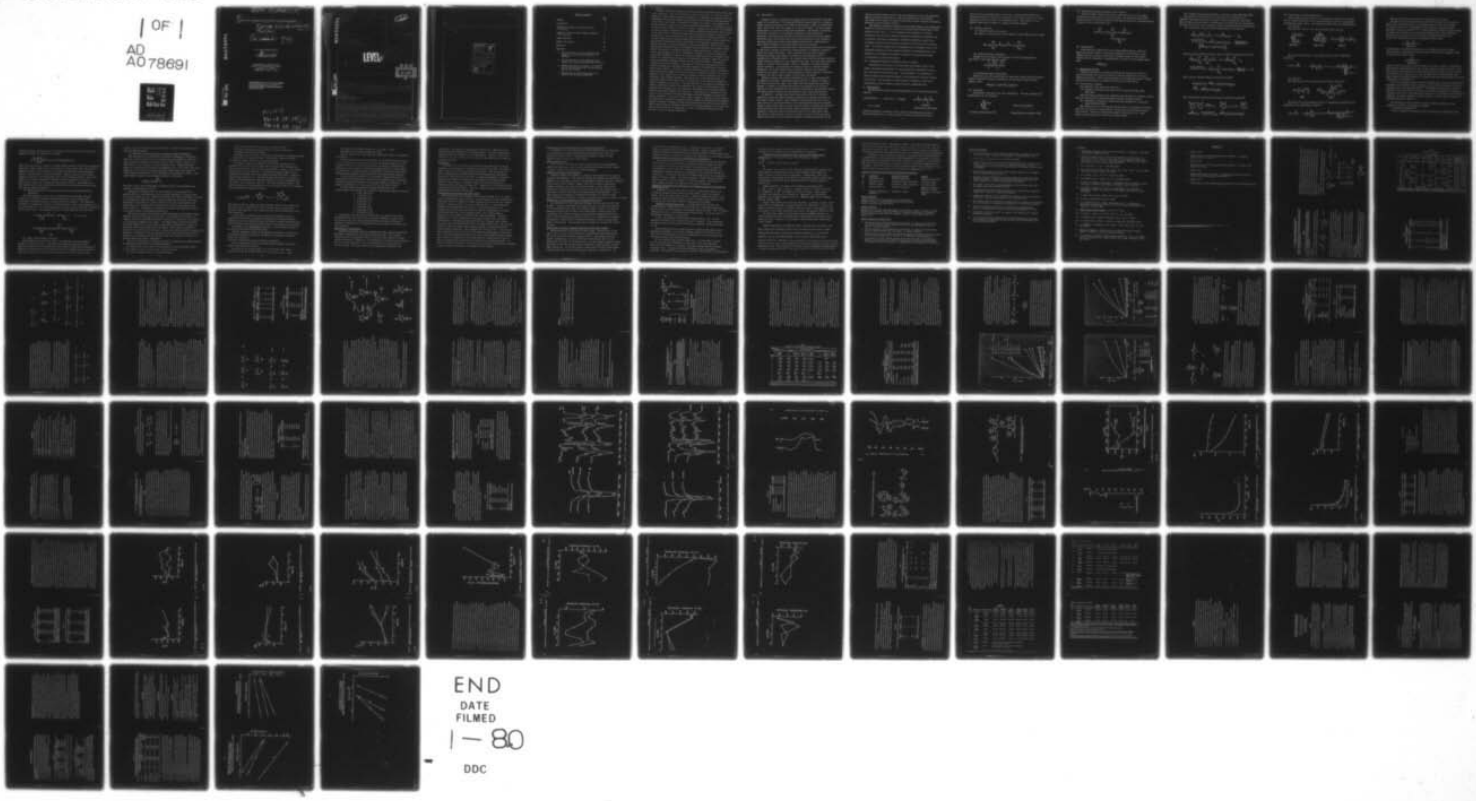
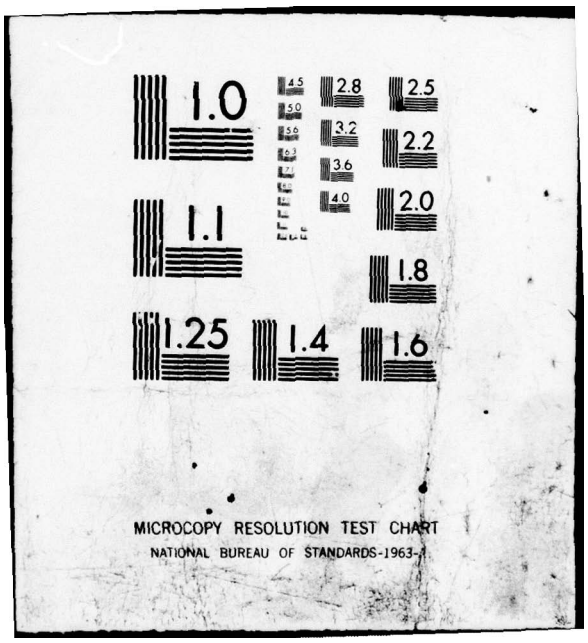
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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propellant binders
thermoplastic elastomers
physical properties

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

It was the objective of the present investigation to conduct a fundamental study of the feasibility of utilizing or developing suitable thermoplastic elastomers for use in propellant technology, and considerable progress has been made toward achieving this objective. A wide variety of thermoplastic elastomers of novel structure have been synthesized, and their fundamental physical properties determined. As a result of this study, a number of carefully selected samples were submitted to personnel at Redstone Arsenal, Alabama for evaluation as thermo-

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20. ABSTRACT CONTINUED

plastic propellant binders. Verbal communication has strongly indicated that the present approach is a feasible one, and has made it possible to extrapolate to a set of "necessary" properties of the material to meet the required objectives.

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1. The Ene Reaction of Triazolinediones with Alkenes. I. Structure and Properties of Products.
2. The Ene Reaction of Triazolinediones with Alkenes. II. Kinetics and Substituent Effects.
3. Chemical Reactions on Polymers. II. Modification of Diene Polymers with Triazolinediones *via* the Ene Reaction.
4. Crosslinking of Diene Polymers *via* 'Ene' Reaction with Bistriazolinediones.

I. Abstract

Polymeric binders in propellants usually constitute from 16-20% of the total weight of the propellant. Both of the problems of original processing of propellants and of disposing or reprocessing of obsolete propellant are formidable ones because of the time requirements for the cross-linking or curing step and the resultant crosslinked nature of the binder, which makes it impossible to dissolve in solvents. The encasement of oxidizer and metal particles in the water-insoluble binder makes it impossible to remove the water-soluble oxidizer by solution in water. Although much effort has been expended to develop methods of degradation of the binders, directed predominantly toward cleavage of the cross-links by solvolytic methods, which might permit economic recovery of the raw materials, these approaches have not proven satisfactory from many standpoints. If a binder system could be developed which would not require formal covalent cross-links, many problems involved with initial processing of the propellant and particularly economic recovery of obsolete propellant, could be accomplished. Within recent years, thermoplastic elastomers have been developed, and such materials have replaced conventional cross-linked or vulcanized elastomers in many applications. However, to the best of our knowledge, the use of thermoplastic elastomers to replace conventional cross-linked elastomers as binders in propellant technology had not been applied technically nor studied from the theoretical or feasibility standpoint before the present research program was undertaken on ARO Grant No. DAAG29-76-G-0223. Thermoplastic elastomers are known to combine in large degree the end-use characteristics of vulcanized elastomers with the rapid processing advantages of thermoplastic materials. They generally exhibit a continuous two-phase domain structure in which a crystalline, highly polar "hard" segment serves as tie points or "pseudo-cross-links" that bind an amorphous "soft" segment into a thermally reversible network resembling that of conventionally cross-linked elastomers. When heated above their melting points, the elastomers soften and flow easily under low pressures, but develop high strength and elastic properties upon cooling. It was the objective of the present investigation to conduct a fundamental study of the feasibility of utilizing or developing suitable thermoplastic elastomers for use in propellant technology, and considerable progress has been made toward achieving this objective. A wide variety of thermoplastic elastomers of novel structure have been synthesized, and their fundamental physical properties determined. As a result of this study, a number of carefully selected samples were submitted to personnel at Redstone Arsenal, Alabama for evaluation as thermoplastic propellant binders. Although no formal nor written report was ever received, limited verbal communication has strongly indicated that the present approach is a feasible one, and has made it possible to extrapolate to a set of "necessary" properties of the material to meet the required objectives.

II. Introduction

Polymeric binders in propellants usually constitute from 16-20% of the total weight of the propellant. The remaining 84-80% is generally made up of oxidizer, usually ammonium perchlorate (AP) 60-82%, aluminum metal, 2-18%, and stabilizers, 0-1%. Binders most often used appear to be one of two types: (1) cross-linked polyurethanes or (2) cured polybutadiene prepolymers. The problem of disposing of obsolete propellants is a formidable one because of the difficulties associated with reprocessing and legal limitations on burning and ocean dumping. The product gases from burning would cause serious pollution of the atmosphere and ocean dumping could cause serious damage to marine life. Reprocessing is quite difficult because of the cross-linked nature of the binder.

A desirable means of overcoming some of these problems would involve separation of the binder, oxidizer and metal by suitable physical or mechanical processes which would permit their reuse. Such a procedure may also offer important economic advantages, particularly if recovery of each component could be accomplished in reasonable purity. The problems associated with processes directed toward mechanical separation of the components are many. The cross-linked polymeric binder is insoluble in all solvents, making it impossible to remove simply by solvent extraction. Its properties are similar to those of vulcanized rubber. Furthermore, the finely divided metal and oxidizer particles are intimately coated with the binder, which is often impervious to water, making it impossible to extract the water-soluble oxidizer from the metal and binder.

Extensive efforts both in these laboratories[1] and in other laboratories[2] to degrade these binders, predominantly *via* solvolytic or chemical cleavage of the cross-links have been made. Such efforts have been moderately successful; however, it remains to be established whether these methods can be utilized effectively after consideration of the possible alternatives, the potential hazards and safety factors involved, and the economics of the various possibilities.

In addition to problems associated with potential recovery of obsolete propellants, there are numerous problems associated with initial processing of the oxidizer-binder mixture. These problems are associated with cure time, i.e. time required for the vulcanization or cross-linking process to occur; residual chemical changes which occur at a lower rate but continue to change the properties of the propellant with time; different storage conditions, particularly the temperature differences which exist between storage areas, which would cause the residual chemical changes referred to earlier to occur at different rates; lack of uniformity in a wide variety of individual components which make up the

finally vulcanized binder; and the lack of reformability of the cast propellant, making it relatively impossible to reuse the components of such a system, for example in the event of an error in processing, without extensive degradation procedures as those proposed earlier.

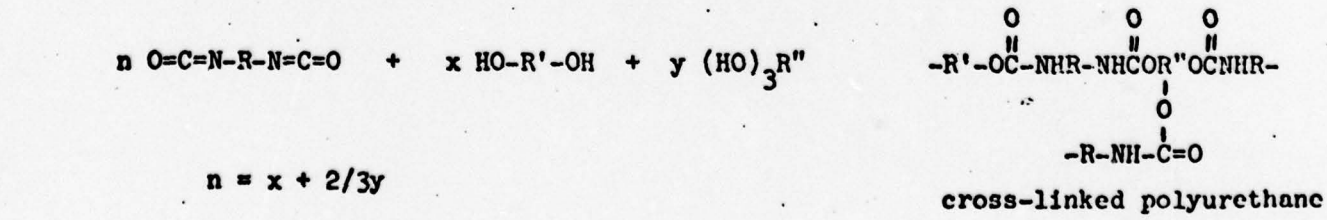
The concept of replacing conventional cross-linked binders with thermoplastic binders is very attractive and success in this area could eliminate many of the problems outlined above. It is the purpose of this proposal to continue a fundamental study presently underway of available thermoplastic elastomers, and to synthesize additional thermoplastic elastomers possessing a specific set of physical properties which have been formulated as the result of the present study. The synthetic program will be supplemented by a systematic study of the fundamental properties of these synthetic materials, and determination of the feasibility of utilizing such materials as binders for propellants instead of conventionally cross-linked binders.

III. Background Information and Present Status of Problem

As pointed out in Section II, the most-often used binders appear to be either cross-linked polyurethanes or cured polybutadiene prepolymers in which the cross-links are of the ester type. A brief summary of the chemistry of these two binder systems and development of the thermoplastic elastomer concept are presented. Also included is a brief summary of progress to date on the investigation presently underway under ARO Grant No. DAAG29-76G-0223.

A. Polyurethanes

The polyurethane binders are produced according to the following generalized reaction:



$n = x + 2/3y$

cross-linked polyurethane

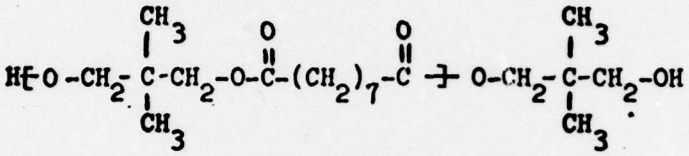
Cross-link density is a function of y/x, since the trifunctional molecule is the cross-linking agent. If y/x is large, cross-link density will be high.

If y/x is low, cross-link density will be low. Since the polyurethanes are cross-linked polymers, they are not expected to be soluble in any solvent unless degradation of the cross-links is accomplished first. The remaining linear polymer should then be soluble in a number of organic solvents.

(1) Dihydroxy Compounds

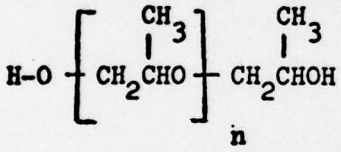
(a) Hydroxyl-terminated Polyesters

An example is neopentylglycol azelate (NPGA) of about 2000 molecular weight:



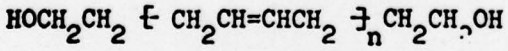
(b) Hydroxy-terminated polyethers

Perhaps the most commonly used polyether is poly-(1,2-oxypropylene)-diol (PPG) of about 2000 molecular weight:



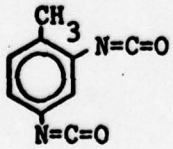
(c) Hydroxy-terminated polybutadiene

Perhaps the most often used product is based upon lithium initiated polymerization of butadiene followed by termination of the anionic chain ends with ethylene oxide.

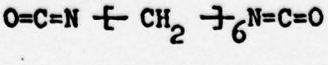


(2) Isocyanates

The isocyanate used must be at least difunctional. The most commonly used diisocyanates are the following:



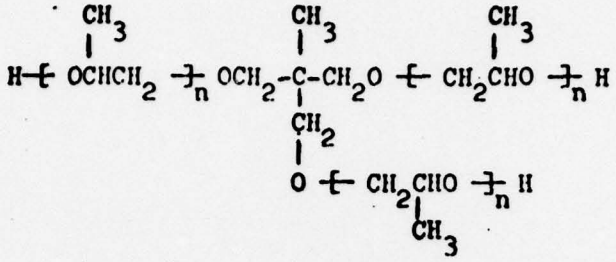
2,4-Toluenediisocyanate (TDI)



Hexamethylene diisocyanate (HDI)

(3) Trifunctional hydroxyl components (cross-linkers)

The cross-linking component must have a functionality of at least three. Trifunctional alcohols have been most often used. The following trifunctional alcohol derived by initiating propylene oxide polymerization with trimethylolpropane is typical of the cross-linkers used:



(4) Bonding Agents

Processing often required the use of certain bonding agents. These are highly polar organic diols or triols which accumulate on the surface of the oxidizer particle yielding a dense layer of hydroxyl groups for the initial reaction with the isocyanate. Triethanolamine is typical of such bonding agents used:

$$(HOCH_2CH_2)_3N$$

B. Polybutadiene Binders

Butadiene prepolymers containing carboxyl groups along with a curing or cross-linking agent have been used widely to make the binder matrix for solid composite propellants. These systems provided 2-3 seconds higher specific impulse and permitted manufacture of composites containing 82 to 88% solids.

