-butadiene (S/B) and acrylonitrile-butadiene (A/B), and homopolymers of cis-trans-butadiene (B), 1,2-butadiene (1,2-B), and cis-isoprene (I). We propose that by modifying the amorphous diene polymers or polymer segments, introducing some intra- and intermolecular interaction, a broad range of properties can be obtained. In the case of triazolinedione-modified polymers, the products contain urazole pendant groups which are capable of undergoing intermolecular hydrogen bonding [Eq. (2)]. Changes in the solubility character, thermal behavior, and tensile properties of the modified polymers are expected. Since the association between molecules is physical in nature, the modified products should remain soluble in appropriate solvents. This certainly has the advantage over chemical crosslinks in situations where soluble polymers are derived.



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EXPERIMENTAL

Materials

Styrene-butadiene ABA block copolymers, 25% styrene (SBS) and styrene-butadiene random copolymer, 23% styrene (S/B) were obtained from Scientific Polymer Products, Inc. Styrene-isoprene block copolymer, 15% styrene (SI) and poly-cis-isoprene, (I) were obtained from Cellomer Associates, Inc. Polybutadiene, cis- and trans-B was obtained from Aldrich Chemical Co., Inc. Poly(acrylonitrile-co-butadiene) with 45% acrylonitrile (A/B) was obtained from Polysciences, Inc. Poly-1,2-butadiene with 93.5% vinyl (1,2-B) was obtained from Firestone. The chemicals and solvents were reagent grade and were used without further purification.

Synthesis

The syntheses of 4-phenyl-1,2,4-triazoline-3,5-dione (PhTD) and 4-methyl-1,2,4-triazoline-3,5-dione (MeTD) have been reported previously [3] and will not be described here. The modification reaction on the olefinic polymers will be described in some detail.

TABLE 1. Some Modification Conditions

Polymer	Reaction solvent	Nonsolvent used in precipitation
SBS	Benzene	Ethanol
SI	Benzene	Ethanol
B	CH_2Cl_2	Ethanol
I	CH_2Cl_2	Acetone
1,2-B	Benzene	Ethanol
S/B	Benzene	Ethanol
A/B	CH_2Cl_2	Ethanol

Modification of Olefinic Polymers

A sample of 1.00 g of polymer was dissolved in 20 ml of dry benzene. The mixture was stirred very slowly until a clear solution was obtained. Triazolinedione, dissolved in 20 ml of benzene, was added to the polymer solution very quickly at room temperature. The reaction mixture was allowed to stand overnight (~ 10 hr) after the red color had faded. The modified polymer was recovered by precipitation into 200 ml of 95% ethanol containing 0.5% 2,6-di-tert-butyl-4-methylphenol (BHT), and then dried in a vacuum desiccator for 24 hr. In the case of B, I, and A/B polymers, dichloromethane was used as the reaction solvent. The amount of triazoline dione used was expressed as a certain percentage of the total unsaturation in the olefinic polymer or polymer segments; in fact, simply in terms of the butadiene or isoprene content in the polymer. Some modification conditions are listed in Table 1.

Characterization of the Modified Polymers

The polymers were characterized via infrared spectroscopy (IR), nuclear magnetic resonance (NMR), measurement of intrinsic viscosity $[\eta]$, gel-permeation chromatography (GPC), differential scanning calorimetry (DSC), solubility tests, and tensile measurements.

Infrared Spectra (IR). IR was primarily used as a qualitative tool to demonstrate the molecular association through hydrogen bonding. Spectra were taken from thin polymer films cast from a 20% polymer solution. The solvent was evaporated in a vacuum desiccator at room temperature for 48 hr. No absorption bands due to residual solvent were observed in the IR spectra. In cases where the products were too brittle, samples in KBr pellets were used.

Nuclear Magnetic Resonance (NMR). NMR spectra were used to determine quantitatively the amount of triazolinedione incorporated into the polymer. The phenyl signal from PhTD and the methyl signal from MeTD are very distinct from those of the parent polymer. Therefore, the extent of modification was obtained by comparing the ratio of the signal from the urazole pendant groups to those of the main chain protons. Solvents for NMR spectra were mainly $CDCl_3$ and DMSO-d_6. Tetramethylsilane (TMS) was used as the internal standard.

Viscosity. The intrinsic viscosity $[\eta]$ of the polymers was determined by means of an Ubbelohde viscometer in reagent-grade benzene or chloroform at 30°C. The original concentration of all the polymer samples was made up to 0.500 g/dl. The intrinsic viscosity was extrapolated from four additional concentrations, obtained by diluting the original solution.

Gel-Permeation Chromatography (GPC). Gel permeation chromatography measurements were made at room temperature (25°C) on a Water Associates ALC/GPC-201 instrument equipped with a differential refractometer and a Model 440 absorbance detector. μ-Styragel columns were calibrated with narrow molecular weight distribution polystyrene samples of known molecular sizes. Approximately 0.10% (w/w) polymer solutions in dichloromethane were used. In all the measurements, the flow rate was set at 1.0 ml/min.

Differential Scanning Calorimetry (DSC). The thermal behavior of the modified polymers was studied by using the Perkin-Elmer DSC-1B model. Samples, approximately 10 mg each, were prepared directly from the dried samples, and the temperature range scanned was from 185°K to 325°K for T_g measurements and 310°K to 490°K for measurements of softening temperature T_s, and decomposition temperature T_d. All measurements were made at heating and cooling rates of 10°C/min. The first value of all T_g measurements was discarded. The recorded T_g values were actual averages of the second and third consecutive measurements. The T_g was defined as the initial point of deviation from the base line. The softening temperatures and decomposition temperatures were defined as the point of maximum excursion of the endotherm or exotherm from the base line.

Solubility Tests. A few milligrams of the polymer samples were added to 1 ml of solvent. The mixture was agitated periodically for 30 min at room temperature. When a clear solution resulted after 30 min, the polymer was recorded to be soluble in that solvent. When the polymer remained insoluble or became swollen in the solvent, the mixture was allowed to stand overnight and re-examined. Appearance of swollen fragments was taken as insolubility. The solvents used in solubility tests were benzene, chloroform, dichloromethane, DMF, DMSO, pyridine, and 10% aqueous NaOH solution.

Tensile Measurements. In the tensile measurements, 4-g samples were dissolved in 400 ml of solvent. The solutions were poured into 9-in. by 9-in. Teflon-coated pans. The solvent was evaporated over a 3-day period, and the resulting polymer films were removed and placed in a vacuum oven at 40°C overnight. Samples (1/2 in. × 1.5 in.) were cut from each film, and the thickness of each sample was measured prior to testing. In general, five measurements were made for sample thickness, elongation to break, Young's modulus, and tensile strength. Three measurements were made for tensile recovery and stress decay. All samples were extended at a rate of 20 in./min. Samples were extended at 20 in./min to half their elongation to break and held there for 1.5 min to measure stress decays. The samples were then returned to zero stress level to measure tensile recoveries. Tensile measurements were performed by Dr. K. Wagener at the American Enka Corp., Enka, N. C.

RESULTS AND DISCUSSION

In general, the ene reaction is so fast that the rate cannot be measured by usual methods such as UV absorption technique. But in the case of A/B copolymer, the rate is very slow. In this copolymer, the acrylonitrile content is 45% and so the steric effect caused by the acrylonitrile units is enough to hinder the approach of the triazolinedione molecules. The reaction rate at 25°C in CH_2Cl_2 was found to be second-order overall. The rate constant K_2 was found to be 1.2×10^{-4} liter/mole-sec for PhTD and 5.8×10^{-5} liter/mole-sec for MeTD.

The relative rate of reaction for PhTD is faster than MeTD. The reactivity of various polymers toward triazolinedione modification can be qualitatively compared in terms of the length of time elapsed for the red triazolinedione color to fade completely. The data are shown in Table 2.

