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Chemical Reactions on Polymers. III. Modification of Diene Polymers via the Ene Reaction with 4-Substituted-1,2,4-triazoline-3,5-diones

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ABSTRACT

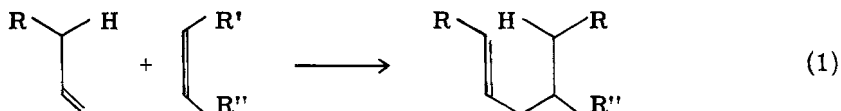
Various diene polymers have been modified at room temperature via the ene reaction with 4-substituted-1,2,4-triazoline-3,5-diones. The resulting modified polymers were characterized by means of IR spectroscopy, nuclear magnetic resonance, differential scanning calorimetry, and solubility tests. Physical properties measurements support the assumption that the highly-polar pendant urazole groups play an important role in both intermolecular and intramolecular hydrogen bonding interaction, and accordingly give thermoplastic properties to the modified polymers. Changes in the thermal analysis and solubility character of the modified polymers agree fairly well with this assumption. The modified polymers remain soluble in suitable solvents because of the physical nature of the association between molecules.

INTRODUCTION

Diene polymers may be modified by adding polar functionalities so as to change the electrostatic and steric characteristics. Chemical conversions due to these changes will correspondingly cause

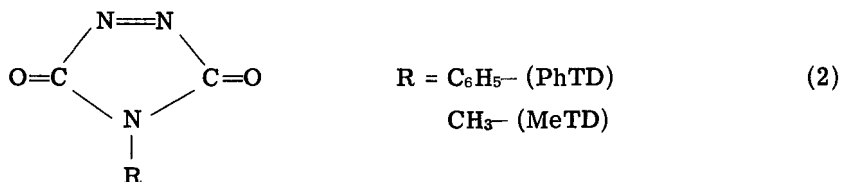
changes in physical properties which are of great value in certain applications.

One of the commonly investigated reactions in organic chemistry is the ene reaction which involves an olefin having active allylic hydrogens and an electron-deficient enophile. During the ene reaction a bond is formed between the enophile and the olefin with an allylic hydrogen being transferred from the olefin to the enophile:



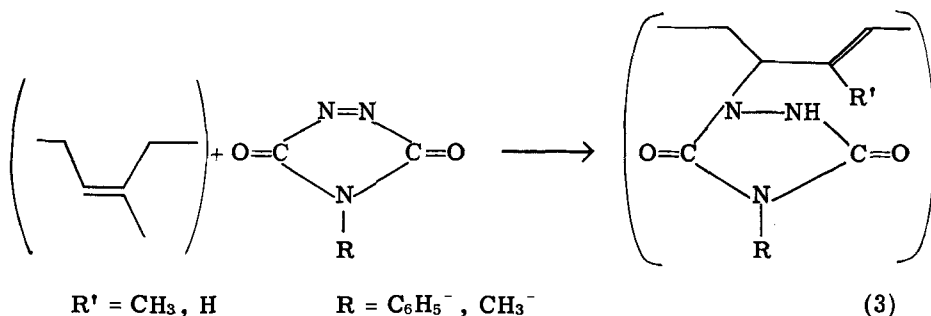
Mechanistically, the reaction may proceed either by stepwise involvement of a 1,4-polar intermediate or in a concerted manner via suprafacial or antarafacial processes.

The purpose of this report is to study the modification of polydienes via the ene reaction at room temperature and the characterization of the modified polymers. The enophiles that we used were 4-substituted-1,2,4-triazoline-3,5-diones:



Both triazolinediones are very reactive dienophiles as well as enophiles. It has been reported that PhTD has a reactivity 10^4 times higher than that of conventional olefins which undergo thermal reaction with allylic systems. The syntheses of triazolinediones have been previously reported in the literature [1, 2] and are not very complicated. There is a special feature of the triazolinedione reaction which makes it convenient to use: the compounds are highly colored (red), and the red color will disappear after completion of the ene reaction. This serves as a good indication for determination of completeness of the reaction. The polydienes that we used were polypentamer (pptm), cis-1,4-polypiperylene (cis-ppp), high vinyl polybutadiene (HVPB), and medium vinyl polybutadiene (MVPB).

Using the polydienes as olefins, we can write the reaction process as shown in Eq. (3). These triazolinedione-modified polymers contain urazole pendant groups which are capable of undergoing intermolecular hydrogen bonding. Thus a variety of properties such as solubility character, thermal behavior, and tensility are expected to occur. Under present conditions the association between molecules is still



of a physical character in nature. Hence the modified polymers should be soluble in suitable solvents. This kind of pseudo-cross-linking modification has some definite advantages in terms of flexibility and recovery of starting materials.