(1) Polybutadiene Prepolymer

The prepolymers most extensively used were:

(a) Copolymer of Butadiene and Acrylic acid of molecular weight 2000-4000 (PBAA)

These were random copolymers and, dependent upon the method of synthesis, varied from zero functionality to polyfunctionality and many problems resulted.

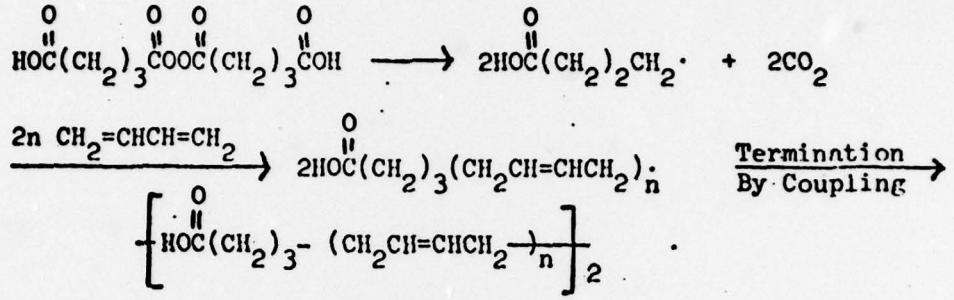
(b) Terpolymers of Butadiene, Acrylic Acid and Acrylonitrile of molecular weight 2000-4000 (PBAN)

Even though the use of this material overcame many of the problems associated with PBAA, the problem of controlling the functionality per prepolymer molecule still existed. Prepolymer functionality should be exactly two, i.e., every molecule should contain two and only two carboxyl groups.

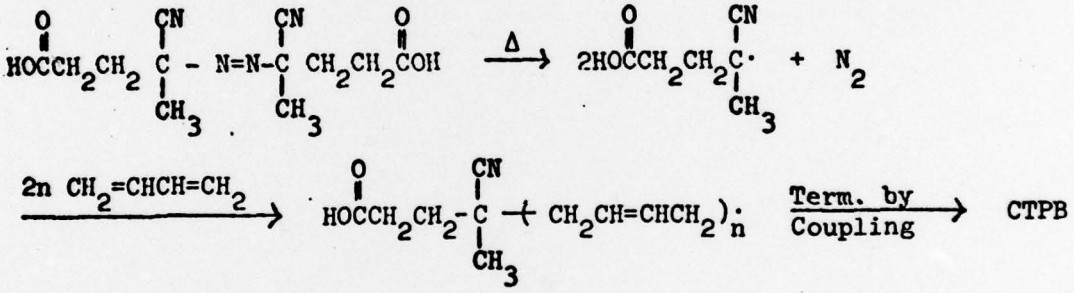
(c) Carboxyl Terminated Polybutadiene of molecular weight 2000-4000 (CTPB)

The problem of functionality was so important to reproducibility of butadiene based propellants that an extensive research program was undertaken both by industry and government to provide means of controlling the functionality. The following reactions were developed to produce carboxy-terminated polybutadiene.

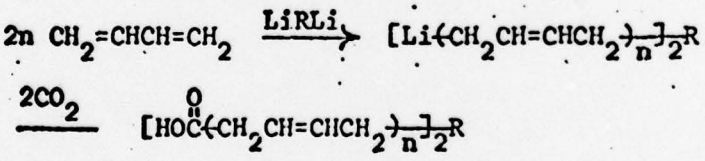
[i] Free-radical Initiated Reaction Using Glutaric Acid Peroxide[3]



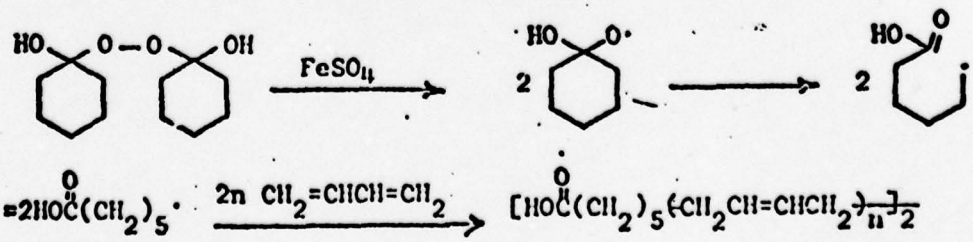
[ii] Free-radical Initiated Reaction using 4,4'-Azobis-4-cyanopentanoic Acid[4]



[iii] Anionic Initiated Reaction Using Lithium Alkyls[5]



[iv] Free-radical Initiated Reaction using Cyclohexanone Peroxide[6]

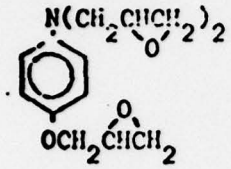


(2) Curing Agents or Cross-linking Agents

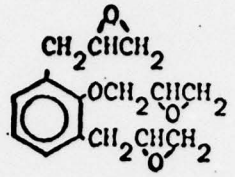
Curing agents often used are di- or trifunctional compounds in the range of 0.2 - 1.0% of total which react with the carboxyl groups of the prepolymer to produce the binder matrix. The following chemical types are representative:

(a) Epoxides

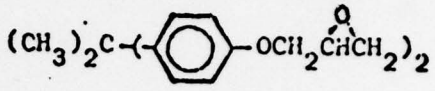
The following structures are typical polyfunctional epoxides:



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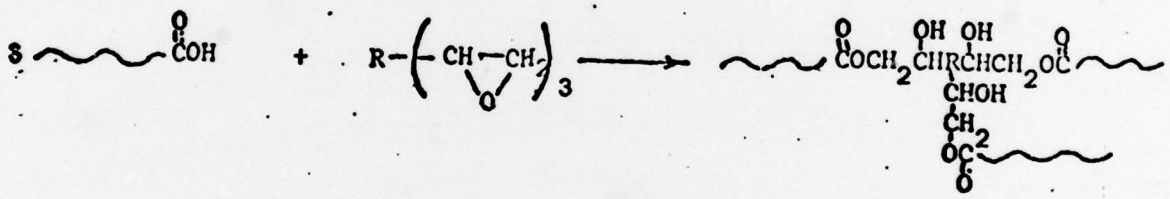


Epon X-801



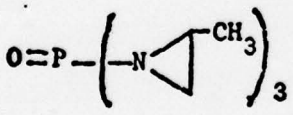
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The nature of the curing or cross-linking reaction can be represented as follows:

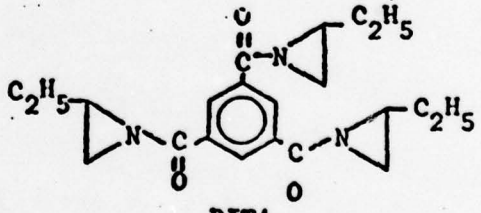


(b) Azirdines

The following structures are typical polyfunctional aziridines:

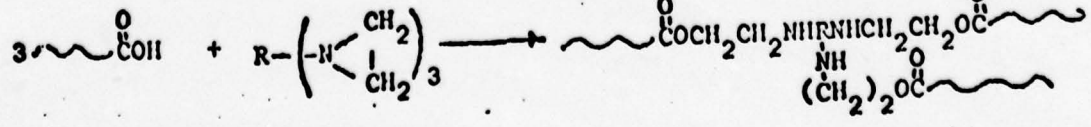


MAPO



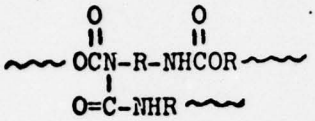
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The nature of the cross-linking reaction of polybutadiene prepolymer with aziridines can be represented as follows:

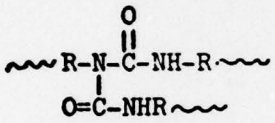


History of Discovery and Development of Thermoplastic Elastomers

The earliest observations that dipole-dipole interactions between polymeric chains, when sufficiently strong could produce materials which would perform in a manner analogous to conventionally cross-linked or vulcanized polymers was made by Bayer and coworkers.[7-10] An early explanation offered by these authors to account for the properties of material developed by them, which possessed vulcanized-like properties, was that terminal isocyanate groups may have reacted with urethane groups to give allophanate branch points:



or that polymers containing urea groups, e.g. by addition of water or amine chain extenders to the system, could have reacted with terminal isocyanate groups to lead to biuret branch points:



either of which could lead to formal covalent cross-links. However, even though it has been shown experimentally that both of the proposed reactions can occur, it was also shown by these authors that cross-linking was not necessary in order to attain the vulcanized-like properties, but that the highly polar urethane groups could exert sufficient interchain attraction to produce materials which exhibited "virtually cross-linked" (VC) properties.[8]

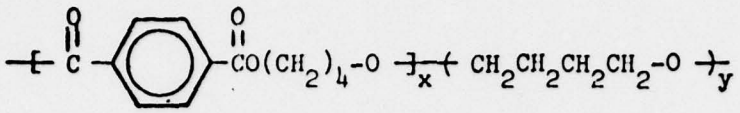
It is now recognized that the urethane elastomers differ from the olefin-derived elastomers in that hydrogen bonding and other Van der Waals forces play a much more pronounced role in the urethane systems.[11] The original investigations showed the beneficial effects of strong intermolecular attraction and considerable rigidity in a portion of the chain. Some additional properties to be associated with thermoplastic elastomers will become apparent from the discussion of certain typical commercially available materials in Section B.

The following are typical examples and most probable structures of some commercially available thermoplastic elastomers:

(1) Copolyester Elastomers[12]

A class of copolyester elastomers which are derived from terephthalic acid,

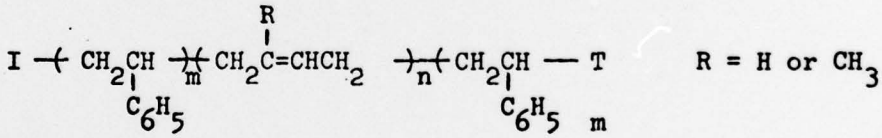
polytetramethylene ether glycol and 1,4-butanediol and which have the following most probable structure are commercially available:



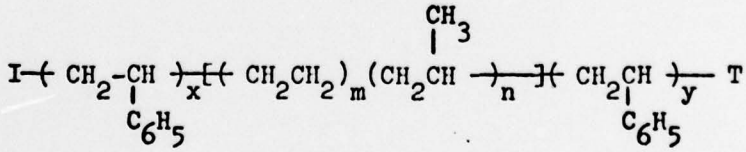
These materials exhibit a continuous two-phase domain structure in which the crystalline short-chain "hard" segments serve as tie points or "pseudo cross-links" that bind the amorphous polyether "soft" segments into a thermally reversible network resembling that of a conventionally cross-linked elastomer. However, because of their unique morphology, they are true thermoplastics and can be processed routinely. They can be molded or extruded at temperatures from 350° to 480°F (176-249°C) and need no post-curing to attain full strength and dimensional stability. They possess good melt stability and low melt viscosities, which provide wide processing latitude without affecting physical properties.

(2) ABA Block Copolymers of Polystyrene-Conventional Hydrocarbon Elastomer-Polystyrene

ABA block copolymers in which the A or end blocks are polystyrene and the B blocks are conventional elastomer-type polyhydrocarbons such as polybutadiene, polyisoprene or ethylene-propylene copolymer blocks are available. The combination of rubbery and thermoplastic behavior is possible because of the block copolymer structure which makes use of the rigid polystyrene end blocks with the elastomeric properties of the center blocks. Most probable structures of these materials are shown below:



R = H or CH_3



EPR

(3) Radial Block Copolymer Elastomers

These materials are believed to consist of essentially the same structural features as example (2) above. They provide good physical properties without requiring vulcanization, and exhibit rubber-like qualities under normal environmental conditions. When heated above their melting points, the elastomers soften readily and flow under low pressures, and develop high strength and elastic properties upon

cooling. They can be processed using conventional equipment, and soften between 200° and 250°F (93-121°C).

(4) Thermoplastic Elastomers Based on Ethylene-Propylene Copolymers

These materials can be processed by conventional thermoplastic techniques. These are four basic grades varying in hardness and other properties; however, in general, service temperatures are limited to about 250°F (121°C); however, up to 300°F (149°C) can be tolerated for short periods of time. Highly stabilized grades are recommended for sustained high temperature use. The nature of the "hard" segment, if any, in this thermoplastic elastomer group, which would impart the "cross-linked effectiveness", is not identified in the published literature. The "soft" segment implied in the published literature is as follows:

$$\left(CH_2CH_2 \right)_x \left(CH_2\overset{CH_3}{\overset{|}{C}}H \right)_y$$

The "hard" segment could conceivably be extended blocks of crystallizable polyethylene, as represented by x above.

Thermoplastic elastomers meet the usual definition of an elastomer as a material which at room temperature can be stretched repeatedly to at least twice its original length and, upon release of the stress, will return immediately with force to its approximate original length". The high elongation and elastic recovery of thermoplastic elastomers are in sharp contrast to the much lower elongation and high permanent-set characteristic of even the most flexible conventional thermoplastic materials. Thermoplastic elastomers also exhibit other properties similar to vulcanized rubber as subsequently pointed out.

Conventional elastomers derive their rubbery properties from permanent bonding together of polymer chains <u>via</u> covalent bonds. The thermoplastic elastomers, in contrast, have their elastomeric properties tailored in as the result of the design of the individual segments of the chain . The dipole-dipole interactions between the "hard" segments of the chain create "cross-linking effectiveness" without the requirement that formal cross-links be introduced. These built-in elastomeric properties are derived in different ways in the several materials which are commercially available. In addition, there are many ways in which other structurally different thermoplastic elastomers possessing the particular set of properties required for a specific application could be synthesized.

The use of thermoplastic elastomers to replace conventional cross-linked binders for propellants would offer the following advantages:

(1) Elimination of the curing or cross-linking cycle with attendant savings in cross-linking agents, processing times, and curing costs.

(2) Reuse of materials such as scrap and trimmings

(3) Better low temperature properties are highly probable.

(4) Good tensile strength and elasticity at normal temperatures.

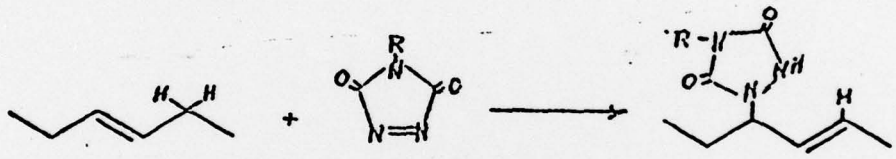
(5) Higher coefficient of friction.

(6) Reduced cost of recovery of materials from obsolete or discarded systems.

Brief Outline of Research Findings - ARO Grant No. DAAG-29-76-G-0223

(1) Synthetic Program--Modification of Diene Polymers

The synthetic program was primarily concerned with modification of preformed diene polymers and copolymers with the objective of incorporating into the polymer chain sufficient polar group content to impart to the polymers thermoplastic elastomer properties. The modification agents employed were N-methyltriazolinedione (MeTD) and N-phenyltriazolinedione (PhTD). Among the diene polymers employed were: styrene-butadiene (SB), ABA block copolymers (75/25), styrene-isoprene (SI) ABA block copolymer (85/15), polybutadiene (PB) (cis/trans), and polyisoprene (PI)(cis). The triazolinediones undergo a very rapid ene reaction, at room temperature, with the allylic system of the polymers, thus introducing the substituted urazole:



The urazole groups are capable of forming hydrogen bonds with one another and have been shown to exhibit "pseudo-cross-linking" effects in the polymer molecules, thus imparting to the polymer chain the desired thermoplastic elastomer properties.