Evidence of Intra- and Intermolecular Association in Polymers Modified with PhTD and MeTD

Infrared Spectroscopy. IR spectra for reacted and unreacted SBS samples are shown in Figs. 1a and 1b. The absorption bands associated with the urazole substituents and their functionality assignments are listed in Table 3. The presence of urazole groups was confirmed by the carbonyl stretching frequencies which appear as very strong bands at 1770 cm^{-1} and 1700 cm^{-1}. The evidence of hydrogen bonding was confirmed by the bonded N–H stretching band around 3190 cm^{-1} and N–H bending band around 1490 cm^{-1}.

In the case of modified poly-cis-isoprene (I), two N–H stretching absorption bands can be observed. One is due to the free N–H

TABLE 2. Relative Reactivity of Different Polymers

Polymer[a]	Solvent	Time for completion[b]
SBS	Benzene	Instantaneous
SI	Benzene	Instantaneous
B	CH_2Cl_2	1 min
I	CH_2Cl_2	Instantaneous
1,2-B	Benzene	1-2 hr
S/B	Benzene	5 min
A/B	CH_2Cl_2	6 hr

[a] 5% solution.
[b] 1% modification.

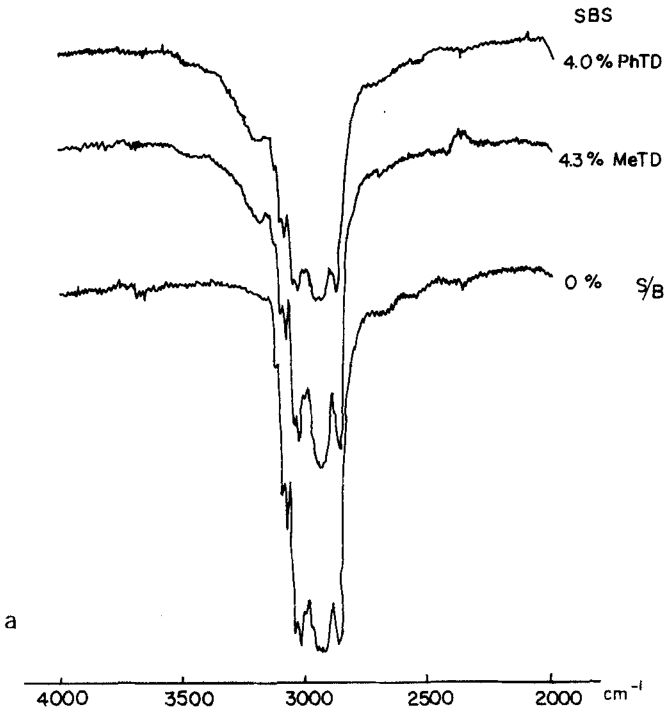


FIG. 1a. Infrared spectra of unmodified and modified SBS samples.

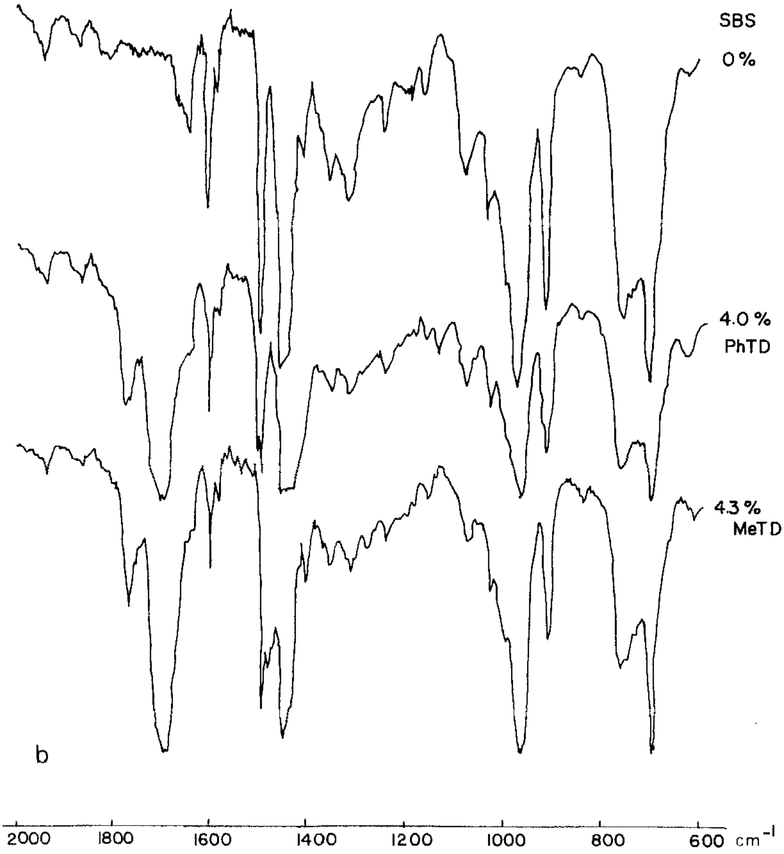


FIG. 1b. Infrared spectra of unmodified and modified SBS samples.

TABLE 3. IR Data from Modified SBS Polymer

	IR band (cm^{-1})[a]			
	SBS-4.0%	PhTD	SBS-4.3%	MeTD
N–H stretching	3190	(m)	3180	(m)
N–H bending	1490	(m)	1480	(s)
C=O stretching	1770	(m)	1770	(m)
	1700	(s)	1700	(s)

[a] Intensity: w = weak, m = medium, s = strong.

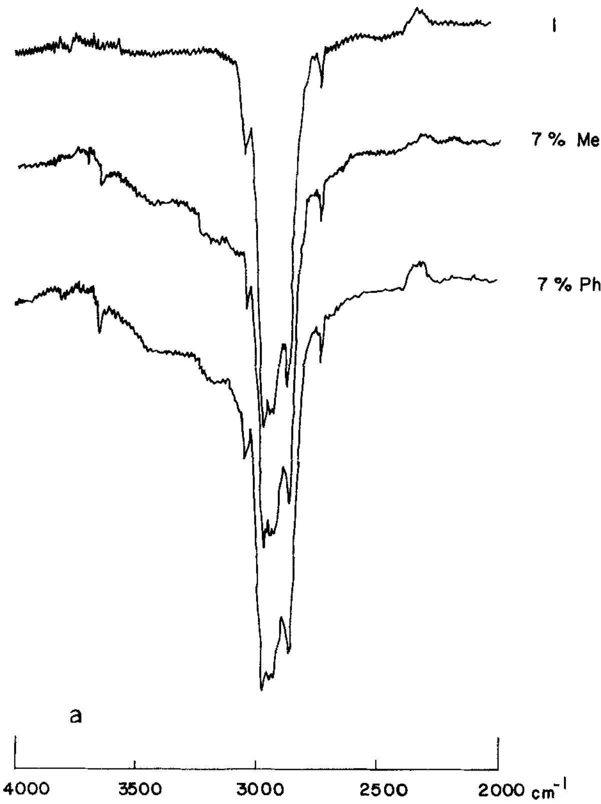


FIG. 2a. Infrared spectra of unmodified and modified I samples.

stretching band which occurs around 3400 cm^{-1}, and the other bonded N–H stretching band at 3170 cm^{-1}. Some of the urazole groups might be physically too far apart to facilitate effective hydrogen bonding. The IR spectra are shown in Figs. 2a and 2b, and the absorption band assignments are shown in Table 4.