EXPERIMENTAL

Materials

All polymers were obtained from the Goodyear Tire and Rubber Co. and were used as received. The solvents and chemicals were reagent grade and were used after being purified by standard procedures.

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) [3] were according to the published methods and are not described in detail here.

Procedure for Modification of Polydienes

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 produced. The required amount of triazolinedione to produce the desired degree of different percentage polymer modification was dissolved in the same amount (20 mL) of dry benzene. The triazolinedione solution was then added to the polymer solution quite rapidly at room temperature. The reaction mixture was allowed to stand overnight with occasional shaking after the red color had disappeared. The modified polymer was precipitated with 200 mL of 95% ethanol containing 0.5% 2,6-di-tert-butyl-4-methylphenol (BHT), filtered

with suction on a Buchner funnel, and dried in a vacuum desiccator for 24 h.

Characterization

The modified polymers were characterized by infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC), and solubility tests as follows.

Infrared (IR). Solvent cast films of the modified polymers were prepared on NaCl plates. IR spectra were recorded on a Perkin-Elmer Model 621 grating IR spectrophotometer. IR was originally used as a qualitative tool to prove the molecular association through hydrogen bonding. No absorption bands due to residual solvent were observed in the IR spectra.

Nuclear Magnetic Resonance (NMR). NMR measurements on the sample were carried out on a Varian A-60-MHz NMR spectrometer in deuterated chloroform using TMS as an internal standard. NMR spectra were used to establish the amount of triazolinedione combined with the polymer. The triazolinedione phenyl and methyl signals are easily distinguished from those of the parent polymer. It is assumed that the degree of modification can be obtained by comparing the ratios from the urazole pendant group to those of the main chain protons.

Differential Scanning Calorimetry (DSC). DSC measurements were performed on a Perkin-Elmer Model DSC II. The scanning speed was 10°C/min in all cases of heating and cooling, and time was used as a calibration standard. Samples, approximately 10-15 mg each, were prepared directly from the dried samples. T_g is taken as the intersection of the extrapolated low temperature baseline with the tangent to the endotherm signal resulting from the heat capacity increase. The decomposition temperatures were defined as the point of maximum expansion of the exotherm from the baseline.

Solubility Tests. A few milligrams of the polymer samples were added to 1 mL of solvent. The mixture was stirred periodically for 1/2 h at room temperature. The polymer was considered to be soluble in that solvent if a clear and transparent solution was obtained after a 30-min stirring period. For some cases the polymer solution remained opaque or the polymer became swollen in the solvent. The reaction mixture was permitted to stand overnight and reexamined. Appearance of swollen fragments was interpreted as insolubility. The solvents used in the solubility tests were xylene, benzene, dichloromethane, pyridine, and chloroform.

RESULTS AND DISCUSSION

Under normal conditions the ene reaction is so rapid that the rate cannot be measured by usual methods such as UV absorption techniques. However, in some situations the steric effect exerted by the

TABLE 1. Relative Reactivity of Different Polymers Modified by PhTD

Polymer (5% solution)	Solvent	Completion time (min) for % modification		
		1%	5%	10%
pptm	Benzene	6	7	8
cis-ppp	Benzene	12	13	14
HVPB	Benzene	8	10	12
MVPB	Benzene	5	6	7

polymers might be strong enough to prevent the triazolinedione molecules from approaching. In general, the relative rate of reaction for PhTD is faster than MeTD. The relative reactivity of various polymers under study toward triazolinedione modification can be qualitatively determined by comparing the period of time needed for the red triazolinedione color to fade fully in each reaction mixture. The data are illustrated in Table 1.

Thus the larger the modification percentage, the longer the completion time required.

Evidence of Intra- and Intermolecular Association in Triazolinedione-Modified Polymers

Infrared Spectroscopy. The absorption bands associated with the urazole substituents and their functionality assignments are listed in Table 2.

The presence of urazole groups was confirmed by the carbonyl stretching frequencies which appear around 1700 cm^{-1} , while the evidence of hydrogen bonding was supported by the bonded N-H stretching band around 3185 cm^{-1} , and N-H bending band around 1490 cm^{-1} . Typical IR spectra for two modified and one unmodified polymers are shown in Fig. 1. Some of the urazole groups might be physically too far apart to produce effective hydrogen bonding, and thus a very weak absorption would be the result. On the contrary, when the extent of triazolinedione modification exceeds 50%, the effective intermolecular association might be influenced by the steric hindrance and conformational changes due to the appearance of a large amount of urazole pendant groups. In general, the higher the modification percentage, the broader the absorption bands as shown in Fig. 2. The amount of free N-H to hydrogen-bonded N-H approaches a ratio of 1:1.