A wide variety of modified diene polymers and copolymers have been synthesized and evaluated, decomposition temperatures and glass-transition temperatures, Tg, were determined using differential scanning calorimetry (DSC): tensile properties and thermoplasticity of most of the samples were detemrined.

Evaluation of the thermoplastic properties of these modified copolymers was done by observing their melting behavior.

Nineteen commercial samples of thermoplastic elastomers of potential use as propellant binders were acquired and submitted to personnel at Redstone Arsenal for evaluation.

(2) Results--Thermoplastic Range for Modified Copolymers

(a) The thermoplastic range for SB-PhTD modified polymers was 0-1.44%. Fusion temperatures were 132-154°C.

The range for the SI-PhTD polymers was 0.15% (fusion temp. range = 103-132°); and for the SI-MeTD polymers was 0.59 (fusion temp. = 103°C)

The range for the PB-PhTD polymers was 0-1% (temp. = 103°C)

The range for the PI-PhTD polymers was 0-10%.

Thus, it appears that a reasonably low modification changes the properties considerably.

(b) The decomposition temperatures (DSC) for the modified polymers appear to be a function of the diene block present in the system; however these temperatures do not show a linear variation with the degree of triazolinedione modification, which indicates considerable hydrogen bonding at certain degrees of modification. At higher degrees of modification steric factors may hinder maximum hydrogen bonding, thus accounting for the discontinuities observed.

(c) The intrinsic viscosities of the modified polymers show minima at a certain degree of modification in each case, thus suggesting that the maximum in hydrogen bonding is attained at this specific degree of modification. This degree of modification is in the range of 25% for the PhTD-SI system.

(d) Eight samples of ABA block copolymer modified with 1-15% triazolinedione were prepared for the purpose of determining physical properties.

1. 1.08% MeTD, 25g
2. 1.44% PhTD, 25g
3. 5.00% MeTD, 21.5g
4. 15.00% PhTD, 27g
5. 4.32% PhTD, 27g
6. 10.80% MeTD, 28g
7. 15.00% MeTD, 23.5g
8. 5.00% PhTD, 19.5 g

Arrangements were made with Borg Warner Corp. for physical properties determination and four of the above samples were submitted. However, before the tests were done, the samples became infusible, presumably through air oxidation. Unfortunately, no antioxidant was used to protect the samples from such reactions.

Modification of Polybutadiene:

Modified polybutadiene samples containing PhTD show a larger decomposition-temperature lowering effect than those modified with MeTD. The intrinsic viscosity at low % incorporation seems to follow the same trend as the decomposition temperature. Between 0 to 1% incorporation, the effect on the molecular size is not very significant in the case of MeTD but it is very drastic in the case of PhTD. The result indicates that hydrophobic interaction also

contributes to strengthen the intramolecular interaction. Samples up to 1% incorporation have thermoplastic properties (170°C). The glass transitions as measured by DSC show increases up to 1% modification. There is a drop in Tg after 5% in the case of PhTD, but the presence of more MeTD does not change Tg of polymer very much.

Polyisoprene:

Polyisoprenes (cis) modified with PhTD but without BHT also show larger decreases in the decomposition temperatures than those with MeTD. The maximum effect occurs around 50% incorporation in both cases. When stabilized with BHT, polyisoprene samples modified with PhTD have decomposition temperatures about 20-50° lower than those with MeTD. The general appearance of intrinsic viscosity plots against % incorporation are similar in both MeTD and PhTD modified polymer samples. Ir spectra confirm the presence of bonded N-H stretching around the region 3500-3100 cm^{-1}. Samples up to 7% incorporation have thermoplastic properties (145°C). There is a general increase in Tg for polymer samples modified by both PhTD and MeTD.

Poly(styrene-co-butadiene) random 23% styrene:

The reaction with this copolymer is much slower probably due to the steric effect of the aromatic group on styrene. In the range of 0-10 mole % modification (with BHT) there is a decrease in thermal stability by 23°C in the case of MeTD whereas a lowering of 37°C in the case of PhTD was noted. A very interesting phenomenon was observed based on Tg data. Tg increases initially to 1% incorporation but then gives two values for higher % incorporation, one higher and one lower than that of the original polymer. This probably means a separation of the copolymer constituents into different domains. Intrinsic viscosity [η] vs mole % incorporation plots show a gradual drop in [η] with % modification. Copolymers modified with PhTD show a slightly larger drop in [η] values than those modified with MeTD at the same% modification. GPC data show a shift of signal to higher elution volume indicative of strong H-bonding or intra-molecular interaction. This coincides with the drop in [η]. Since GPC and [η] are measured in dilute solution--intra-molecular interactions are manifested here. One interesting point though; in the case of MeTD modified styrene-isoprene block copolymer, broadening of the peak was observed, indicating that intra- as well as inter-molecular interactions are effective in the polymer solution. In order to evaluate the extent of inter-molecular interaction (H-bonding) melt rheology as well as tensile properties of the polymers must be studied.

Polychloroprene and Poly(acrylonitrile-co-butadiene)(A/B) 45% A:

In efforts to test the reactivity of other polyolefins--it was discovered that polychloroprene and poly(acrylonitrile-co-butadiene) gave very slow reaction with PhTD and MeTD. Polychloroprene required 24 hours to react completely even at fairly low % modification.

Model Compound Studies:

In an effort to establish the course of the reaction of triazolinedione (PhTD) with polyisoprene, model compound studies were carried out with 2-methyl-1-pentene, 2-methyl-2-pentene, and 1-methylcyclohexene.

Submission of Samples for Evaluation:

Seventeen samples were submitted to American Enka Laboratories for physical properties determination. Also, fourteen samples were prepared and submitted to: Commander, U.S. Army Missile Research and Development Command, Attention: DRDMI-TKC (Henry Allen) Redstone Arsenal, Alabama 35809, for testing as thermoplastic elastomer binders in the solid fuel research program. Eleven samples were prepared for biological testing in view of the fact that many polyanions have been shown to possess anti-tumor and interferon-generating properties. Four of these samples were submitted to Professor Ray Ottenbrite of Virginia Commonwealth University for evaluation. Complete evaluation results are not present available.

Modification of Poly(acrylonitrile-co-butadiene)(A/B) 45% A:

As indicated above, this copolymer undergoes very slow reaction with PhTD and MeTD. Complete discolorization occurred only after six hours upon reaction of 1% of unsaturation with PhTD. DSC analysis showed a variation of softening temperature between 400° and 380°K when triazolinedione content varied from 0-15 mole %, and a general increase of glass transition temperature (Tg) from 247° to 260°K, indicating the influence of inter- or intramolecular interaction. GPC analysis of sample with 1% TD modification showed a shift of peaks toward higher elution volume. The molecular size was reduced to one-half when 1% MeTD was used.

Modification of Poly(1,2-butadiene)(Firestone--93.5% vinyl content):

NMR analysis ($CDCl_3$) indicated 76% vinyl content. Reaction with TD was fairly slow, 1-2 hours being required for 1% modification with MeTD and PhTD. This is in accord with the model compound studies. DSC analysis indicated thermal decomposition to occur at 235°C for 1% modification, 160°C for 5% modification, and 180°C for 10% modification. Tg (DSC) showed a general increase from 266°K to 280°K for 10% modification indicating a steady increase in interchain interaction. GPC analysis showed a general shift in peaks toward higher elution volumes with increased modification, indicating a reduction in the

molecular size or hydrodynamic volume. Thermoplastic properties are retained only up to modification of 0.2% MeTD and 0.3% PhTD. Samples of unmodified poly(1,2-butadiene), 0.2% PhTD modified, 0.2% MeTD modified, 5% PhTD modified, and 5% MeTD modified were submitted to American Enka Laboratories for properties evaluation.

Physical Properties Evaluation on Modified Poly(1,2-butadiene):

The report by American Enka Co. on physical properties evaluation indicated that this series of modified polymers illustrate most convincingly the effect of the urazole unit in the polymer backbone in providing sites for physical crosslinking; in other terms, this series demonstrates without question that thermoplastic elastomer properties are imparted to these materials through the urazole unit. The results show that 5% TD modification doubles the elongation-to-break, the Young's modulus and tensile strengths. Tensile recoveries become greater than 90%, and stress decays of 42-53% are obtained. The results on other polymers evaluated are supportive of the above conclusions.

Preparation of Thermoplastic Elastomers of Low Tensile Strength, High Elongation and Low Mp and Tg:

On April 6, 1978, Mr. Henry Allen of the U.S. Army Missile Research and Development Command, Redstone Arsenal, Alabama 35809, visited our research center. Based upon discussions with him, a synthetic program designed to yield potentially useful materials having low tensile strength, high elongation, and low melting point and glass transition temperature was initiated.

Reactants and Abbrevations Used: B-Poly(butadiene)diol $\overline{M}_n$-2800; S/B-Poly(butadiene-co-styrene)diol (25% styrene) $\overline{M}_n$-2400; C-Poly(caprolactone)diol, $\overline{M}_n$-2000, mp 55°C: E-Poly(ethylene succinate)diol, $\overline{M}_n$-1100 mp 86°C. TDI = 2,4-diisocyanatotoluene; HDI = 1,6-hexamethylenediisocyanate; BHT - 2,6-di-tert-butyl-4-methylphenol (stabilizer) or antioxidant.

B and C were obtained from Scientific Polymer Products, Inc. S/B was obtained from Aldrich, and contained 25% by wt. of styrene. E was synthesized by reacting excess ethylene glycol with succinic anhydride. $\overline{M}_n$ was determined by VPO.

Using varying ratios of the above reactants, nineteen base polymers were prepared and evaluated. One of these polymers composed of B, 77.3%, E, 9.4%, S/B, 8.5% and chain-extended by HDI in an OH/NCO ratio of 1.3 was selected for modification studies with triazolinediones.

The Tg measured by DSC occurred around -80°C. The MW by GPC is between 31,600 and 14,100 with distribution occurring more on the lower MW range. When filled with 80% by wt. of NH_4ClO_4, the sample remained soft but retained structural shape. The molecular weight distribution could be reproduced repeatedly. The synthesis was repeated and modified with different triazolinediones,

as indicated below, using both 10% and 5% modifications. The preliminary evaluation results indicated that 5% modification is sufficient.

4-N-Substituted Triazolinediones Used in Modification Reactions and Abbreviations: R = CH_3-, MeTD: C_6H_5-, PhTD: CH_3-$(CH_2)_3$-, n-BuTD; CH_3-$C(CH_3)_2$-, t-BuTD: and CH_3-$(CH_2)_{17}$, $C_{18}H_{37}$TD.

The polymer can be modified with different triazolinediones separately and mixed together or modified with several triazolinediones simultaneously in order to obtain a broad spectrum of properties. Theoretically, 100% of the unsaturation in the polymer can be reacted but preliminary results indicate that the maximum percentage that yields modified products of suitable properties would be 10%.

Samples modified to the extent of 5% required the following times: R = CH_3-, 1 min; R - C_6H_5-, 1 min; R - n-butyl, 3 min; R = t-butyl, 20 min; and R = n-hexadecyl, 15 min. All samples are soluble in CH_2Cl_2. Eight samples (5 g each) were submitted for evaluation to: Cammander, U.S. Army Missile Research and Development Command, Attention: DRDMI-TKC (Henry Allen), Redstone Arsenal, Alabama, 35809.

(Sample code, polymer description, $\overline{M}_w$ GPC peaks) A, Unmodif. polymer, 31,600 and 14,000; B, 5% MeTD modif., 31,600 and 9,330; C, 5% PhTD modif., 1,700; D, 5% n-BuTD, 31,600 and 4,470; E, 5% t-BuTD, 35,500 and 13,500; F, 5% $C_{18}H_{37}$TD, 31,600 and 13,500; G, 10% n-BuTD, 26,900 and 5,010; and H, 10% $C_{18}H_{37}$TD, 28,100 and 7,410.

The GPC results showed that PhTD imparts better H-bonding efficiency in dilute solution than other triazolinediones as indicated by the shifting of MW to much lower value. However, in solid samples t-BuTD provides more reinforcement to the polymer.

Verbal communication with Redstone Arsenal indicated that evaluations of the above samples gave promising results, and on the basis of these tests, further modifications and larger samples were requested and submitted: B_{10} (10% MeTD modified), 5g; C_{10} (10% PhTD modified), 6.6g; G (same as above) 90g; and H (Same as above) 52g. Although no formal reporting of results was ever received during the course of this work, verbal communication with Redstone Arsenal personnel indicated promising results. Smaller samples of the above were also submitted to American Enka for physical properties studies. Only sample C_{10} gave a useful film in these tests

with the following results: Film thickness (mils): 3.6; tensile strength (kg/cm^2): 12; elongation-to-break (%): 500; initial modulus (kg/cm^2): 31; stress decay (%): 74; and tensile recovery (%): 60. The initial modulus is below the range of 100 desired. It is quite likely that this property will have to be increased by further modification.

In addition to the polymers and copolymers of conjugated dienes described above, a polypentenemer, derived *via* ring-opening polymerization of cyclopentene, and poly-*cis*-piperylene were modified with both MeTD and PhTD to the extent of 1,5,10, and 15%, and their thermal decomposition temperatures and glass transition temperatures were determined. Trends were similar to those previously reported with thermoplastic elastomer properties being apparent in the low ranges of modification of 1 - 5%.

Summary of Modified Polymer Samples Submitted for Evaluation:

No.	Laboratory	Evaluation Desired	Results
4	Borg Warner Corp.	Physical properties	Samples deteriorated
19	Redstone Arsenal	Propellant binder properties	No formal report
26	Redstone Arsenal	Propellant binder properties	No formal report
32	American Enka Co.	Physical properties	Results included in Paper No. 3 below.
4	Virginia Commonwealth University	Biological testing	Negative as anti-tumor agents

Papers Published:

Modification of Styrene Copolymers *via* the Ene Reaction, George B. Butler, A. Grady Williams, and Koon-Wah Leong, Polymer Preprints, 18, 11843 (1977).

Papers Presented:

Modification of Styrene Copolymers *via* the Ene Reaction, George B. Butler, A. Grady Williams, and Koon-Wah Leong, Macromolecular Secretariat, Symposium on Toughened Styrene Polymers, Polymer Division, American Chemical Society, New Orleans, LA, March, 1977.

Papers Submitted for Publication:

1. The Ene Reaction of Triazolinediones with Alkenes, I. Structure and Properties of Products, Shinichi Ohashi, Koon-Wah Leong, Kristoff Matyasjewski and G.B. Butler, J. Organic Chemistry.
2. The Ene Reaction of Triazolinediones with Alkenes, II. Kinetics and Substituent Effects, Shinichi Ohashi and G.B. Butler, J. Organic Chemistry.
3. Modification of Diene Polymers and Copolymers *via* the Ene Reaction With Triazolinediones, Koon-Wah Leong and G.B. Butler, J. of Macromol. Science-Chemistry.
4. Crosslinking of Diene Polymers *via* the Ene Reaction with Bis-Triazolinediones, Swayom P. Rout and George B. Butler, Polymer Bulletin (Special issue dedicated to the 60th birthday of Professor C.I. Simioneseu, Jassy, Romania, by invitation.)

General Conclusions

1. Time for reaction to reach completion ranges from a fraction of a minute to several minutes depending on the amount of triazolinedione used.