In the SBS polymer samples, the styrene segments are already associated into a plastic phase and this tends to pull the butadiene segments closer to one another, thus enhancing the hydrogen bonding through urazole groups. That is why the free N–H stretching band is not present in modified SBS polymers. On the other hand, when the concentration of urazole groups is high, for example when the extent of modification exceeds 50%, more factors have to be considered. The steric effects and conformational changes due to the presence of urazole pendant groups might increase or reduce the effective intermolecular association. For instance, when poly-cis-isoprene (I)

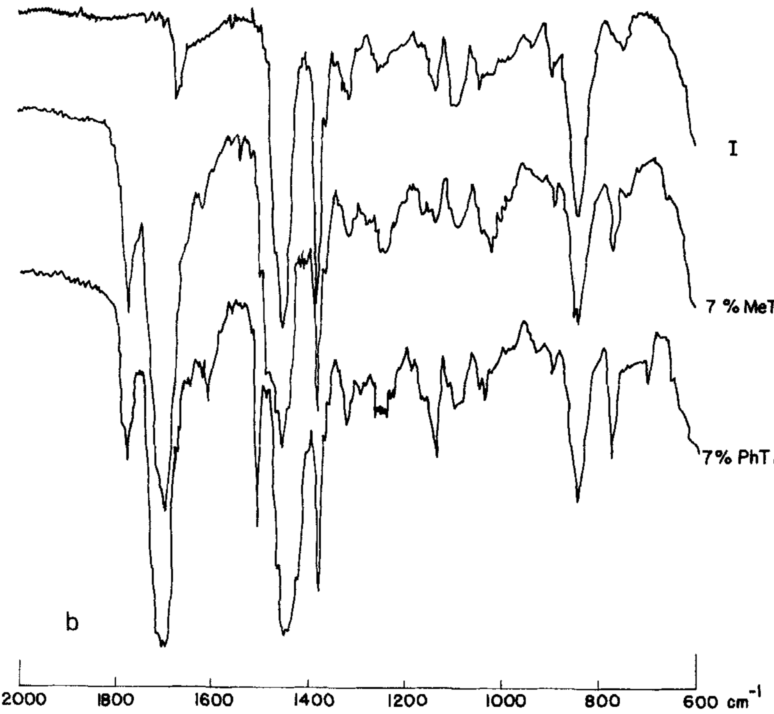


FIG. 2b. Infrared spectra of unmodified and modified I samples.

TABLE 4. IR Data from Modified I Polymer

	IR band (cm^{-1})			
	I - 7%	PhTD	I - 7%	MeTD
N–H stretching (free)	3400	(m)	3440	(m)
N–H stretching (bonded)	3180	(m)	3170	(m)
N–H Bending	1490	(w)	1480	(m)
C=O stretching	1770	(m)	1770	(m)
	1700	(s)	1700	(s)

FIG. 3a. Infrared spectra of I at 50% modification.

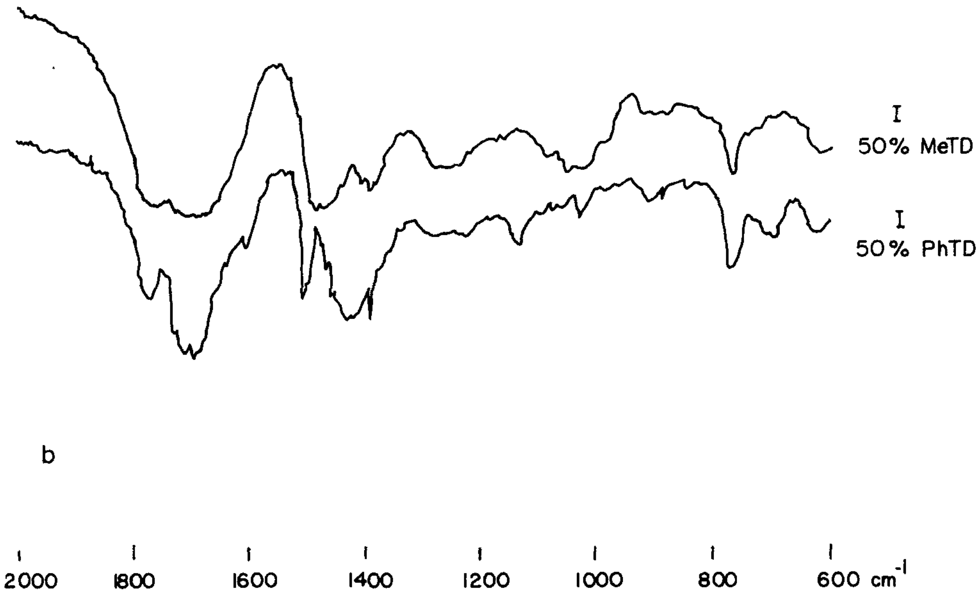
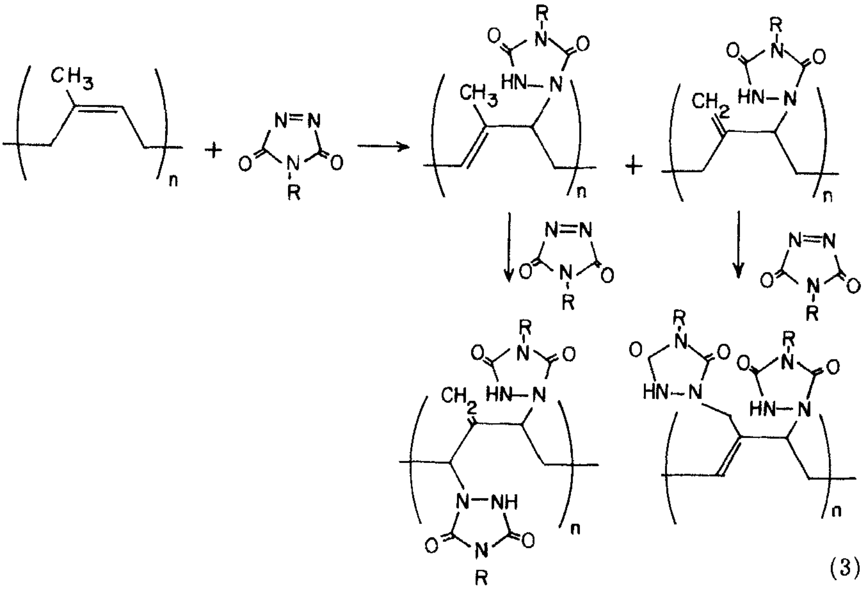


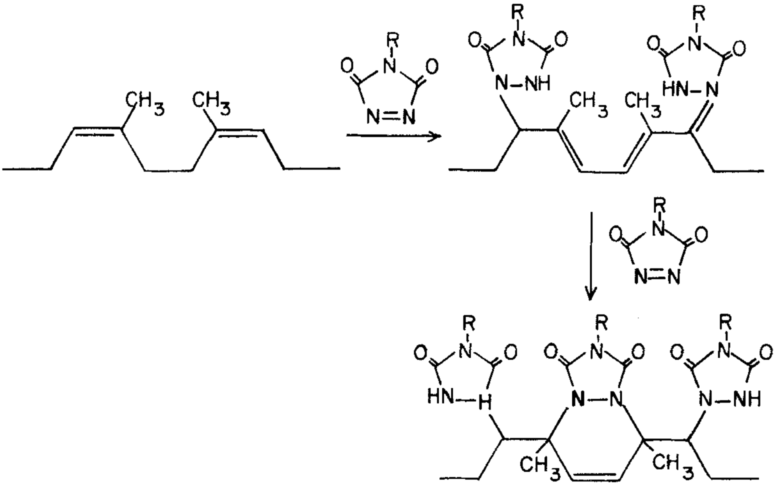
FIG. 3b. Infrared spectra of I at 50% modification.

has undergone 50% modification with PhTD and MeTD, the product becomes very brittle, and the IR spectra (KBr pellets) show very broad absorption bands as illustrated in Figs. 3a and 3b. The ratio of free N–H to bonded N–H is approximately 1:1.

NMR Analysis. The NMR technique is not very accurate in determining the extent of modification. From NMR integration, an actual 4.0% PhTD feed gave only 3.3% modification on the SBS polymer. The spectra of modified I were very complicated to interpret. There are several possible products that can be obtained in the modification reaction, and they are shown in Eq. (3). The second ene reaction is generally slow and might not occur at all. On the other hand, if these were head-to-head isoprene units in the polymer chain, a second triazolinedione molecule could add onto the conjugated ene product via the Diels Alder (4 + 2) reaction as shown in Eq. (4). This could generate a very complicated NMR spectrum. In fact, the NMR spectra are very complicated as shown in Fig. 4. Therefore, elemental analysis of the nitrogen content should be used to determine the actual amount of urazole pendent groups incorporated into the modified polymer. This was examined [4], and the average incorporation of urazole groups was found to be 90% of the triazolinedione feed.