NMR Analysis. The NMR technique is not very accurate in finding the degree of modification, since the absorption spectra are

TABLE 2. IR Absorption Data From Modified Polymers^a

Modified polymers	IR absorption		
	C=O stretching (cm ⁻¹)	N-H stretching (cm ⁻¹)	N-H bonding (cm ⁻¹)
pptm -5% MeTD	1697 (m)	3180 (w)	1460 (w)
pptm -5% PhTD	1685 (w)	3175 (vw)	1496 (w)
cis-ppp-5% MeTD	1690 (m)	3190 (vw)	1470 (w)
cis-ppp-5% PhTD	1710 (m)	3185 (w)	1450 (w)
HVPB -5% MeTD	1700 (s)	3140 (w)	1485 (m)
HVPB -5% PhTD	1720 (w)	3165 (vw)	1475 (w)
MVPB -5% MeTD	1696 (m)	3090 (w)	1470 (w)
MVPB -5% PhTD	1705 (m)	3130 (w)	1480 (w)

^avw = very weak, w = weak, m = medium, s = strong.

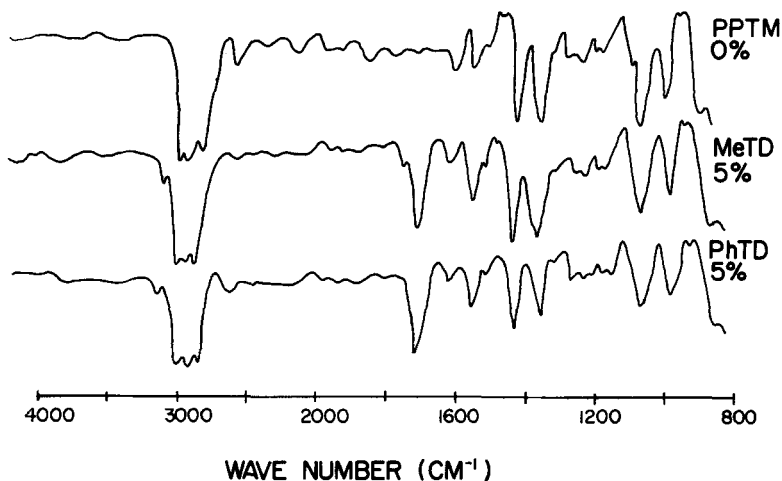


FIG. 1. Infrared spectra of unmodified and modified pptm samples.

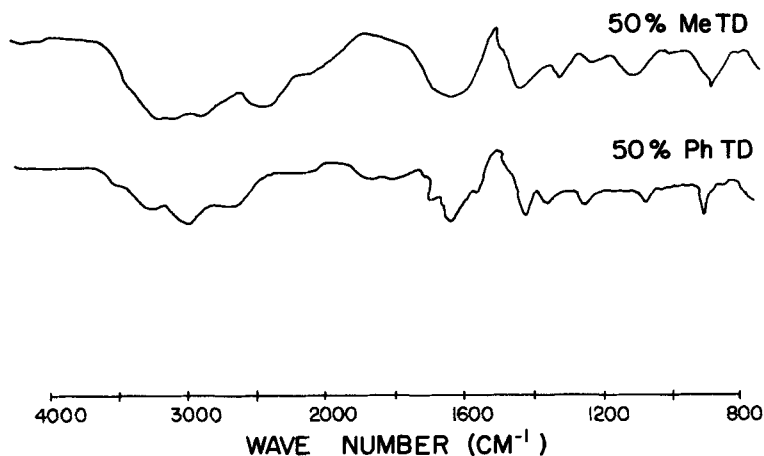
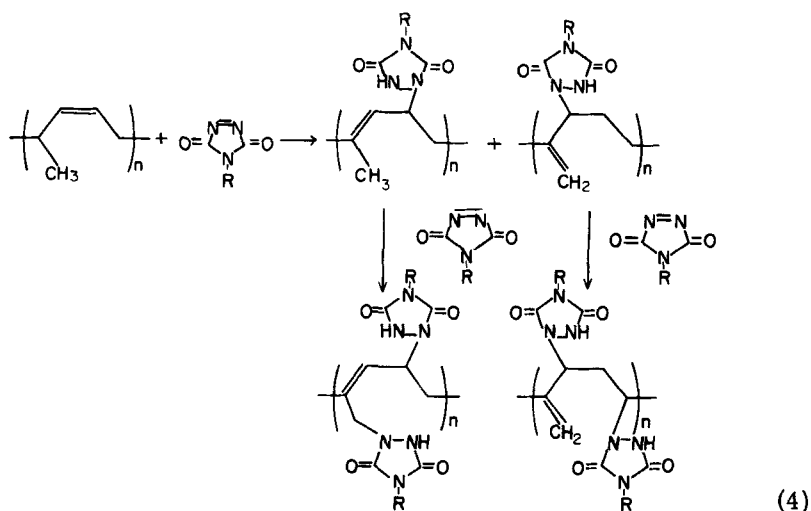