2. The % yield, in general, is in the range of 90-95%.

3. Polymers modified with more than 20% triazolinedione are insoluble in most organic solvents but they become more soluble in pyridine. When the % incorporation of triazolinedione exceeds 40%, the polymers become soluble in 10% NaOH.

4. The styrene/butadiene series has higher thermal stability (10° higher) than the styrene/isoprene series.

5. Polymers modified with PhTD have a yellow color and are brittle at high PhTD incorporation. Polymers modified with MeTD have white color and remain tough and not brittle at high MeTD incorporation.

6. The tensile moduli for the styrene/butadiene series modified with MeTD are higher than those modified with PhTD.

7. Triazolinedione modified diene polymers must be protected from oxidative conditions if they are to remain thermoplastic.

8. Further work must be done to establish the chemical mode of cross-linking (oxidative or chemical characteristics of the urazole unit).

9. The styrene block in the ABA block copolymer does not appear to be desirable in the development of thermoplastic elastomers of the type being studied.

10. Further work should be devoted to modification of cis-polyisoprene since the thermoplasticity range for these modified polymers is 0-10%.

11. Antioxidants should be used in all samples to be submitted for physical properties evaluation.

12. It now appears entirely feasible that suitable thermoplastic elastomers can be prepared by procedures utilized in the present investigation for use as propellant binders.

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APPENDICES

1. (Pages 1-16)

   The Ene Reaction of Triazolinediones with Alkenes. I. Structure and Properties of Products.

2. (Pages 1-18)

   The Ene Reaction of Triazolinediones with Alkenes. II. Kinetics and Substituent Effects.

3. (Pages 1-49)

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

4. (Pages 1-11)

   Crosslinking of Diene Polymers *via* Ene Reaction with Bistriazolinediones.

THE ENE REACTION OF TRIAZOLINEDIONES WITH ALKENES. I. STRUCTURE AND PROPERTIES OF PRODUCTS

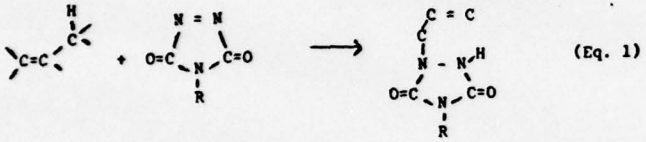
Shinichi Chashi, Koon-wah Leong, Kristoff Matyjaszewski, and George B. Butler+
Department of Chemistry and Center for Macromolecular Science, University of Florida, Gainesville, Florida, 32611

Summary

The structures of the ene products from reaction of triazolinediones with alkenes and polyisoprene were studied by using ^1H nmr. The pKa values of the ene products were measured. The reactivity and stability of the ene products were also studied.

Introduction

The ene reaction of 4-substituted-1,2,4-triazoline-3,5-diones (4-R-TD) with alkenes (Eq. 1) was first studied by Pirkle and Stickler[1] and 4-methyl-TD



(Eq. 1)

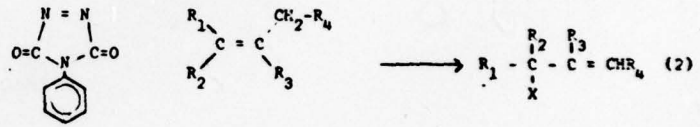
(MeTD) was found to be at least thirty thousand times more reactive toward cyclohexene than is ethyl azodicarboxylate. Saville[2] used this reaction for crosslinking of natural rubber. We[3, 4] have been successfully using this reaction for modification of polybutadiene, polyisoprene, and copolymers of butadiene and isoprene. However, no systematic studies on this reaction itself have been reported.

A study was undertaken to obtain fundamental background information on the ene reaction between TD and alkenes. In this paper we would like to report the structures of the ene products for a series of model compounds as well as for polyisoprene. We also wish to report pKa data and some reactions of the ene products.

Results and Discussion

Ene reaction between PhTD and alkenes: An excess (5-10 moles/1 mole PhTD) of the alkene was permitted to undergo reaction with PhTD in dichloromethane at room temperature. Usually the typical red color of PhTD was quickly discharged by mixing with the alkenes. After removal of solvent and recrystallization of the residual solids, pure ene products were obtained. The products from certain alkenes (especially 1-alkenes) required chromatographic purification to obtain high purity. The structures of the products were confirmed by ^1H nmr analysis and all alkenes which were studied gave normal ene reaction products. Yield and m.p. of these products are listed in Table I and ^1H nmr data are shown in Table II. In the case of alkenes which may give several isomeric structures, ^1H nmr of the crude product was also checked just after removal of solvent.

Alkenes 2 - 7 (Eq. 2) gave structures which could be predicted from the normal ene reaction. However, the purity of the products from 1-alkenes



(2)

1 2 - 7 8 - 13

	R_1	R_2	R_3	R_4
2, 8	H	H	H	H
3, 9	H	H	H	CH_3
4, 10	H	H	CH_3	H
5, 11	CH_3	H	H	H
6, 12	CH_3	CH_3	CH_3	H
7, 13	H	H	H	$CH_2CH_2CH_3$

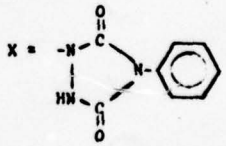


Table II

^{1}H NMR Data of Ene Products

δ ($CDCl_3$) ppm

Product			$-CH_2-$							
8					4.15, d[a]		5.27, w	5.9 , m	7.47, s	8.65, brs
9		1.70, d			4.17, d			5.73, m	7.52, s	8.9, brs
10		1.72, d			4.10, s		4.94, s		7.46, s	8.75, brs
11	1.35, d					4.80, m	5.15, m	5.83, m	7.47, s	8.4, brs
12	1.62, s	1.85, s					5.04, s		7.50, s	9.0, brs
13	0.85, t		1.37, m	1.99, q	4.13, d			5.65, m	7.48, s	9.0, brs
21	1.43, d	1.82, s				4.80, q	5.07, s		7.53, s	8.7, brs
26		1.72, s			4.20, d			5.28, t	7.48, m	8.8, brs
27		1.64, s			4.0 brm		4.87, brm		7.30, s	8.3, brs
33				2.70, t	4.05, d		4.7-6.05, m		7.40, s	9.0, brs
52			1.85, m	1.98, m		4.85, s		5.83, m	7.52, s	

[a] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Table I

Ene Reaction[a] of Alkenes with PhTD
Yield and mp of Products

Alkene	Product	Yield[b] (%)	mp (°C)
2	8	54	116.5-117.5
3	9	58	129 -130
4	10	86	105 -106
5	11	80	99 -100
6	12	88	130 -131
7	13	38	111 -112
14	15 + 16	85	77 - 78
17	18 + 19	38	78 - 79
20	21	97	147 -148.5
22	23 + 24	76	106 -107
25	27	--	85 - 87
32	33	87	102 -105
51[c]	52	89	171 -172

[a] Reaction in dichloromethane at room temperature. [Alkene]/[PhTD] = 5-10

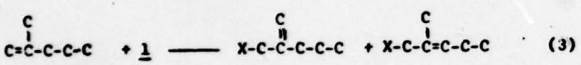
[b] After complete purification

[c] [Diene]/[PhTD] = 28

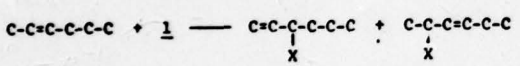
(2, 3, and 7) was low so that chromatographic purification was necessary. This fact suggests the possibility of a secondary 1:2 reaction and possibly some other side reactions; however, the presence of these side products was not detectable by ^1H nmr analysis. On the other hand, 2-methyl-1-pentene (14) (Eq. 3) gave products consisting of almost equal amounts of 15 and 16 in spite of the stability of the internal olefin. trans-2-Hexene (17) (Eq. 4) gave a slight excess of the internal olefin (18:19 = 2:3). However, 2-methyl-2-butene (20) (Eq. 5) gave only one product, 21. PhTD also attacked 1-methyl-1-cyclohexene (22) (Eq. 6) exclusively at the 2-position and the ratio between two isomers, 23 and 24 was 1:1.

Although 26 would be predicted to be the only product from the reaction between 1 and 25 (Eq. 7), the reaction product was a mixture. After chromatographic purification, it was found that more than 80% of the product was the 1:2 adduct, 27. In the case of 3-methyl-1-pentene (28) (Eq. 8), the product was a mixture of 25% of 1:1 adduct, 29, and 75% of the 1:2 adducts 30 and 31.

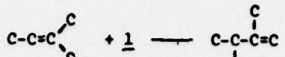
1,5-Hexadiene (32)(Eq. 9) also underwent reaction with PhTD at a molar ratio of 28:1 to yield a 1:1 ene product, 33. If 32 were reacted with PhTD at a molar



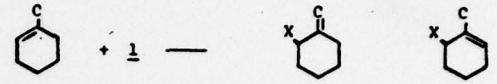
14 15 16 (3)



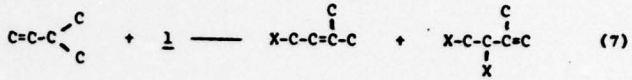
17 18 19 (4)



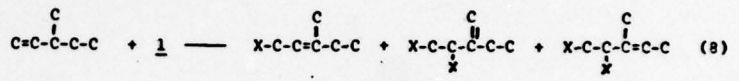
20 21 (5)



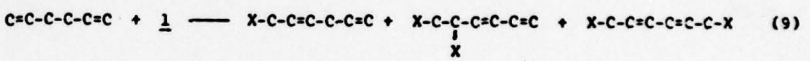
22 23 24 (6)



25 26 27 (7)



28 29 30 31 (8)



32 33 34 35 (9)

ratio of 1:2, a complicated mixture was obtained; however, the major product appears to have structure, 34, instead of the symmetrical one, 35. Theoretically, a normal Diels-Alder reaction could occur after the two ene reactions to form a 1:3 adduct. This was not observed, probably due to steric effects.

From a qualitative comparison of the rate of color discharge of PhTD, the order of reactivity of the alkenes appears to be as follows:

2, 3, 7 < 5, 14, 17 ≪ 20 ≪ 6

This order suggests that reactivity of the alkene increases markedly with increased substitution at the carbon-carbon double bond of the alkene. Taking this fact into consideration, the result that 25 and 28 gave more 1:2 adduct than 1:1 adduct can be easily understood. Since 25 and 28 are 1-alkenes, their reactivity is very low. On the other hand, the 1:1 adducts (26 and 29) have similar structure to that of 18 and are expected to have relatively high reactivity. Usually, the second addition is not fast enough to give an appreciable amount of the 1:2 adduct (for example 7, 17). However, in this case, once the 1:1 adduct is formed, it seems to react with another PhTD even faster than the starting alkene. The reason why 34 is the major 1:2 adduct from 32 can be also explained by comparing the reactivity of two double bonds in 33.

Structure of polymers modified with triazolinedione: Usually ^{1}H nmr spectra of polymers modified with TD are too complicated to give sufficient information for structural determination. However, if we use the results of the model studies, we can predict the structure reasonably well. 1,4-cis-Polyisoprene (36)(Eq. 10) has possibilities to give several different structures by reaction with TD. But, the results from 20 and 22 suggest that only two structures, 37 and 38, are formed. Furthermore, 39 seems to be the only 1:2 adduct formed, because 37 would be predicted to be much more reactive than 38. Based on these assumptions, we tried to calculate the ratio of each structure for 1,4-cis-polyisoprene modified with MeTD. Those peaks between δ 1-3, which should arise from allylmethyl,

allylmethylene, and N-methyl proton, were used for the calculation. The results are shown in Table III. The presence of structure, 39, was neglected in method A and considered in method B.

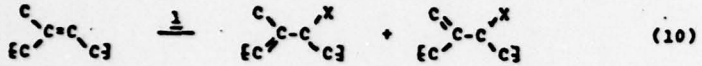
In spite of the complexity of the spectra, the ratio between 37 and 39 was found to be very close to 1:1 and very good agreement with the model study was obtained in method A. In method B, the ratio of 39 was much higher than that expected from the model study, which means that the presence of structure 39 can be neglected at lower extent of modification.

In the cases of 1,4-cis or trans-polybutadiene (41)(Eq. 11) and 1,2-polybutadiene (44), the structures can be predicted more easily. Structure 41 will give mostly 42 and only a small amount of 43 at the higher extent of modification. Structure 44 (Eq. 12) will give more of 1:2 adduct 46, because of the high reactivity of structure 45.

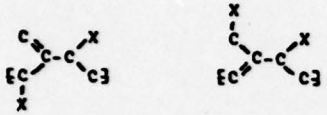
The pKa of ene products: The urazole derived via the ene reaction of TD with alkenes has one NH proton, which seems to be very acidic. Actually we[3] have observed that polymers modified with TD are soluble in alkaline solution if the extent of modification is 40-50% or more. So the measurement of pKa of the ene products was considered to be very important to provide information on the properties of modified polymers.

The pKa of ene products was measured by using an acid-base titration method. As most of the ene products are not soluble in pure water, an N,N-dimethylformamide-water mixed solvent was used and the pKa in pure water was estimated by extrapolation method. The resutls are shown in Table IV.

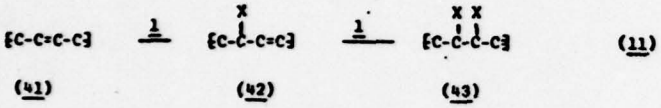
As expected, these compounds are quite strongly acidic and the pKa of 8 is almost the same as that of acetic acid. The increase of the number of substituents on the alkenyl group causes a decrease of acidity, but the difference is not so pronounced. Thus, polymers modified with TD are expected to have similar acidity to that of polyacrylic acid.



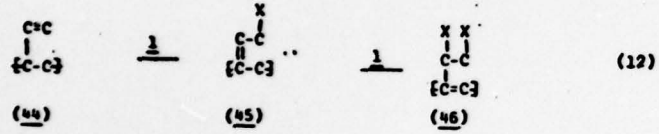
(36) (37) (38) (10)



(39) (40)



(41) (42) (43) (11)



(44) (45) (46) (12)

Table III
Structure of 1,4-cis-Polyisoprene Modified with MeTD

Extent of Modification %	Method A		Method B		
	37 %	38 %	37 %	38 %	39 %
12.8	43	57	--	--	--
22.1	47	53	--	--	--
38.2	58	42	38.5	30.5	31
44.7	50	50	39	41	20
55.6	62	38	42	25	33
100.0	--	--	43.5	30.5	26

Table IV

pKa of PhTD-Alkene Ene Products

Compounds	pKa[a] in water	pKa[a] in DMF-water (1/1)
8	4.71	5.97
10	(4.80)[b]	6.05
21	(4.86)	6.16
12	(5.33	6.72
52	(5.10)	6.31
Phenylurazole	5.29	6.44

[a] Measured at 25°C

[b] Values in parentheses were obtained by extrapolation

Reactivity of ene products: In order to get further information on the stability and reactivity of modified polymers, reactions of the NH group and carbon-carbon double bond were studied by using model compounds.