Viscosity Measurement. The intrinsic viscosity $[\eta]$ of modified polymers was plotted against the triazolinedione incorporation. The plots are shown in Figs. 5-9. In general, a significant decrease in $[\eta]$ is recognizable even at 1% modification. This is due



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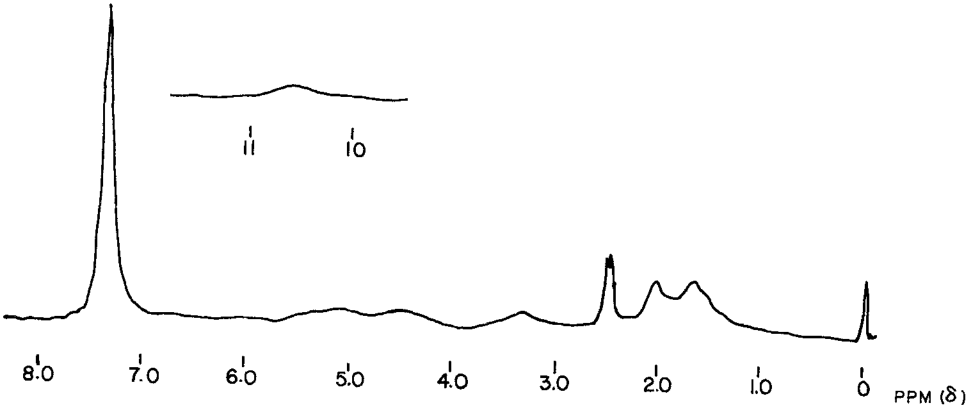

FIG. 4. NMR spectrum of I 100% modified with PhTD. Solvent: DMSO-d_6).

to the intramolecular interaction between the urazole pendant groups. The modified polymer chains became tightly coiled and decreased in molecular size, when dissolved in nonassociating solvent such as benzene and chloroform. A comparison of $[\eta]$ between the unmodified polymer and the modified polymer at 1% and 5% modification is shown in Tables 5 and 6, respectively. Diethylamine is a fairly strong base, as well as a very polar solvent. Theoretically, it can break up the hydrogen bonding between urazole groups. In the absence of intramolecular interaction, the modified polymer should have a higher

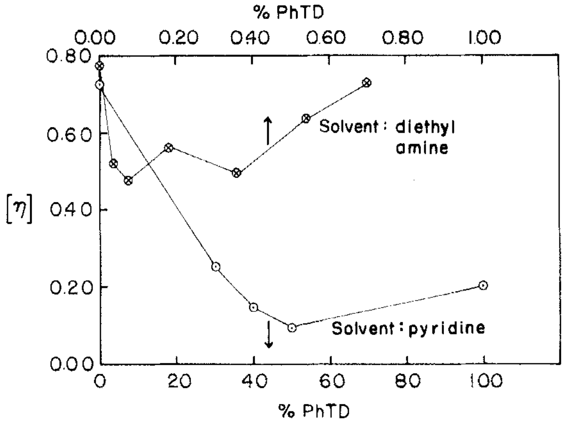

FIG. 5. Intrinsic viscosity plot of styrene/butadiene (SBS) block copolymer modified with PhTD (31.2°C).

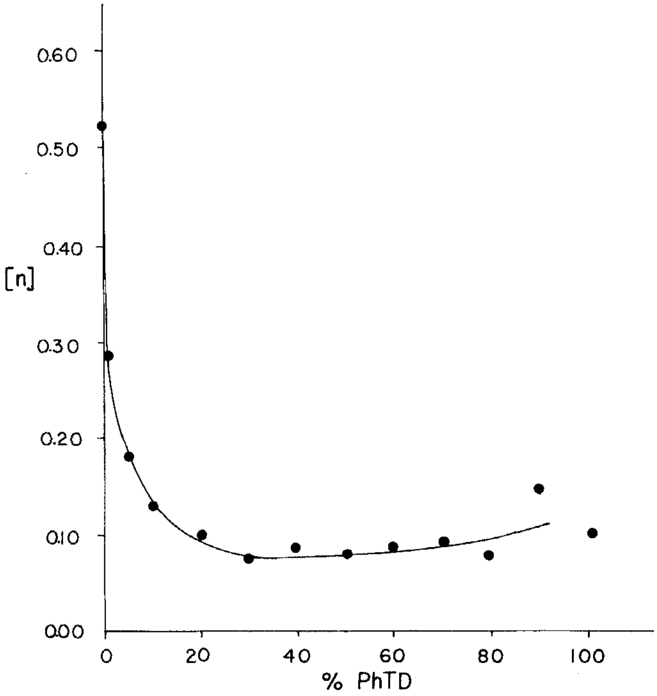

FIG. 6. Intrinsic viscosity plot of SI modified with PhTD. Solvent: pyridine.

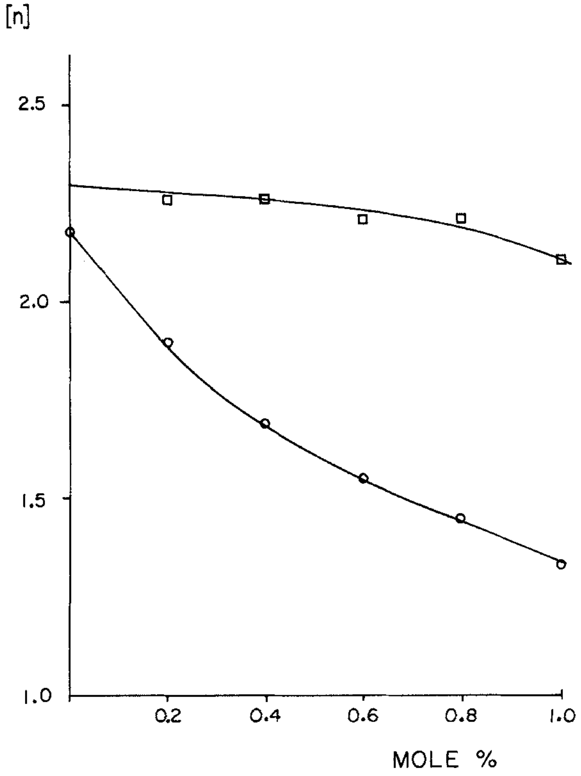

FIG. 7. Intrinsic viscosity plot of B modified with PhTD (○) and (□) MeTD. Solvent: benzene.

intrinsic viscosity value due to the increase in molecular weight. The experimental results shown in Table 6 indicate that even in diethylamine, the [η] of 5% PhTD modified SBS is lower than that of unmodified SBS polymer.

In most cases, the intrinsic viscosity decreases to a much lower value with an increase in triazolinedione addition. In the cases of SBS and S/B, where the polymer systems were already associated through physical interaction between polymer blocks, little change in [η] was observed at low degree of modification. The styrene segments interact with each other via hydrophobic interaction, even in dilute solution. As a result, the effect due to a small amount of hydrogen bonding becomes insignificant.

The hydrogen-bonding character of phenyl- and methylurazole groups can be observed through the [η] data. In general, the phenylurazole groups cause slightly larger decreases in [η] than the methyl

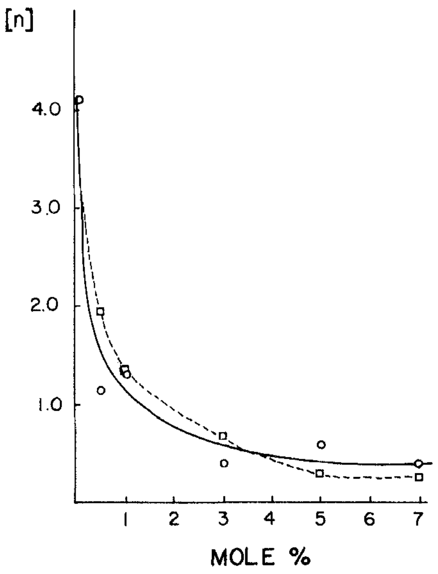

FIG. 8. Intrinsic viscosity plot of I modified with (—○) PhTD and (- - □) MeTD. Solvent: $CHCl_3$.