FIG. 2. Infrared spectra of HVPB at 50% modification.

quite complicated. There are several possible products that can be produced in the modification reaction with *cis*-ppp. These are shown in Eq. (4).



Based upon model compound studies, the second ene reaction is usually slow and may not occur at all. After modification, the N-H proton signal and the methyl (or phenyl) signal from TD are not very

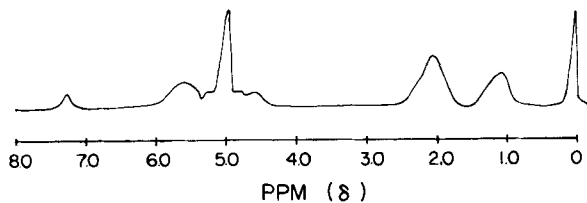


FIG. 3. NMR spectrum of HVPB modified by PhTD.

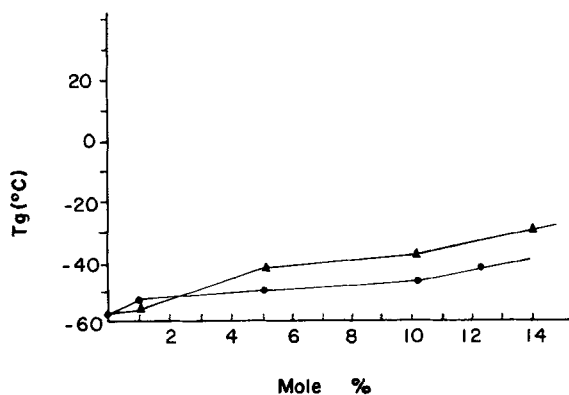


FIG. 4. Glass transition temperature of ptpm modified with PhTD (●) and MeTD (▲).

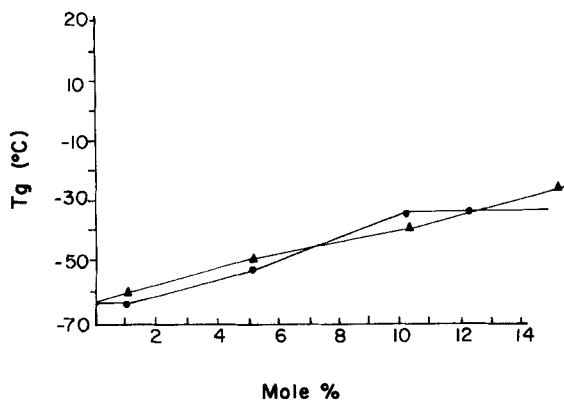


FIG. 5. Glass transition temperature of cis-ppp modified with PhTD (●) and MeTD (▲).

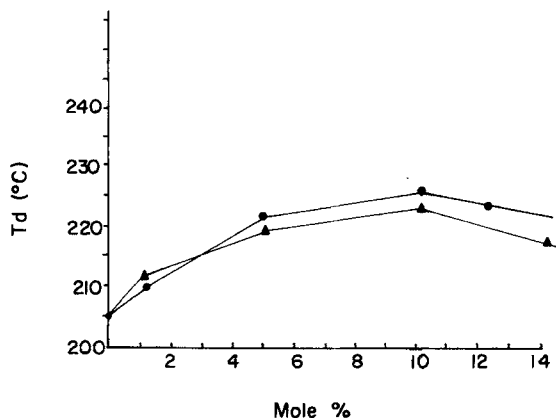


FIG. 6. Decomposition temperature (T_d) for pptm modified with PhTD (●) and MeTD (▲).

pronounced or may be too weak to be detected. Consider the absorptions of HVPB, for example, as shown in Fig. 3. The resonances ranging from 4.6 to 5.9 ppm are assigned to the pendant vinyl groups. The very strong band at 5.05 ppm is due to the high percentage of 1,2-polybutadiene, while the band at 2.05 ppm indicates 1,4-polybutadiene. On the other hand, it is quite difficult to locate the absorptions due to either N-H proton or methyl or phenyl signals from TD. Hence the actual amount of urazole pendant groups incorporated into the polydiene should be dependent upon the elemental analysis of the nitrogen content [5]. The average urazole-group incorporation, according to elemental analysis, was found to be 90% of the triazolinedione feed.