As would be expected from its pKa value, the NH group of the ene product is very reactive. Compound 8 reacts with acetic anhydride at room temperature to give an N-acetyl compound (47)(Eq. 13). Compound 8 also reacts with methyl iodide in the presence of potassium hydroxide (eq. 14) and with phenyl isocyanate in the presence of triethylamine as catalyst (eq. 15). These reactions could be useful for further modification of TD modified diene polymers and TD copolymers.[5]

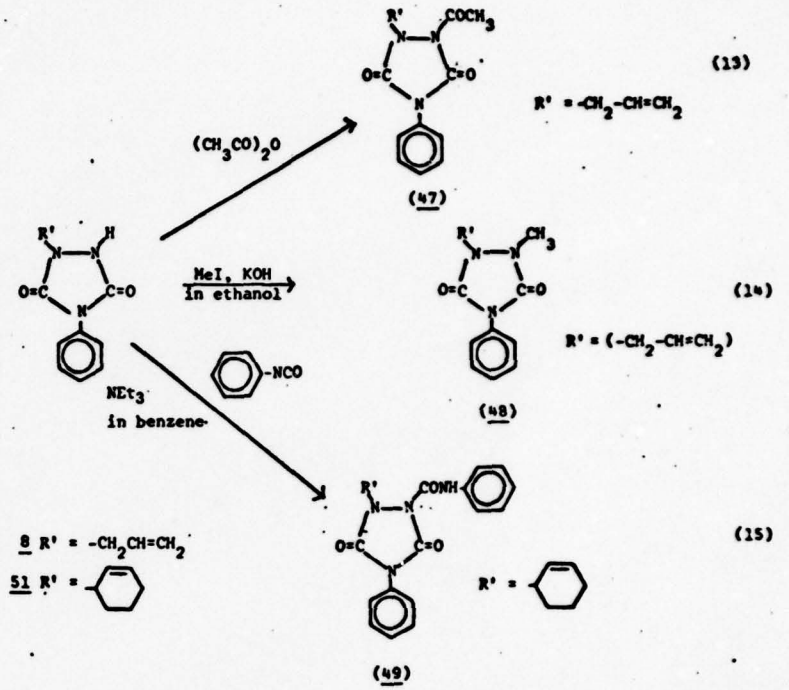
The ene product still possesses a carbon-carbon double bond, which should have interesting reactivity. This double bond can undergo reaction with bromine or another TD molecule. However, the reactivity is much lower than that of the corresponding simple alkene. N-Acetylated compound 47 (Eq. 16) yielded epoxy compound 50 by the action of m-chloro peroxybenzoic acid. Compound 50 could be useful as another type of monomer or modifier which has a urazole ring.

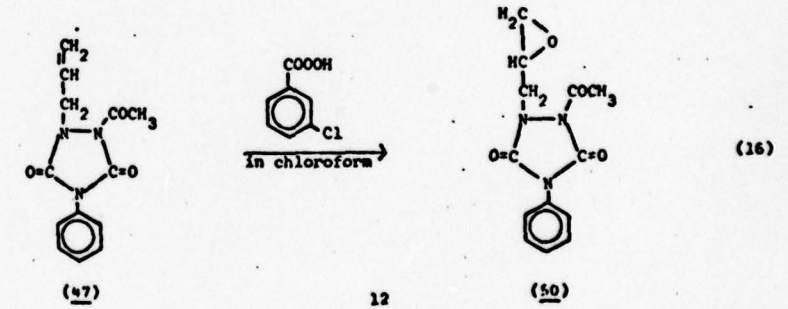
These ene products were found to be very stable. The ene product of cyclohexene with PhTD, 51, was heated in 3N potassium hydroxide methanol-water (3/1 v/v) solution at 110°C for 46 hrs or treated with dinitrogen tetroxide at room temperature to result in only the recovery of 51. However such an N-methylated compound as 48 was completely hydrolyzed by the action of potassium hydroxide at 110°C.

From these results, it can be concluded that polymers modified with TD have a homogeneous structure as long as the extent of modification is not too high and that these polymers can be converted to the polyanion which would be very stable even under strongly basic conditions.

Experimental

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H nmr spectra were taken on a Varian A-60A spectrometer.





A Corning pH meter 125 was used for pH measurement. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Ene reaction and isolation of products: The alkene was dissolved in or bubbled into dichloromethane (ca. 0.1 mol/l) and TD in the same solvent (ca. 0.01 mol/l; alkene/TD = 5-10 mole/mole) was added slowly to the alkene solution with stirring. After complete discharge of the red color of TD, the solvent was removed on a rotary evaporator. The residual slightly yellow oil or solid was purified by recrystallization from benzene-hexane or by column chromatography (silica gel).. Yield and mp of these products are shown in Table I and ^1H nmr data are shown in Table II.

The ratios of isomers for the products from alkenes 14, 17, 20, 22, 25, 28, and 32, were determined by comparing two peaks which are assigned to vinyl and vinylene protons, respectively, in ^1H nmr spectra.

Modification of 1,4-cis-polyisoprene by MeTD - 0.97 g of polyisoprene was dissolved in 40 ml CH_2Cl_2 during 20 hrs. MeTD (0.38 g) was dissolved in 9.3 ml DMSO-d_6. To a known amount of the polymer solution, the solution of MeTD was added dropwise during stirring, keeping the solution slightly pink. The color disappeared in less than 5 min. when less than an equimolar amount of MeTD was added. No precipitation was observed. Dichloromethane was removed on a rotary evaporator and DMSO-d_6 solutions of modified polymers were tested by ^1H nmr. When the polymer was modified to an extent of less than 20% it was insoluble in pure DMSO. Thus chloroform-d (30 v/v%) was added to give a homogeneous solution.

Nmr analysis was used to assign structures for the modified polymers.

pKa Measurement: The ene product (ca. 5×10^{-4} mole) was weighed accurately into a 100 ml beaker and dissolved in 50 ml of deionized water. In the case of DMF-water mixed solvent, the sample was first dissolved in DMF and then water was added to adjust the volume. The electrode of the pH meter was dipped into this solution, which was maintained at 25.0°C using a water bath. The pH of

the solution was measured after each addition of 0.5 ml of 0.08 N aqueous sodium hydroxide solution. The pKa was calculated at each point by using Eq. 17 and these values were averaged. In the case of the compounds which are insoluble in pure water, the pKa in 10%, 30%, and 50% DMF-water was measured and the pKa in pure water was estimated by extrapolation.

$$pKa = pH + \log([AH]_{st} - [H^+] + [OH^-] - \log([A^-]_{st} + [H^+] - [OH^-]) \quad \text{Eq. 17}$$

1-(2-Propenyl)-2-acetyl-4-phenyl-1,2,4-triazolidine-3,5-dione (47)

- 2.28 g (10.5 mmole) of 8 was dissolved in 50 ml acetic anhydride and left at room temperature overnight. Excess acetic anhydride and acetic acid were removed on a rotary evaporator and the residue was dried in vacuo. After chromatography (silica gel) and recrystallization from benzene-hexane, 2.1 g (77%) of 47 was obtained: mp 103-104°C; nmr ($CDCl_3$) δ 2.58 (s, 3), 4.60 (d, 2), 5.27 (d, 1), 5.30 (d, 1), 5.83 (d,d,t,1), 7.47 (s, 5).

Anal. Calcd. for $C_{13}H_{13}N_3O_3$: C, 60.22; H, 5.05; N, 16.21.

Found: C, 60.21; H, 5.09; N, 16.19.

1-(2-Propenyl)-2-methyl-4-phenyl-1,2,4-triazolidine-3,5-dione (48) - 0.75 g of potassium hydroxide was dissolved in 50 ml ethanol and 2.5 g (11.5 mmole) of 8 was added to this solution. After complete dissolution, 3.5 ml methyl iodide was added and the mixture was left at room temperature overnight. After separation of salt, ethanol and excess methyl iodide were removed on a rotary evaporator. The residual oil was dissolved in ethyl acetate, washed with water and dried with sodium sulfate. After removal of ethyl acetate, the product was purified by column chromatography (silica gel) and 2.64 g (82%) of colorless oil was obtained.

NMR ($CDCl_3$) δ 3.22 (s, 3), 4.27 (d, 2), 5.32 (d, 1), 5.33 (d, 1), 5.92 (d, d, t, 1), 7.47 (m, 5).

Anal. Calcd. for $C_{12}H_{13}N_3O_2$: C, 62.32; H, 5.67; N, 18.17.

Found: C, 62.13; H, 5.73; N, 18.10.

1-(2-Cyclohexenyl)-2-(N-phenylaminocarboxy)-4-phenyl-1,2,3-triazolidine-3,5-dione (49) - 0.52 g (2 mmole) of 51 was dissolved in 10 ml benzene, and 0.45 ml phenyl isocyanate and 2 drops of triethylamine were added to the solution. After 1 day, solvent was removed on a rotary evaporator and the residual solid was recrystallized from benzene-hexanes.

NMR ($CDCl_3$) δ 2.67 (s, 3), 2.70 (d, d, 1), 2.86 (d, d, 1), 3.22 (m, 1), 3.97 (d, d, 1), 4.38 (d, d, 1), 7.51 (s, 5).

Anal. Calcd. for $C_{13}H_{13}N_3O_4$: C, 56.72; H, 4.76; N, 15.27.

Found: C, 56.89; H, 4.82; N, 15.30.

1-Glycidyl-2-acetyl-4-phenyl-1,2,3-triazolidine-3,5-dione - To 1.04 g (4 mmole) of 47 dissolved in 15 ml of 1,2-dichloroethane (DCE), 0.89 g of m-chloroperoxybenzoic acid in 20 ml $CHCl_3$ was added. The mixture was kept at room temperature for 3 hrs and then heated at 70°C overnight. After cooling, the mixture was treated with sodium sulfite to remove excess peroxide and then washed with 5% sodium bicarbonate, followed by drying with sodium sulfate, and the solvent removed. The residue was purified by column chromatography (silica gel) and recrystallized from benzene-hexanes to yield 0.62 g (56%) of white crystals: m.p. 116-119°C.

NMR ($CDCl_3$) δ 2.1 (brm, 6), 4.9 (brm, 1), 5.85 (brm, 2) 7.48 (m, 10), 9.55 (brs, 1).

Acknowledgements

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THE ENE REACTION OF TRIAZOLINEDIONES WITH ALKENES, II. Kinetics and Substituent Effects

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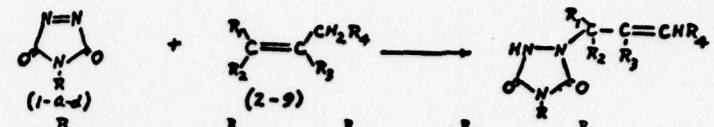
Summary

The kinetic measurements for the reaction of 4-R-1,2,4-triazoline-3,5-diones(4-R-TD, R = Ph, Me, p-$MeOC_6H_4$, p-$NO_2C_6H_4$) with alkenes have been undertaken. The reactivity of alkenes was found to be very sensitive to substituent effects. The effects of solvent and substituent on TD were small. In the reaction of TD with ene products, side reactions as well as second-step ene reactions were observed. The reactions of 1-alkyl-4-phenyl-1,2,4-triazolidine-3,5-diones were investigated and the reaction products were isolated.

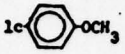
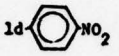
Introduction

Since Pirkle and Stickler[1] reported the high reactivity of 4-substituted-1,2,4-triazoline-3,5-diones (TD) as an enophile, the ene reaction of TD (eq. 1) has been used for synthesis of hydrazine derivatives,[2] synthesis of copolymers with styrene[3] and modification of polydienes.[4, 5] However, no systematic studies on this reaction have been reported.

In the previous paper, we[6] have reported the structure of ene products obtained from a series of alkenes as well as polyisoprene. In this paper, we would like to report the results of kinetic studies on the ene reaction of TD with a series of alkenes. Kinetic measurements have been made for the ene reaction of four different TDs (1a-b) with various alkene structures (2 - 9). The effect of the alkene structure as well as that of the TD, and also the effect of solvent on the reaction rate have been studied. The reaction of TD with the ene product was also studied and the mechanism of the second step reaction is discussed.



(1)

R		R_1	R_2	R_3	R_4
1a - 	2	H	H	H	$CH_2CH_2CH_3$
	3	H	H	CH_3	C_2H_5
1b $-CH_3$	4	H	CH_3	H	C_2H_5
	5	H	C_2H_5	H	CH_3
1c 	6	CH_3	CH_3	H	H
	7	CH_3	CH_3	CH_3	H
1d 	8	R_1-R_4 = $-CH_2CH_2CH_2-$; R_2=R_3=H			
	9	R_1-R_4 = $-CH_2CH_2CH_2-$; R_2=CH_3; R_3=H			

Results and Discussion

Reactivity of Alkenes and Triazolinediones

The reactivities of C_5 and C_6 alkenes in the ene reactions with TD were examined by measuring the reaction rates. The reaction of TD with an excess of alkene ([alkene]/[TD] = 5) was carried out in a UV cell using benzene as solvent. The decrease of absorbance was recorded by use of a UV -visible photometer. It has been confirmed that under such conditions only the 1:1 reaction product is formed, especially during the early stages of the reaction.[5]

The reaction was treated as a second-order reaction. The second order rate constant, k_2, and the reactivity ratio (based on trans-3-hexene, 5) are shown in Table I. As shown in the table, the reactivity of alkene was markedly dependent on the structure. 1-Alkene (2) was the least active and one substituent on the double bond increased the reactivity 10-20 times. Further substitution on the double bond increased the reactivity extraordinarily and the reactivity of 2,3-dimethyl-2-butene (7) was too high to measure the reaction rate by the method used here. In the ene reaction of ethyl azodicarboxylate with C_4 and C_5 alkenes, a similar increase of reactivity of the alkenes was

observed.[7] However, in that case, the difference of reactivity was very small and the reactivity ratio of 2-methyl-2-butene (6) and 2-methyl-1-butene based on 1-pentene was 4.33 and 3.64, respectively. The reactivities of cyclohexene (8) and 1-methyl-cyclohexene were much lower than those of the corresponding linear alkenes (3 and 6).

As for the reactivity of TD, p-nitrophenyl-TD (1d) was the most reactive and methyl-TD (1b) was the least reactive. Ph-(1a) and p-methoxyphenyl-TD (1c) showed similar reactivity. These results are quite reasonable if we consider the electron-donating or withdrawing effect of the substituents at the 4-position of TD. A similar order of TD reactivities was also observed in the ene reaction by Butler and Williams[8] and in the Diels-Alder reaction by Burrage, Cookson, Gupte, and Stevens.[9] The effect of structures of alkenes on k_2 was almost the same for all four triazolinediones studied.

In methylene chloride the reaction was about five times as fast as that in benzene. Since TD decomposes slowly in this solvent, accurate measurement of k_2 was not easy for such an inactive alkene as 2. However, quite similar tendencies were observed concerning the reactivity ratio of alkenes and reactivity of triazolinediones.

In order to get further information on the reaction mechanism, the effect of solvent was examined. 1,2-Dichloroethane,(DCE), tetrahydrofuran (THF), ethyl acetate and nitrobenzene as well as benzene and dichloromethane were used as solvents. In nitrobenzene, dichloromethane, and tetrahydrofuran 1a decomposed gradually, so the rate constants in these solvents were corrected for such decomposition. The results are shown in Table II.

Solvent effects, in general, were small. Even in such a polar solvent as nitrobenzene k_2 was not greatly different from that in benzene. The reaction in THF and ethyl acetate was slower than that in other solvents. As shown in Table IV, λ_{max} of TD in THF and ethyl acetate is almost 15 nm lower than λ_{max} in benzene. This result indicates the strong interaction between TD and

Table I

Ene Reaction[a] of Triazolinedione Second-Order Rate Constant

Olefin	$10^2 \times k_2$ (1/mol·sec) Benzene -R				Methylene Chloride -R			
		-CH_3	-OCH_3	-NO_2		-CH_3	-OCH_3	-NO_2
2	0.29 (0.08)[b]	0.13 (0.09)	0.28 (0.10)	0.94 (0.07)	1.1 (0.07)		13.8 (1	
4	3.54 (1.03)	1.77 (1.24)	3.30 (1.15)	14.3 (1.10)	16.5 (1.01)	7.8 (1.13)	13.8 (1.05)	75.6 (1.07)
5	3.44 (1.00)	1.43 (1.00)	2.87 (1.00)	13.0 (1.00)	16.4 (1.00)	6.9 (1.00)	13.1 (1.00)	70.4 (1.00)
3	5.46 (1.59)	1.95 (1.36)	4.39 (1.53)	17.8 (1.37)	21.1 (1.29)	9.4 (1.36)	18.0 (1.37)	95.4 (1.36)
6	157.3 (45.7)	47.8 (33.4)	115.0 (40.1)	609.0 (46.8)	c	300 (43.5)	c	c
8	1.12 (0.33)	0.56 (0.39)	0.93 (0.32)	4.37 (0.34)	5.4 (0.33)	2.5 (0.36)	4.4 (0.34)	25.5 (0.36)
9	7.86 (2.28)	2.64 (1.85)	6.22 (2.17)	36.6 (2.82)				

[a] At 25°C, [b] The values in parentheses are reactivity ratios based on 5., [c] The reaction was too fast to measure by the method used.