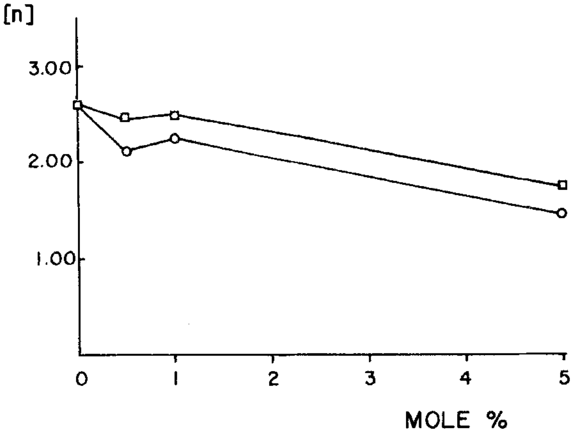

FIG. 9. Intrinsic viscosity plot of S/B modified with (○) PhTD and (□) MeTD. Solvent: benzene.

TABLE 5. Intrinsic Viscosity Data of Various Modified Polymers at 1% Modification

		$[\eta]$		
Polymer	Solvent	Unmodified	With PhTD	With MeTD
SBS	Benzene	1.05	1.07	1.05
SI	Pyridine	0.53	0.28	
B	Benzene	2.18	1.33	2.09
I	Chloroform	4.10	1.31	1.36
S/B	Benzene	2.60	2.25	2.50

TABLE 6. Intrinsic Viscosity Data of Various Modified Polymers at 5% Modification

		$[\eta]$		
Polymer	Solvent	Unmodified	With PhTD	With MeTD
SBS	Diethylamine	0.78	0.64	
SI	Pyridine	0.53	0.19	
I	Chloroform	4.10	0.60	0.30
S/B	Benzene	2.60	1.47	1.75

derivatives. This implies that the hydrogen-bonding tendency is stronger in phenylurazole than methylurazole. The phenyl groups are capable of undergoing hydrophobic interaction with one another and this would enhance the intramolecular H-bonding effect.

Gel-Permeation Chromatography. In GPC, molecules are separated according to their hydrodynamic volumes. The relationship is represented by Flory's viscosity equation:

$$\Phi_0 V_n = [\eta] M = K V_r$$

where V_n is hydrodynamic volume, Φ_0 is a universal constant = 2.8 × 10^{21}, $[\eta]$ is intrinsic viscosity, M is molecular weight, V_r is the retention volume or elution volume, and K is a constant.

Since V_n is proportional to V_r, any change in the hydrodynamic

TABLE 7. GPC Data of Modified Polymers Expressed in MW[a]

	Molecular size as MW		
Polymer	Unmodified	1% PhTD added	1% MeTD added
SBS	224,000	178,000	148,000
SI	29,500	2,510	2,510
B	126,000	14,800	22,400
I	74,100	7,940	9,330
1,2-B	196,000	200,000	132,000
S/B	66,100	56,200	41,700
A/B	1,122,000	794,300	63,100

[a] All measurements were done in CH_2Cl_2 at room temperature, 25° C, and the MW values were calibrated against polystyrene standards of narrow MWD.

TABLE 8. GPC Data of Modified Polymers Expressed in V_n[a]

	Molecular size as Vn (Å)		
Polymer	Unmodified	1% PhTD added	1% MeTD added
SBS	4,677	4,467	3,631
SI	708	63	63
B	3,162	355	537
I	1,778	178	224
1,2-B	5,129	5,623[b]	3,388[b]
S/B	1,995	1,413	1,000
A/B	26,920	19,050	1,349

[a] At 5% modification, molecular size of 1,2-B is reduced to 2399 Å with PhTD and 2690 Å with MeTD.

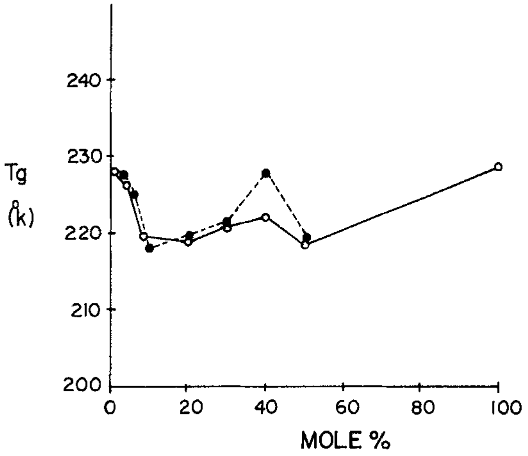

FIG. 10. Glass transition temperature plot of SBS modified with (○) PhTD and (●) MeTD.

volume due to intramolecular interaction would result in increase or decrease of retention volume in GPC. As the urazole pendant groups form hydrogen bonds within the polymer molecule, the hydrodynamic volume in nonprotic solvent should decrease, resulting in increase in retention volume, V_r. In fact, this behavior is observed among all polymer samples modified with PhTD and MeTD. Some of the typical data are listed in Table 7 in which the apparent GPC molecular weights are used in comparison. If we express the retention volume in terms of molecular size (in Å), we can get a better feeling of the size reduction due to intramolecular hydrogen bonding effect of the urazole pendant groups. The data are shown in Table 8. A very dramatic change in molecular size can be observed in the case of SI, B, I, and A/B polymers. The average size of polymers at 1% modification due to intramolecular interaction is about ten times smaller than the parent unmodified polymers. This magnitude of size reduction is comparable to that of chemically crosslinked polymer systems.

Differential Scanning Calorimetry. Any changes in the molecular association forces would be reflected in the glass transition temperature T_g and melting temperature T_m of the polymer, although the former is more sensitive to those changes. The increase in intra- or intermolecular interaction, in fact, imposes a higher energy barrier to the free rotation of the polymer chain and decreases its free volume, resulting in increase in T_g value. In general, this is true among the polymer samples modified with PhTD and MeTD. Specifically,

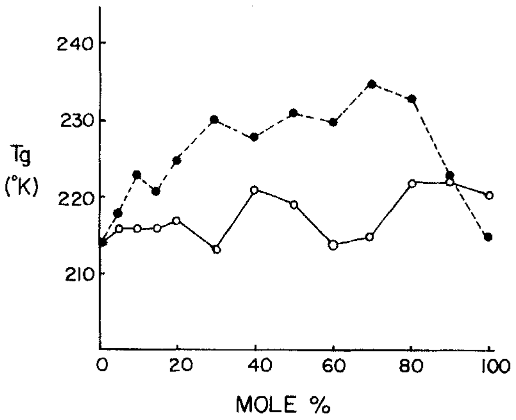

FIG. 11. Glass transition temperature plot of SI modified with (○) PhTD and (●) MeTD.

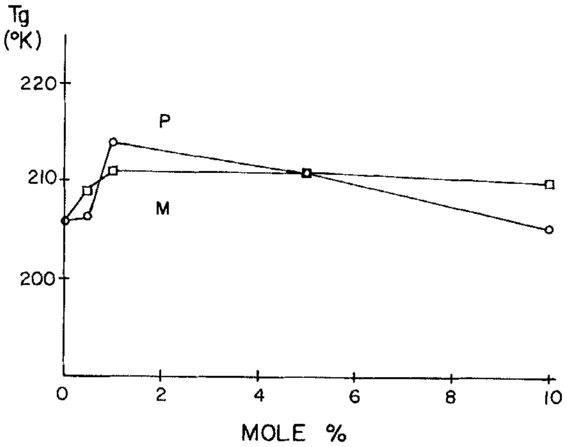

FIG. 12. Glass transition temperature plot of B modified with (○) PhTD and (□) MeTD.

the T_g of the olefinic polymer segments increases with the amount of urazole pendant groups present in the segments. Some of the data are shown in Figs. 10-15.

There are several interesting features among the T_g data. First of all, the T_g of S/B copolymer modified with PhTD and MeTD is split

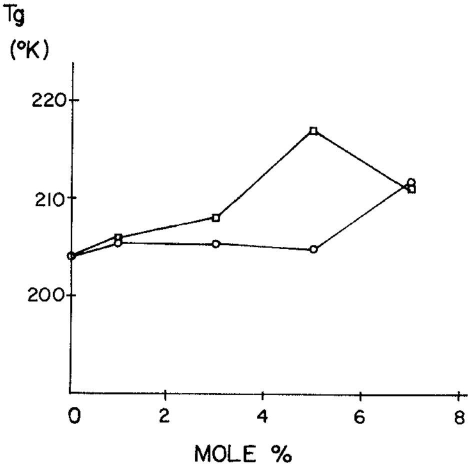

FIG. 13. Glass transition temperature plot of I modified with (○) PhTD and (□) MeTD.