Differential Scanning Calorimetry. Any increase in intra- or intermolecular interaction usually results in contraction of free volume of polymer molecules and a higher energy barrier set up to the free rotation of the polymer chain. The glass transition temperature, T_g , would be increased. The experimental results show that this is true among the polymer samples modified with PhTD and MeTD. Particularly, the T_g of the olefinic polymer segments increases proportionally with the amount of urazole pendant groups occurring in the segments. An example is shown in Figs. 4 and 5. In some cases at low percent modification an initial decrease in T_g may result because of an increase of free volume, which is due to the urazole side groups. As more and more urazole groups are attached to the polymer chain, the probability of the urazole groups interacting with each other thus increases, consequently increasing intramolecular hydrogen bonding. When the attractive forces exerted by

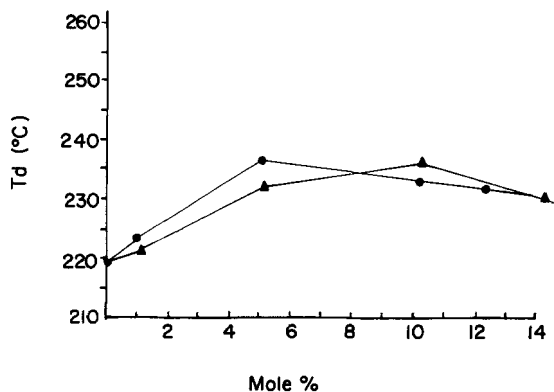


FIG. 7. Decomposition temperature (T_d) for cis-ppp modified with PhTD (●) and MeTD (▲).

intramolecular hydrogen bonding surpasses the repulsive forces due to the presence of urazole pendant groups, the T_g would increase again.

The decomposition temperatures do not follow any trend. Typical data are shown in Figs. 6 and 7. We speculate that at high percent of modification the urazole pendant groups furnish additional thermal stability to the polymer, whereas at low percent modification, i.e., below the 10% level, they might have a destabilizing influence.

Since thermal decomposition of a polymer is always a complicated process with respect to thermal stress, thermal oscillation, and the strength of hydrogen bonding, each polymer system should be dealt with in a separate way.

The polymer samples lose their thermoplastic properties as the quantity of polar groups incorporated increases. The degree of modification possible before thermoplasticity is adversely changed is summarized in Table 3. It appears that MeTD is able to inimically affect the thermoplasticity to a greater extent than PhTD.

TABLE 3. Maximum Percent of Modification Permissible before Loss of Thermoplasticity

Polymer	% PhTD	% MeTD
PPTM	1	1
cis-ppp	12	5
HVPB	1	1
MVPB	5	5

TABLE 4. Maximum % Modification for Polymer to Retain Solubility in Various Solvents

Solvent	Solubility parameter δ	pptm	cis-ppp	HVPB	MVPB
Xylene	8.8	5	5	10	5
Benzene	9.2	<12	<15	<15	<12
Chloroform	9.3	12	5	12	10
Chlorobenzene	9.5	12	10	15	5
Dichloromethane	9.7	10	5	5	5
Pyridine	10.7	10	12	10	5

Solubility Test. The effect of intermolecular forces is characterized by the solubility parameter δ . It is well known that branching increases the solubility of high polymers, while increased polarity decreases their solubility in nonpolar solvents. The introduction of polar groups into a polymer main chain would be expected to decrease its solubility in the original solvent as strong polymer-polymer interactions develop. Our studies show that the modified polymer samples were precipitated from the reaction solvent when the modification percentage was greater than 20%. Obviously the strong hydrogen bonding found by the urazole pendant groups prevents the solvent molecules from entering the polymer coils. In general, the solubility parameter of the polymer samples increases as a function of urazole content. Some of the representative solubility characteristics of the polymers modified with PhTD and MeTD are shown in Table 4.

CONCLUSION

The present method of modifying polydienes is quite simple and effective. Triazolinediones as enophiles have a great advantage because of their high reactivity. The substituents on the triazolinedione molecule can be readily changed in order to provide commercially useful polymers with properties tailor-made to fit specific applications. The extent of modification is subject to no specific restrictions, and the modification reaction can be carried out readily at room temperature or lower. The highly polar modifying groups provide hydrogen bonding sites which have a remarkable effect on T_g , solubility character, viscosity, and tensile properties of the polymer.

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