Table II

Reaction of PhTD with Alkenes[a] Solvent Effects on Second-order Rate Constants

Solvent \ Olefin	$10^2 k_2$ (l/mol·sec) 5	4	3	6
Dichloromethane	16.4 (1.0)[b]	16.5 (1.0)	21.1 (1.3)	c
1,2-Dichloroethane	14.4 (1.0)	15.3 (1.1)	20.4 (1.4)	c
Benzene	3.44 (1.0)	3.54 (1.0)	5.46 (1.6)	157 (45.6)
Nitrobenzene	5.18 (1.0)	5.82 (1.1)	7.57 (1.5)	208 (40.2)
Ethyl Acetate	0.46 (1.0)	0.51 (1.1)	0.65 (1.4)	16.5 (35.9)
Tetrahydrofuran	0.32 (1.0)	0.38 (1.2)	0.39 (1.2)	9.58 (29.9)

[a] At 25°C., [b] The values in parentheses are reactivity ratios based on 5., [c] The reaction was too fast to measure by the method used.

solvent, which seems to cause the lower reactivity of TD. Also, this interaction between TD and solvent seems to affect the reactivity ratio of alkenes. The reactivity ratio of 6 in these solvents is obviously lower than that in benzene.

Considering such a small effect of solvent and the results of studies on the structure of ene products,[6] it appears that the reaction proceeds via a concerted mechanism.

Second Step ene Reaction

The ene products of alkenes with TD still have carbon-carbon double bonds, which may react with another TD. In the reaction of TD with inactive alkenes like 2, the presence of unknown impurities suggested the possibility of other side reactions. In order to investigate these possibilities, the reaction of TD with 1:1 ene product[6] was studied.

Figure 1 shows the time-conversion curves for the reaction of 1a with ene products. Although the reactivity of most of the ene products was lower compared with that of the corresponding simple alkenes, they obviously undergo reaction with another TD. However, the reaction was so complicated that rate constants could not be calculated.

Among the 1:1 ene products, those obtained from 1-alkenes showed reasonably high reactivity. Especially, the product from propylene (10) showed comparable reactivity with that of propylene itself. If we consider the order of reactivity of alkenes shown in Table I, the results are rather unusual. Furthermore, all attempts to isolate the reaction products always resulted in failure. These reactions gave very complicated mixtures even in such a simple reaction as that of propylene adduct (10) with 1a and no evidence for 1:2 ene reaction was obtained.

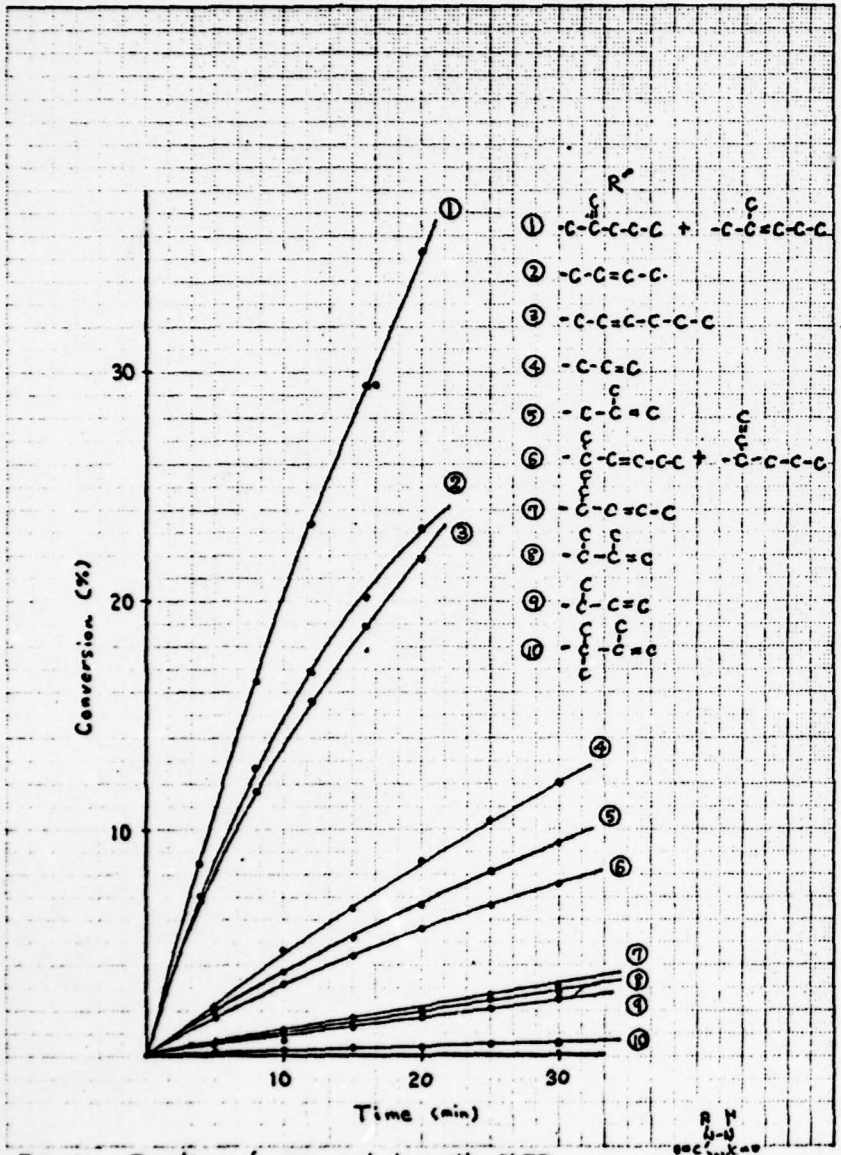
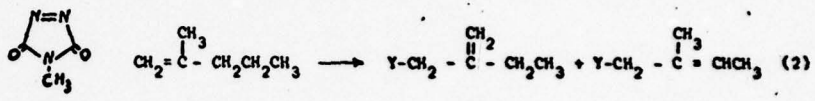


Fig. 1 ... Reaction of ene products with PhTD in benzene at 25 °C [PhTD] = 4.60 × 10^{-3} mol/l, Cene products] = 2.30 × 10^{-2}

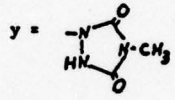
It is well known that TD has high ability for hydrogen abstraction. TD reacts with hydrazine derivatives[10] and alcohol,[11] and even with ethers[13] like THF or diethylether. Taking this fact into consideration, it seems more probable that TD reacts with the NH hydrogen of urazole ring.

In order to prove this possibility, the NH group of 10 was substituted by the acetyl group (11) or the methyl group (12). As expected, 11 and 12 showed no detectable reactivity toward 1a (Fig. 2, No. 4 and No. 5).

The reaction of 1b with 3 (Eq. 2) gave two isomers, 13 and 14, in the ratio of 1:1. Structures 13 and 14 were separated from each other by recrystallization. The results of the reaction of 13 and 14 are shown in Fig. 3 with that of the product (15) from 1a and 3. In the case of these compounds, even



1b 3 13 14 (2)



the acetylated compounds (16, 17, and 18) reacted with PhTD. The reaction product (19 + 20) from 1a and 17 was purified by column chromatography and confirmed to be the 1:2 ene product. The ratio between 19 and 20 was found to be 3:2 from nmr analysis. These reactions were treated as second-order reactions and k_2 values for 16, 17, and 18 were 1.07x10^{-3}, 2.23x10^{-2} and 4.3x10^{-4} l/mol·sec, respectively. By comparing the reactivity of 17 and 18 with that of 6 and 4, respectively, we can estimate that the substitution at the allyl position by the urazole ring causes the decrease of reactivity by 1/50 or less. The reaction of isoprene with 1a gives the Diels-Alder product,

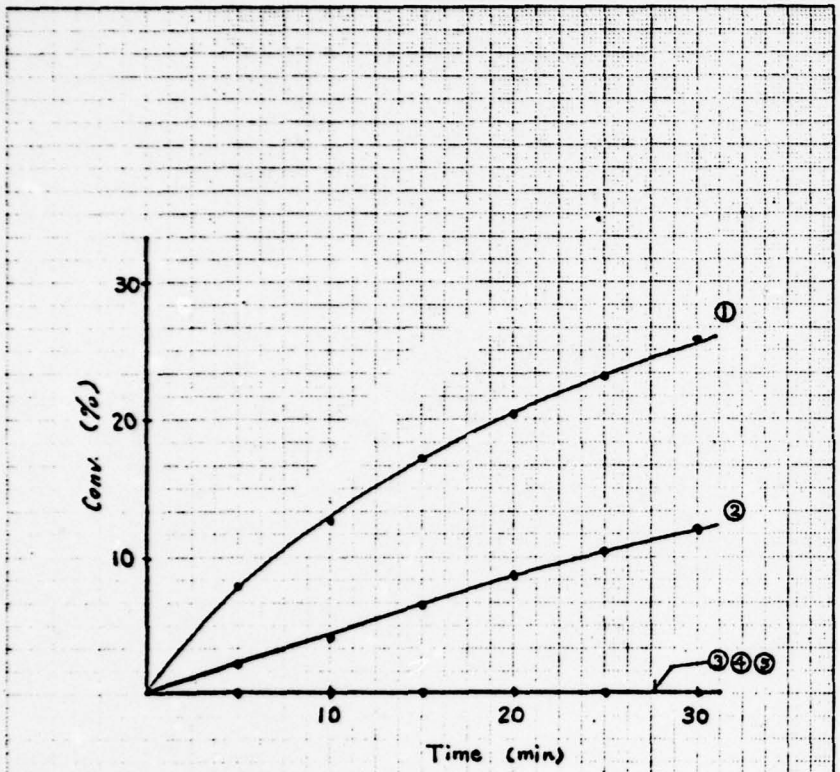
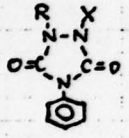


Fig. 2 Reaction of PhTD with N-Substituted Urazole



	R	X
①	$-CH_2-CH_2-CH_3$	H
②	$-CH_2-CH=CH_2$	H
③	$-CH_2-CH_2-CH_3$	$-COCH_3$
④	$-CH_2-CH=CH_2$	$-COCH_3$
⑤	$-CH_2-CH=CH_2$	$-CH_3$

in ~~1,2-dichloroethane~~ benzene at 25°C

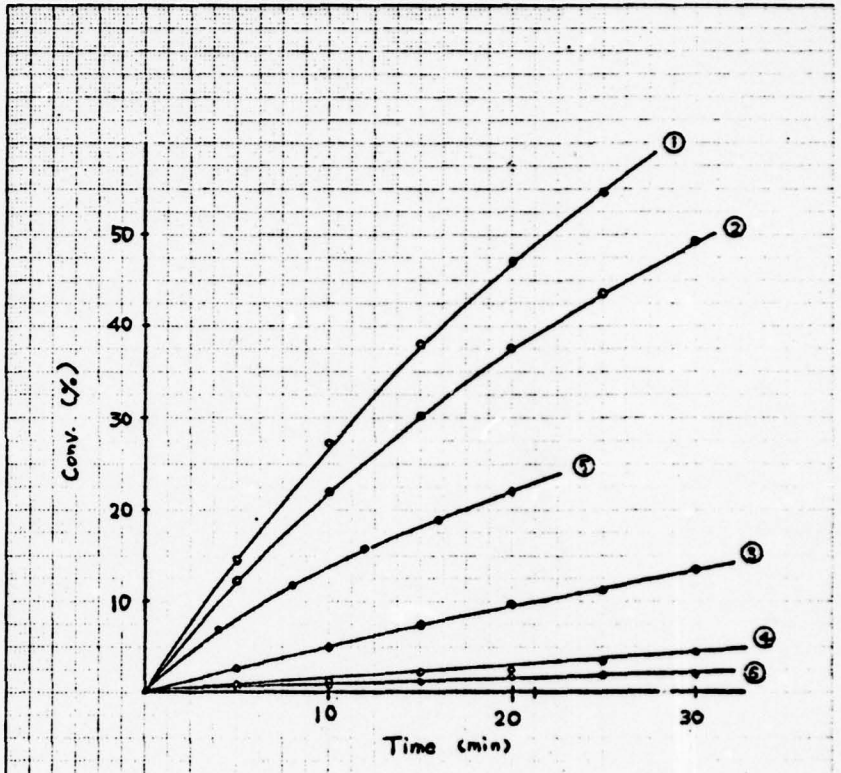
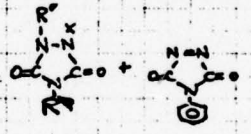
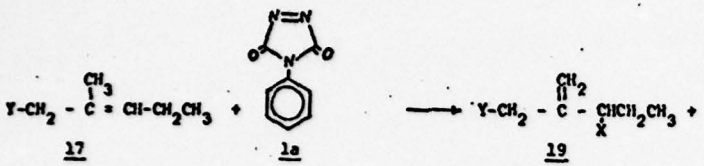


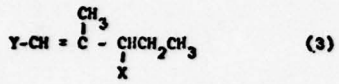
Fig. 3 Reaction of PhTD with Ene Products in benzene at 25°C



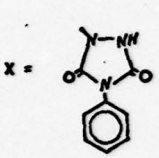
	R	R′	X
①	$-CH_3$	$-C-C=C-C-C$	$-H$
②	$-CH_3$	$-C-C=C-C-C$	$-COCH_3$
③	$-CH_3$	$-C-C-C-C-C$	$-H$
④	$-CH_3$	$-C-C-C-C-C$	$-COCH_3$
⑤	⬡	$-C-C=C-C-C-C$	$-H$
⑥	⬡	$-C-C=C-C-C-C$	$-COCH_3$

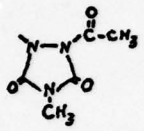


17 1a 19



20 (3)





which has a similar structure to 9. But this compound showed no reactivity toward TD, probably because the deactivation effect of the urazole ring is even stronger than that in the case of 17.

Reaction of 1-Alkyl-4-phenyl-1,2,4-triazolidine-3,5-dione with PhTD

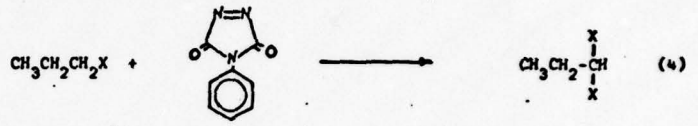
As described above, it was found that side reactions were caused by the presence of the NH group of the ene products. However, the reaction between the ene products and 1a was so complicated that the structure of the products could not be determined.

In order to simplify the system, 1-propyl-4-phenyl-1,2,4-triazolidine-3,5-dione (1-propyl-4-phenylurazole, 21) was synthesized by the reaction of 1-iodopropane with the potassium salt of 4-phenylurazole and permitted to react with 1a in benzene. Structure 21 does not have a carbon-carbon double bond, so only the reaction between NH and 1a was expected to occur.