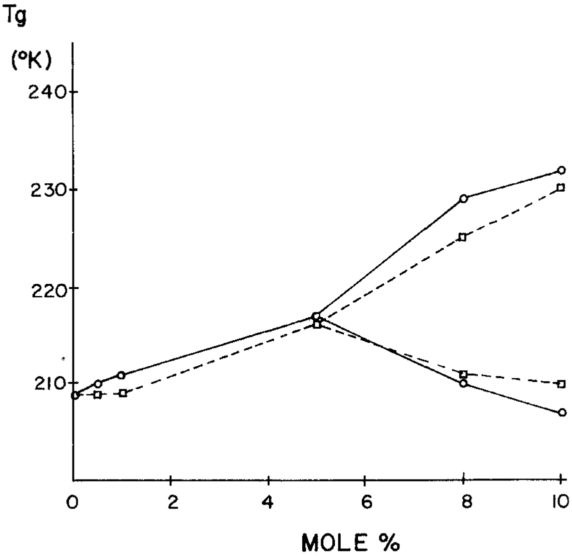

FIG. 14. Glass transition temperature plot of S/B modified with (○) PhTD and (□) MeTD.

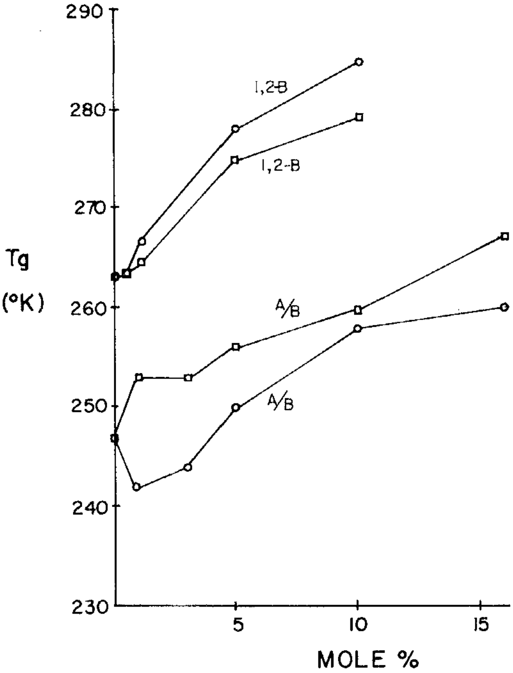

FIG. 15. Glass transition temperature plot of 1,2-B and A/B modified with (○) PhTD and (□) MeTD.

into two values when the extent of modification exceeds 5%. Secondly, the T_g of A/B copolymer decreases instead of increases with percent modification when the PhTD content is below 5%. In the case of S/B copolymer system, the styrene and the butadiene units are arranged in a random fashion. But they can be treated as a random distribution of small blocks of styrene and butadiene units. The reaction time of S/B copolymer with triazolinedione indicates that there exists some steric hindrance to the approach of the triazolinedione molecule onto the butadiene double bond due to adjacent styrene phenyl groups. In other words, the reaction is nonhomogeneous. The unmodified S/B segments might be so isolated from the rest of the modified S/B segments that they form a separate phase. This might account for the occurrence of two separate T_g values on the DSC thermogram. The upper value accounts for the modified segments whereas the lower one, the unmodified segments as shown in Fig. 14.

In the case of A/B copolymer system, the initial decrease in T_g can be explained in terms of changes in free volume of the polymer molecules. It is well known that the introduction of nonreactive

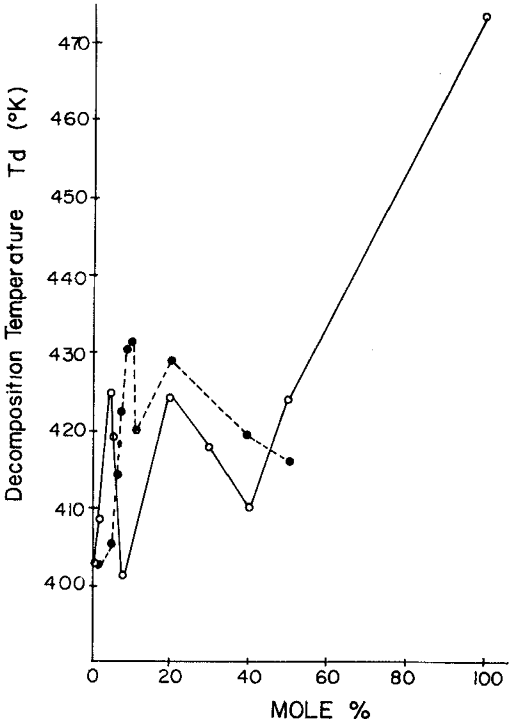

FIG. 16. Plot of decomposition temperature T_d for SBS modified with (○) PhTD and (●) MeTD.

branches or side chains would result in increase of free volume and subsequent decrease in T_g. Since at low modification the probability of one urazole pendant group interacting with another one is very low, the intramolecular interaction due to hydrogen bonding becomes negligible. Therefore, the increase in free volume due to the urazole side groups becomes significant, resulting in decrease in T_g value. As more and more urazole groups are added to the polymer chain, the probability of one urazole group interacting with another one increases. When the attractive forces due to intramolecular hydrogen bonding exceeds the repulsive forces due to presence of pendant groups, the T_g value would increase again. This expansion and contraction of free volume might account for the fluctuation in T_g values among the modified SBS and SI polymers shown in Figs. 10 and 11, respectively.

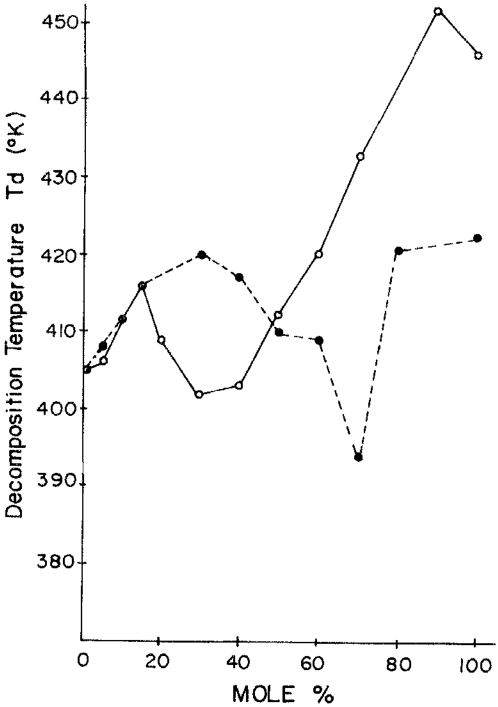

FIG. 17. Plot of decomposition temperature T_d for SI modified with (○) PhTD and (●) MeTD.

As we have mentioned before, T_m is not sensitive to molecular changes in amorphous polymer systems, but we noticed some effect on the decomposition temperature T_d (an exotherm) of the polymer samples as PhTD or MeTD was added. Some representative data are shown in Figs. 16-22. The decomposition pattern does not seem to follow any trend. At high degrees of modification, the urazole groups seem to provide additional thermal stability to the polymer, but at low modification, i. e., below 10% level, they have a destabilizing effect. The methylurazole groups appear to stabilize the I polymer but destabilize the B and 1,2-B polymers towards thermal decomposition. At low modification, the phenylurazole groups have destabilizing effects, whereas at high modification, they appear to stabilize the polymer. This peculiar behavior about the phenylurazole might be due to the increase in thermal oscillation during heating as a result of the presence of large phenyl rings. At low concentration, the hydrogen bonding of the phenylurazole groups can be overcome easily, since the strength of hydrogen bonding is only about 5 kcal/mole. At

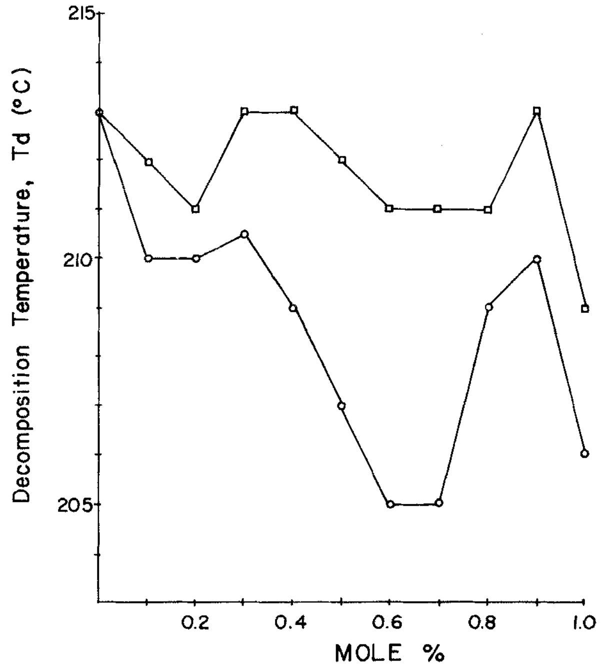

FIG. 18. Plot of decomposition temperature T_d for B modified with (○) PhTD and (□) MeTD.

high concentration, the hydrogen bonding as well as the hydrophobic interaction via the phenyl groups might develop enough strength to withstand the thermal stress. Of course, we are just speculating on the mode of action of the modifying groups, because thermal decomposition of polymer is a very complicated process. Each polymer system has to be studied separately. As the amount of polar groups increases, the polymer samples lose their thermoplastic properties, i. e., they fail to melt without undergoing decomposition. A summary of the degree of modification before thermoplasticity is adversely altered is shown in Table 9. It appears that MeTD can adversely affect the thermoplasticity to a greater degree than PhTD.

Solubility Tests. The effect of intermolecular forces is quantified by cohesive energy density or solubility parameter δ. Branching increases the solubility of high polymers, whereas polarity decreases it. In general, the introduction of polar groups into a polymer chain tends to decrease its solubility in the original solvent as strong polymer-polymer interaction develops. In our studies, the modified polymer samples precipitated out of the reaction solvent when the modification exceeded 10-20%. The strong hydrogen bonds formed by the urazole groups prevent the hydrating solvent molecules

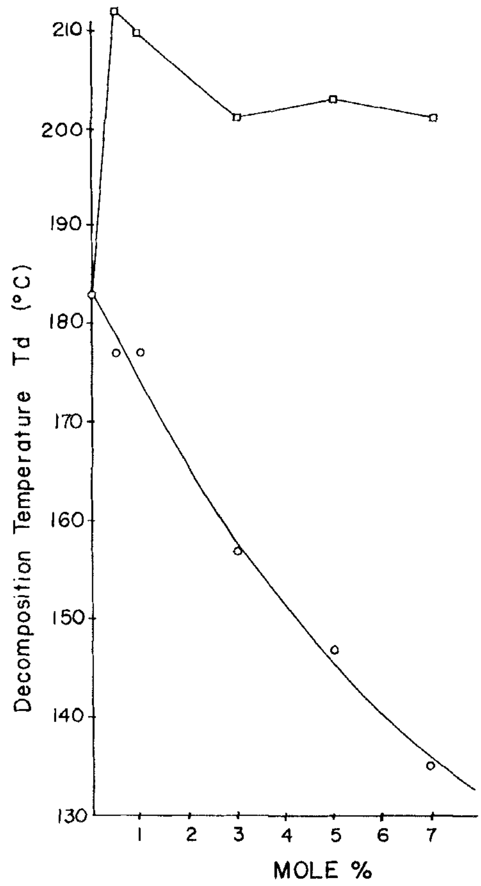

FIG. 19. Plot of decomposition temperature T_d for I modified with (○) PhTD and (□) MeTD.

from penetrating the polymer coils. The addition of more urazole pendant groups on the olefinic polymer leads first to solubility in organic and inorganic bases, which only swell the parent polymer, and then to water solubility. At higher degree of modification or triazolinedione addition, water solubility is accompanied by alcohol solubility, and then solubility in polar organic solvents such as DMF and DMSO. In other words, the solubility parameter of the polymer sample increases with increase in urazole content. Some of the typical solubility characteristics of the polymers modified with PhTD and MeTD are shown in Table 10. A sample of polybutadiene (B)

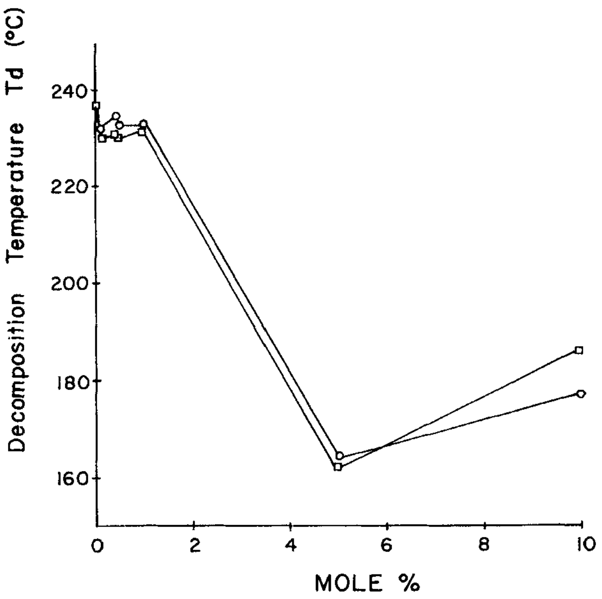

FIG. 20. Plot of decomposition temperature T_d for 1,2-B modified with (○) PhTD and (□) MeTD.

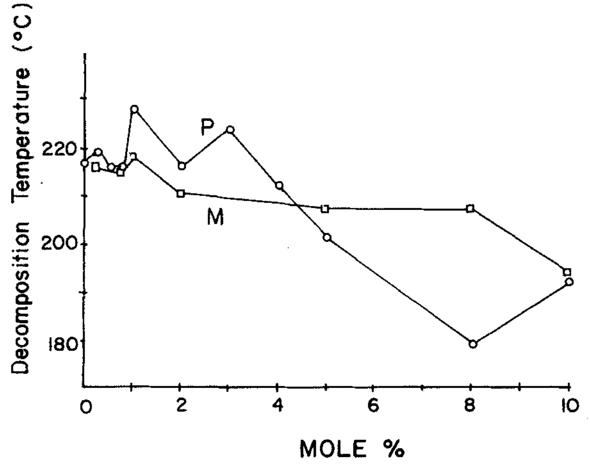

FIG. 21. Plot of decomposition temperature T_d for S/B modified with (○) PhTD and (□) MeTD.

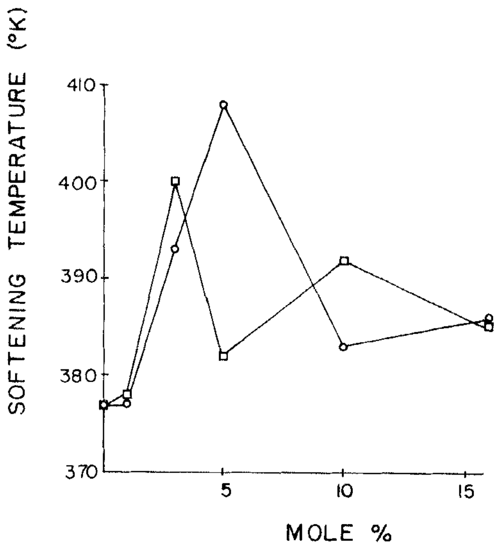

FIG. 22. Plot of softening temperature T_s for A/B modified with (○) PhTD and (□) MeTD.