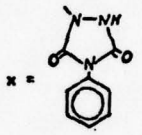
As shown in Fig. 2, 21 reacted with 1a even faster than 10. On the other hand, the N-acetylated derivative (22) of 27 did not react with 1a.

In order to determine the structure of the reaction product, an equimolar reaction between 21 and 1a was carried out in DCE at 60°C. The reaction gave white crystals (25), which are soluble in DMSO and slightly soluble in acetone and water, in very high yield (ca. 85%). The same reaction at room temperature also gave 25 in high yield, however, the reaction was very slow (after 10 days, the solution was still red). Nmr analysis of 25 indicated the structure shown in Eq. 4. Elemental analysis also supported this structure.

In the reaction of 1-ethyl-4-phenylurazole (23) with 1a the same type of product was obtained. On the other hand, the reaction of 1-methyl-4-phenyl-



21 1a 25 (4)



urazole (24) with 1a was much slower than that of 21 or 23. ^{1}H nmr peaks of the product from 24 was very broad and a very small peak for methyl protons was observed.

1a is reported to form adducts with ether[12] by heating or irradiation with UV light ($\lambda > 313$ nm) and with 1,3-dimethyluracil[13] by heating. However, 22 did not react with 1a which suggests that the reaction mechanism of 21 with 1a is different from these examples. 1a is also known to react with hydrazine derivatives or 4-phenylurazole to form radicals. In the case of 21, the NH group appears to react or at least to have a very strong interaction with PhTD. This reaction or interaction would make the hydrogen abstraction

from the methylene group adjacent to the urazole ring easier.

In the case of 24, hydrogen abstraction from the methyl group appears to be more difficult and the radical which is formed by hydrogen abstraction appears to react by different ways. Structure 10 has a carbon-carbon double bond, which seems to make the reaction of the radical much more complicated.

Experimental

Visible spectra were recorded on a Beckman ACTA V photometer. ^1H nmr were obtained by use of a Varian A-60 spectrometer. All melting points were taken on a Thomas Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc. Atlanta, Georgia.

Preparation of the triazolinediones - 4-Substituted-1,2,4-triazolidine-3,5-diones (4-R-urazole) were synthesized according to the procedure described in ref. 14. These urazoles were dispersed in dichloromethane with anhydrous sodium sulfate and oxidized at 0°C by bubbling dinitrogen tetroxide[15] to give 4-R-1,2,4-triazoline-3,5-diones (1a-d). These triazolinediones were purified by sublimation under reduced pressure. λ_{max} and ε in the visible region are shown in Tables III and IV.

Kinetic measurements - Alkene solution (1 ml) and 2 ml of TD solution were mixed in 1 cm cubic UV cell. The TD absorbance at λ_{max} in visible region was measured vs time. The reaction was determined to be second order overall by fitting the data to Eq. 5.

$$\log\left(1+\frac{K}{A_t}\right) = \frac{b-a}{2.30}k_2 t = \log\frac{b}{a} \qquad (5)$$

In Eq. 5, A_t=absorbance at time t, A_0 = initial absorbance, a = initial concentration of TD, b = initial concentration of alkene, k_2 = second-order rate constant and $K = \frac{b-a}{a}A_0$.

Table III

Visible Absorption of 4-R-1,2,4-Triazoline-3,5-dione in Dichloromethane and Benzene

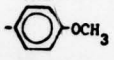
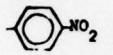
R \ Solvent	Dichloromethane		Benzene	
	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}
$-CH_3$	537.5	185.9	540	247.0
	546	160.0	543.5	240.7
	549	181.5	546	242.9
	540	170.9	541	240.7

Table IV

Visible Absorption of 4-Phenyl-1,2,4-triazoline-3,5-dione

Solvent	λ_{max} (nm)	ε_{max}
Dichloromethane	546	160.0
1,2-Dichloromethane	544.5	183.0
Benzene	543.5	240.7
Nitrobenzene	538	178.8
Ethyl Acetate	531	170.8
Tetrahydrofuran	528	171.9

The products

The 1:1 ene products of PhTD with alkenes were prepared according to the procedure described in Ref. 6.

1-(2-Methylenepentyl)-4-methyl-1,2,4-triazolidine-3,5-dione (13) and 1-(2-methyl-2-pentenyl)-4-methyl-1,2,4-triazolidine-3,5-dione (14). - To 10.3 g (0.12 mole) of 2-methyl-1-pentene in 100 ml of 1,2-dichloroethane (DCE) 2.80 g (0.025 mole) of 1a in 150 ml DCE was added slowly at room temperature with stirring. After 3 hrs, the color of 1a had been completely discharged to result in a slightly yellow solution. DCE was removed on a rotary evaporator. The resulting yellow oil was dissolved in benzene and hexane was added to the solution until the solution became cloudy. After one day in the refrigerator, the solution gave 1.81 g (36.7%) of white needle-like crystals which were found to be almost pure 13 (purity >95%).

The filtrate was concentrated and the yellow oil was purified by column chromatography on silica gel using chloroform and 5% methanol in chloroform as eluent. The main fractions were combined and concentrated. The almost colorless oil was dissolved in benzene and hexane was added. From this solution, 1.89 g (38.3%) of white needlelike crystals were obtained. These crystals consisted of 75% of 14 and 25% of 13, m.p. 77-78°C (dec); nmr ($CDCl_3$) δ 0.93 (t, 3), 1.51 (hex, 2), 2.06 (t, 2), 3.10 (s, 3), 4.13 (s, 2), 5.04 (s, 2), 8.44 (brs, 1). Data for 14: m.p. 51.53°C (dec); nmr ($CDCl_3$) δ 1.00 (t, 3), 1.65 (s, 3), 2.10 (q, 2), 3.09 (s, 3), 4.06 (s, 2), 5.48 (t, 1), 8.4 (brs, 1).

1-(Methylenepentyl)-2-acetyl-4-methyl-1,2,5-triazolidine-3,5-dione (15) and 1-(2-Methyl-2-pentenyl)-2-acetyl-4-methyl-1,2,4-triazolidine-3,5-dione (16) - 13 was treated with acetic anhydride[6] and 15 was obtained as a colorless oil after chromatographic purification. 16 was also synthesized from 14.

Reaction of 16 with 1a - 370 mg (1.54 mmole) of 16 and 245 mg (1.40 mmole) of 1a were dissolved in 30 ml DCE and left at room temperature. After 3 days, DCE was removed on a rotary evaporator and the residue was purified by column chromatography (silica gel). The main fractions were combined and concentrated. After twice recrystallization from benzene-hexane, 433 mg (74.6%) of 19 + 20 was obtained. The ratio between 19 and 20 was found to be 3:2 from ^1H nmr analysis.

Data for 19 + 20: m.p. 166.5-167.5$^{(dec)}$; nmr ($CDCl_3$) δ 0.93 (t), 0.97 (t), 1.90 (quin), 1.97 (s, 2.53 (s), 2.58 (s), 3.10 (s), 3.13 (s), 4.45 (t), 4.6 (s), 5.33 (d), 5.98 (s), 7.48 (s); Anal. Calcd. for $C_{19}H_{22}N_6O_5$: C, 55.06; H, 5.35; N, 20.98. Found: C, 54.54; H, 5.37; N, 20.12.

1-Propyl-4-phenyl-1,2,4-triazolidine-3,5-dione (21) - To 5.26 g of potassium hydroxide (85% purity, 0.080 mol) in 200 ml ethanol, 14.16 g (0.08 mole) of 4-phenylurazole was added. To this solution, which was heated to 60-65°C, 41.0 g (0.24 mole) of 1-iodopropane was added. The mixture was kept at 70°C for 3 hrs during which the salts precipitated. The mixture was left at room temperature overnight. After filtration, ethanol and excess of 1-iodopropane were removed on a rotary evaporator. The resulting yellow oil was dissolved in ethyl acetate and the ethyl acetate solution was washed with water and then dried over anhydrous sodium sulfate. The slightly yellow solid residue, after evaporation of the ethyl acetate, was purified by column chromatography (silica gel). After concentration and recrystallization from benzene-hexane, 8.78 g (50.7%) of pure 21 was obtained: m.p. 98-99°C (dec); nmr ($CDCl_3$) δ 0.90 (t, 3), 1.66 (six, 2), 3.56 (t, 2), 7.49 (s, 5), 8.6 (brs, 1), Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.98; N, 19.17. Found: C, 60.90; H, 6.17; N, 19.30.

1-Propyl-2-acetyl-4-phenyl-1,2,4-triazolidine-3,5-dione (22) - 21 was acetylated by using acetic anhydride: m.p. 107-108°C nmr ($CDCl_3$) δ 0.93 (t, 3), 1.64 (six, 2), 2.65 (s, 3), 4.04 (t, 2), 7.50 (s, 5).

1-Methyl-4-phenyl-1,2,4-triazolidine-3,5-dione (24) - The potassium salt of 4-phenylurazole was permitted to react with methyl iodide in ethanol to give, after purification, 24: m.p. 158-160°C; nmr (Acetone-d_6) δ 3.23 (s,3), 7.48 (m, 5).

Reaction of 21 with 1a - To 2.00 g (0.1 mmole) of 21 in 150 ml DCE, 1.59 g (9.1 mmole) of PhTD was added at 60°C. After one day, the red color was completely discharged and a large amount of white crystals was formed. The crystals were collected by filtration and washed with dichloromethane to give 2.79 g (77.8%) of 25. The filtrate was concentrated and the residue was washed with benzene to give 0.28 g (7.8%) of 25: m.p. 193-195°C (dec); nmr (DMSO-d_6) δ 1.03 (t, 3), 2.23 (quin, 2), 5.63 (t, 1), 7.45 (s, 10); Anal. Calcd. for $C_{19}H_{18}N_6O_4$: C, 57.86; H, 4.60; N, 21.31. Found: C, 57.72; H, 4.64; N, 21.29.

This work was supported in part by the Polymer Program, Division of Materials Research of the National Science Foundation, under NSF Grant No. DMR-7723437, and in part by the Army Research Office under ARO Grant No. DAAG-76-G-0223, for which we are grateful.

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

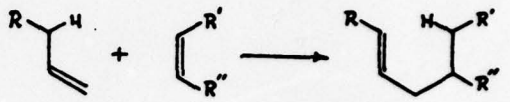
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Summary

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 cross-linked 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%.

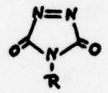
Introduction

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



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 doubly 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.

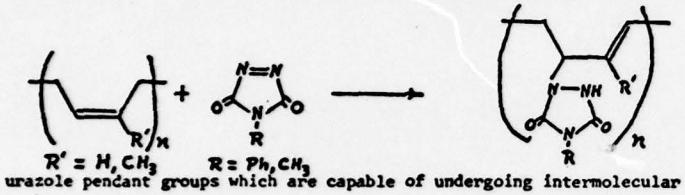


R = Ph, Me

The substituents for this study were phenyl and methyl 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 butadiene, cis-trans (B), butadiene, 1,2- (1,2-B), and isoprene, cis (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. 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.

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 Ceilomer Associates, Inc. Poly(butadiene), cis and trans (B) was obtained from Aldrich Chemical Co., Inc. Poly(acrylonitrile-co-butadiene), 45% acrylonitrile (A/B) was obtained from Polysciences, Inc. Poly(1,2-butadiene), 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)[3] have been reported previously and will not

be described here. The modification reaction on the olefinic polymers will be described in some detail.

Modification of Olefinic Polymers

General Procedure: 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 was 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 hours) 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 hrs. In the case of B, I, and A/B polymers, dichloromethane was used as the reaction solvent. The amount of triazolinedione 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

Polymer	Reaction Solvent	Non-solvent 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

Characterization of the Modified Polymers

The polymers were characterized via infrared spectroscopy (IR), nuclear magnetic resonance (NMR), measurement of intrinsic viscosity ([η]), gel permeation

chromatography (GPC), differential scanning calorimetry (DSC), solubility tests, and tensile measurements.

Infrared (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 hours. 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, [η] 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 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 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°C for Tg measurements and 310°K to 430°K for softening temperature, Ts, and decomposition temperature, Td, measurements. All measurements were made at heating and cooling rates of 10°C/min. The first value of all Tg measurements was discarded. The recorded Tg values were actual averages of the second and third consecutive measurements. The Tg 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 minutes at room temperature. When a clear solution resulted after 30 minutes, 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:[4] Four gram samples were dissolved in 400 ml of solvent. The solutions were poured into 9" by 9" Teflon coated pans. The solvent was evaporated over a three day period, and the resulting polymer films were removed and placed in a vacuum oven at 40°C overnight. Samples (1/2" x 1 1/2") 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 Moduli, and tensile strengths. Three measurements were made for tensile recoveries and stress decays. All samples were extended at a rate of 20"/min. Samples were extended at 20"/min to 1/2 their elongation to break and held there for 1 1/2 min. to measure stress decays. The samples were then returned to zero stress level to measure tensile recoveries.

Results and Discussion

In general, the ene reaction is so fast that the rate connot 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} l mole^{-1} sec^{-1} for PhTD and 5.8×10^{-5} l mole^{-1} sec^{-1} 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 I.

Table I

Relative Reactivity of Different Polymers

Polymer[a]	Solvent	Time for Completion[b]
SBS	Benzene	Instantaneous
SI	Benzene	Instantaneous
B	CH_2Cl_2	1 minute
I	CH_2Cl_2	Instantaneous
1,2-B	Benzene	1-2 hours
S/B	Benzene	5 minutes
A/B	CH_2Cl_2	6 hours

[a] 5% Solution
[b] 1% Modification

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 Figure 1a and 1b. The absorption bands associated with the urazole substituents and their functionality assignments are listed in Table II. 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}.

Table II

IR Data from Modified SBS Polymer

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

w-weak, m-medium, s-strong.

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 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 Figures 2a and 2b, and the absorption band assignments are shown in Table III.