TABLE 9. Maximum Percent Modification Allowed in Order to Retain Thermoplasticity

Polymer	% PhTD	% MeTD
SBS	1	1
SI	15	5
B	1	1
I	7	7
1,2-B	0.3	0.2
S/B	1	1
A/B	1	1

TABLE 10. Data Showing Maximum Modification for Polymer to Remain or Become Soluble in Various Solvents

		Maximum modification (%)					
Solvent	δ $(cal/cc)^{1/2}$	SBS	SI	I	B	1,2-B	S/B
Benzene	9.2						
$CHCl_3$	9.3	<20	<20	<10	<15	<15	<10
CH_2Cl_2	9.7						
Pyridine	10.7	0-100	0-100	>90			
DMF	12.1						
EtOH	12.7						
DMSO	12.9	>80	>70		$>45^{a}$		
Acetone	14.5						
H_2O	23.4						
10% NaOH		>40	>40	>40	$>45^{a,b}$		

[a] Reported by Williams [5].

[b] 0.8 M KOH used; modification > 60%, the samples are soluble in 1.0 M $NaHCO_3$.

was modified to 75% PhTD incorporation and converted to potassium salt. The salt is soluble in MeOH, DMF, DMSO, and H_2O. It has a decomposition maximum at 255°C and it is very brittle in nature.

Tensile Measurements. The Young's modulus data are not reliable, based on our methodology, but gross differences do have significance. The tensile data are shown in Table 11. The 1,2-B series (samples 20-24) best illustrates the effect of urazole pendent groups in the polymer. A 5.0% modification doubles the elongation to break, the Young's modulus, and tensile strength values. The tensile recoveries become greater than 90%, and the stress decay values become measurable.

In the B series (samples 7-11), the urazole groups appear to increase tensile strength, improve tensile recoveries, and reduce stress decays even at the 1% modification level.

The I series (samples 12-14, 18, 19) was difficult to work with and in every case either solubilization was never achieved or the films were weak and tacky.

No changes at all are noted for the A/B series (samples 15-17) as physical association already exists between the acrylonitrile units.

The SBS series (samples 1-3) and SI series (samples 4-6 and 25-27) are not particularly revealing as far as supplying evidence

TABLE 11. Tensile Data

Sample no.	Description	Casting solvent[a]	Sample thickness (mils)[b]	Elongation to break (%)[b,c]	Young's modulus (kg/cm^2)[b]	Tensile strength (kg/cm^2)[b,c]	Tensile recovery (%)[b]	Stress decay (%)[b,d]
1	SBS	Toluene	4.2 (0.3)	648 (30)	218 (95)	138 (37)	95 (0.2)	20 (2.7)
2[e]	SBS 1% PhTD	Toluene	3.8 (1.0)	879 (167)	758 (82)	77 (13)	87 (0.9)	45 (4.5)
3	SBS 1% MeTD	Toluene	4.1 (0.7)	794 (38)	1038 (142)	226 (52)	94 (0.2)	23 (0.2)
4	SI	Toluene	3.0 (0.4)	1245 (20)	25 (1.3)	234 (21)	97 (0.4)	15 (0.4)
5	SI 1% PhTD	Toluene	2.1 (0.4)	788 (46)	22 (1.8)	220 (1.3)	90 (1.4)	32 (0.9)
6	SI 1% MeTD	Toluene	3.2 (0.7)	1361 (48)	16 (2.4)	80 (7.1)	94 (0.4)	13 (0.5)
7	B	Toluene	1.3 (0.3)	1453 (167)	32 (2.0)	14 (0.7)	82 (2.2)	44 (1.1)
8	B 1% PhTD	Toluene	3.3 (0.5)	1782 (58)	22 (5.0)	28 (2.7)	88 (0.9)	28 (0.8)
9	B 1% MeTD	Toluene	3.0 (0.9)	1680 (216)	20 (43)	23 (3.9)	89 (0.5)	28 (1.4)
10	B 75% PhTD	Pyridine	Sample too brittle to test; wide angle x-ray photo shows polymer to be amorphous					
11	B 75% PhTD K salt	Water	Sample too brittle to test; wide-angle x-ray photo shows polymer to be amorphous					

12	I	Toluene	Unable to cast a useful film					
13	I 1% PhTD	Toluene	Unable to cast a useful film					
14	I 1% MeTD	Toluene	Unable to cast a useful film					
15	A/B	Chloroform	3.2 (0.3)	1124 (35)	62 (3.4)	39 (1.7)	64 (2.0)	40 (1.8)
16	A/B 1% PhTD	Chloroform	3.4 (0.2)	1286 (47)	61 (5.5)	27 (2.8)	66 (1.4)	39 (2.3)
17	A/B 1% MeTD	Chloroform	3.3 (0.3)	1028 (58)	69 (9.2)	36 (6.7)	63 (1.4)	38 (2.0)
18	I 5% PhTD	Chloroform	Unable to cast a useful film					
19	I 5% MeTD	Chloroform	Unable to cast a useful film					
20	1,2-B	Chloroform	3.3 (0.5)	136 (13)	46 (8.9)	97 (21.3)	f	f
21	1,2-B 0.5% MeTD	Chloroform	3.4 (0.3)	126 (8)	45 (3.4)	107 (9.7)	f	f
22	1,2-B 0.5% MeTD	Chloroform	3.2 (0.6)	150 (11)	40 (5.3)	111 (11)	f	f
23	1,2-B 5.0% PhTD	Chloroform	3.4 (0.1)	367 (17)	112 (3.0)	267 (32)	92 (0.5)	52 (1.0)
24	1,2-B 5% MeTD	Chloroform	3.2 (0.2)	394 (24)	96 (12)	229 (49)	93 (0.2)	43 (1.7)
25	SI 5.0% PhTD	Chloroform	3.8 (0.5)	650 (65)	59 (4.4)	82 (11)	76 (0.2)	61 (0.2)

(continued)

TABLE 11 (continued)

Sample no.	Description	Casting solvent[a]	Sample thickness (mils)[b]	Elongation to break (%)[b,c]	Young's modulus (kg/cm^2)[b]	Tensile strength (kg/cm^2)[b,c]	Tensile recovery (%)[b]	Stress decay (%)[b,d]
26	SI 5.0% MeTD	Chloroform	3.1 (0.2)	773 (52)	25 (2.7)	133 (14)	86 (0.4)	42 (0.3)
27	SI 15% PhTD	Chloroform	3.8 (0.5)	650 (65)	59 (4.4)	82 (11)	65	69

[a] In casting, 4g samples were dissolved in 400 ml of solvent (800 ml for samples 7, 8, and 9).

[b] Data in parentheses are standard deviations. Unless otherwise indicated, five measurements were made for sample thickness, elongation to break, Young's modulus, and tensile strength. Three measurements were made for tensile recovery and stress decay.

[c] Samples were extended at a rate of 20 in./min.

[d] Samples were extended at 20 in./min to half their elongation to break and held there for 1 and 0.5 min to measure stress decay. The sample was then returned to a zero stress level to measure tensile recovery.

[e] Fourteen measurements were made for sample thickness, elongation to break, Young's modulus, and tensile strength. Five measurements were made for tensile recovery and stress decay.

[f] Stress decay too high for measurement of tensile recovery; sample fractured in less than 1 min.

for intermolecular hydrogen bonding is concerned, but a phenomenon involving phase mixing can be recognized. The MeTD-modified samples are not much different from unmodified films, since unmodified samples are already physically associated by the styrene phase. Thus, a small increase in physical association by methylurazole groups might not be noticed in the tensile data. The PhTD-modified samples exhibit poorer tensile recoveries and increased stress decays, which could be manifestations of phase mixing or a perturbation of the phase interface. The increased phase mixing might be a result of the increased solubility of the phenyl substituent on the urazole ring in the styrene phase.

CONCLUSION

A relatively simple method to modify polydienes and copolymers of dienes has been developed. The modification reaction can be done at room temperatures or lower. The degree of modification can be controlled, almost at will. The modifying group is highly polar, offers the opportunity for hydrogen bonding, and, as predicted, has a marked influence on the glass transition temperature, solubility character, and tensile properties of the polymer. The choice of substituents on the triazolinedione molecule can be varied very easily to provide "tailor-made" polymers of desired properties for specific applications.

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