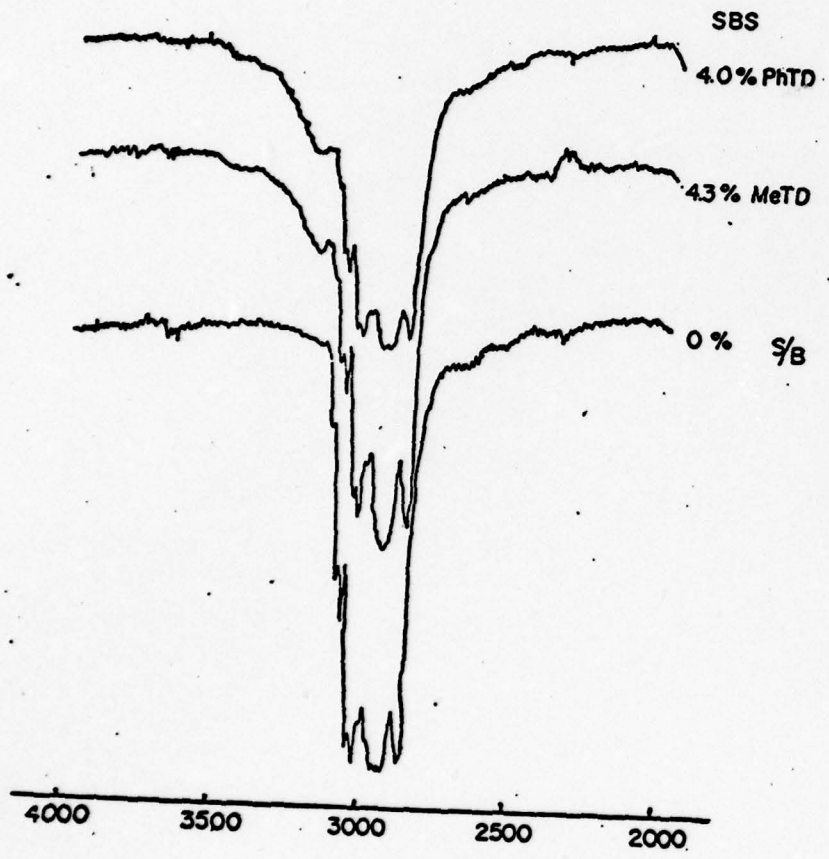


Figure 1a: Infrared Spectra of Unmodified and Modified SBS Samples

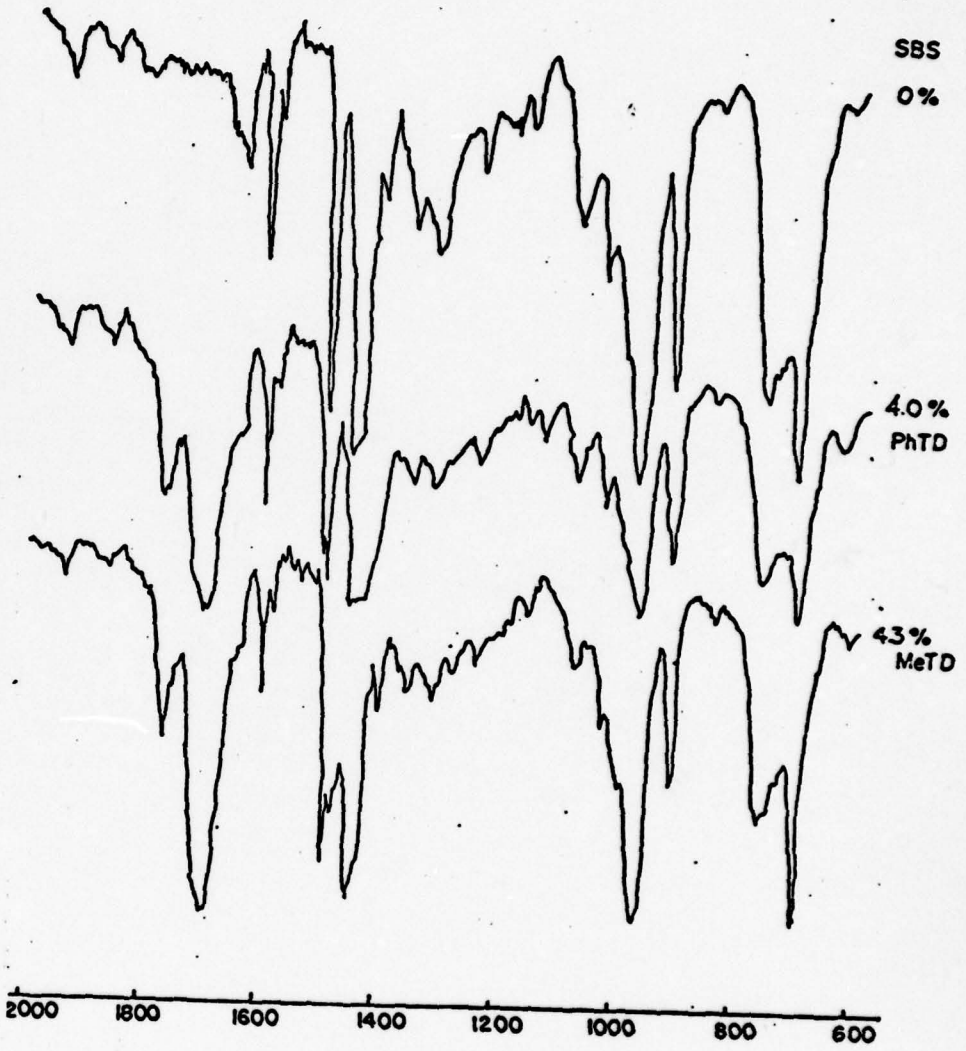


Figure 1b: Infrared Spectra of Unmodified and Modified SBS Samples

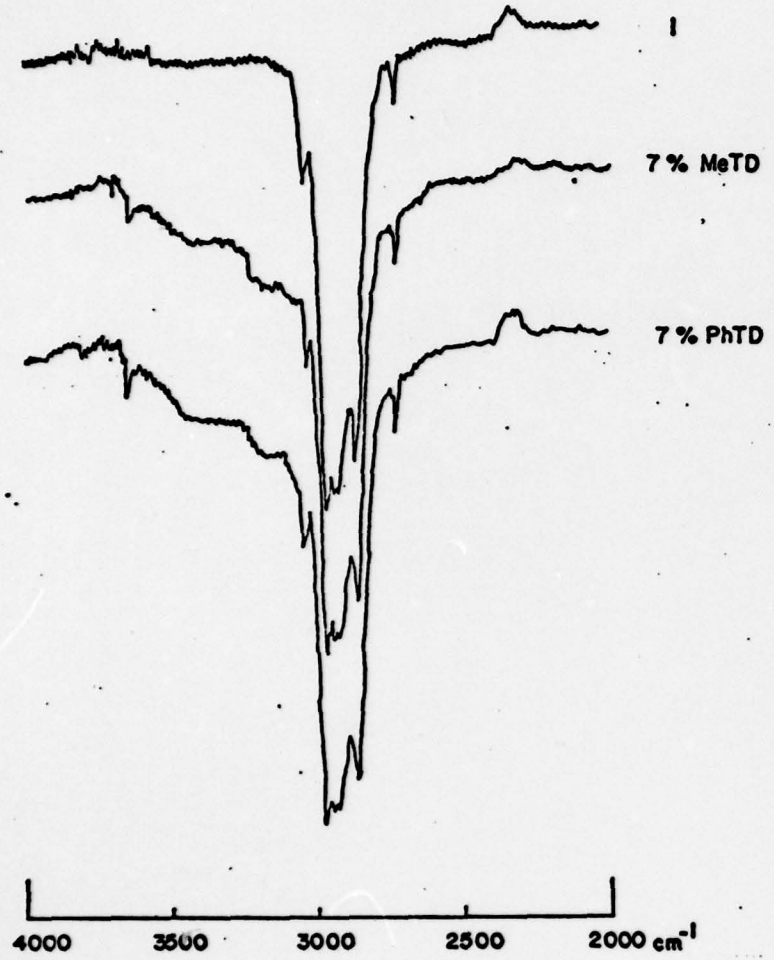


Figure 2a: Infrared Spectra of Unmodified and Modified I Samples

Fig 2a

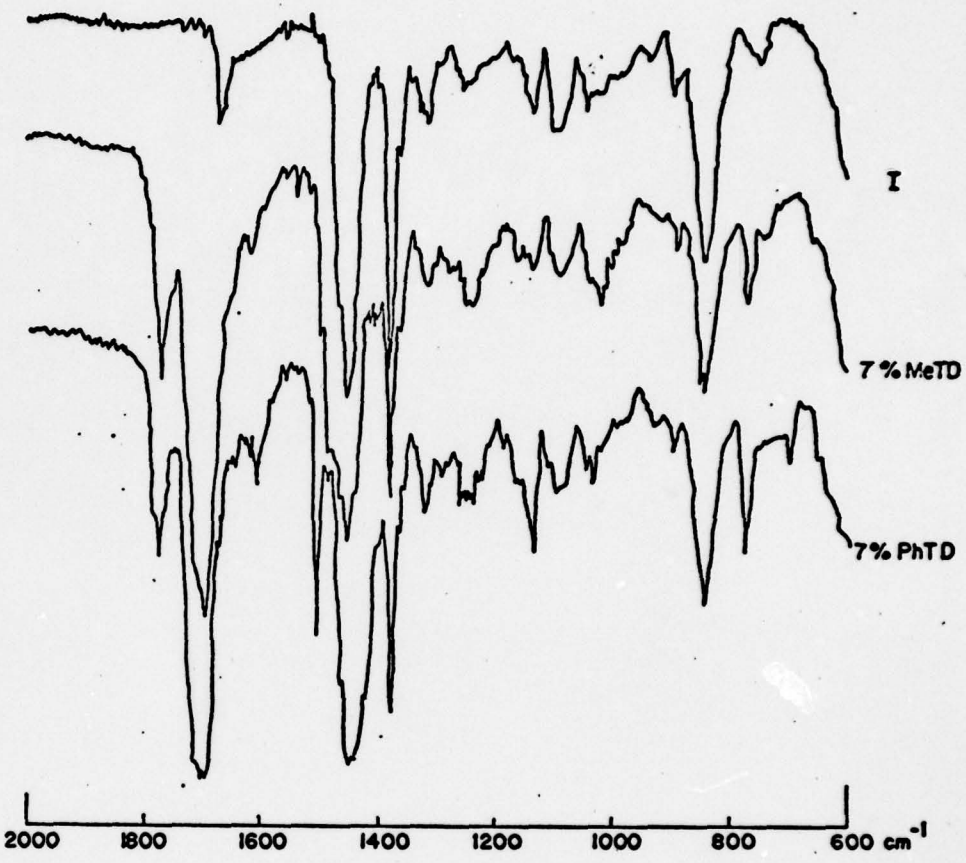


Figure 2b: Infrared Spectra of Unmodified and Modified I Samples

Fig 2b.

Table III

IR Data from Modified I Polymer

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

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 bond 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 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 Figures 3a and 3b. The amount of free N-H to bonded N-H approximates 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 Figure 4. 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

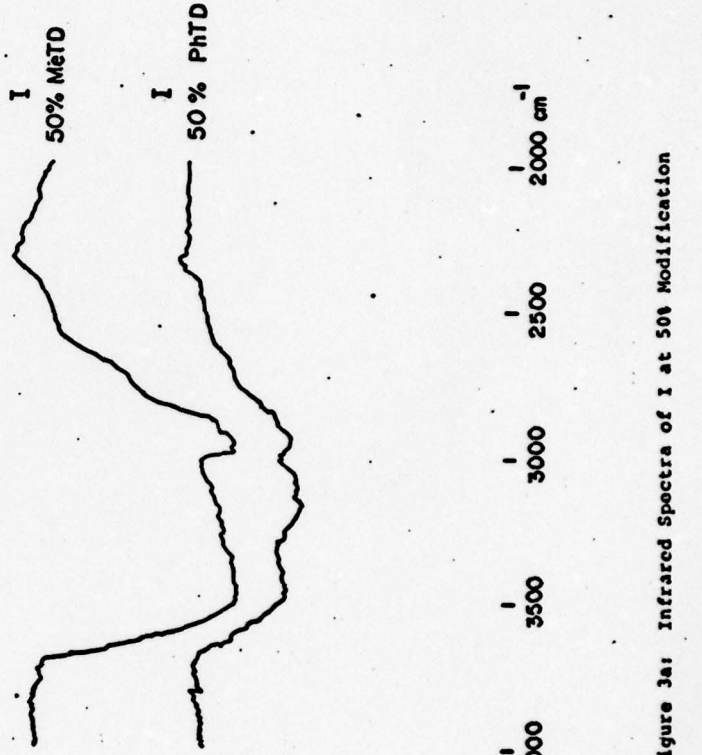


Figure 3a: Infrared Spectra of I at 50% Modification

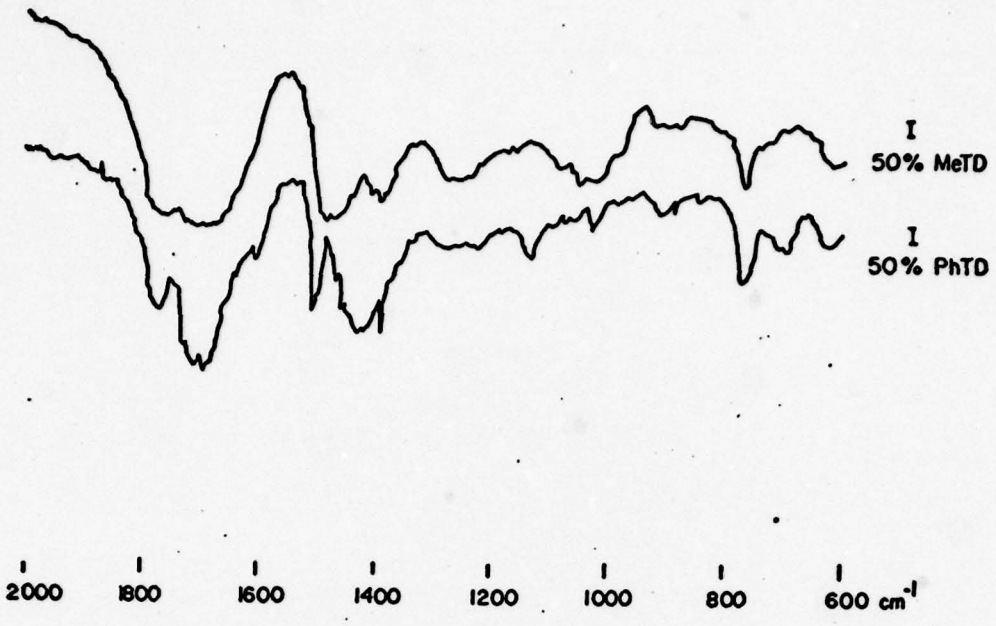


Figure 3b: Infrared Spectra of I at 50% Modification

Fig 3b

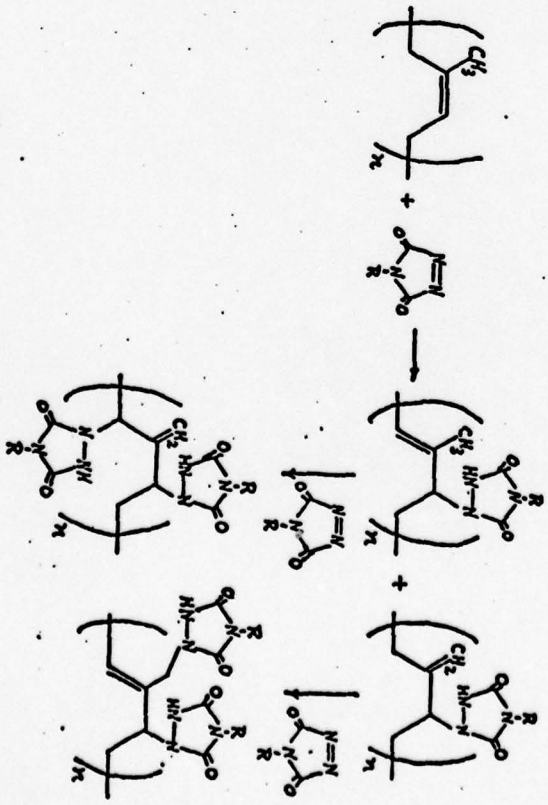


Figure 4: Possible Structures in Modified Poly(cis-isoprene)

the Diels Alder (4 + 2) reaction as shown in Figure 5. This could generate a very complicated NMR spectrum. In fact, the NMR spectra are very complicated as shown in Figure 6. 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[5] and the average urazole groups incorporation was found to be 90% of the triazolinedione feed.

Viscosity Measurement: The intrinsic viscosity, [η] of modified polymers was plotted against the % of triazolinedione incorporation. The plots are shown in Figure 7. In general, a significant decrease in [η] is recognizable even at 1% modification. This is due to the intramolecular interaction between the urazole pendant groups. The modified polymer chains became tightly coiled and decreased in molecular size, when dissolved in non-associating solvent such as benzene and chloroform. A comparison of [η] between the unmodified polymer and the modified polymer at 1% and 5% modification is shown in Table IV and Table V 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 intra-molecular interaction, the

Table IV

Intrinsic Viscosity Data of Various Modified Polymers at 1% Modification

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

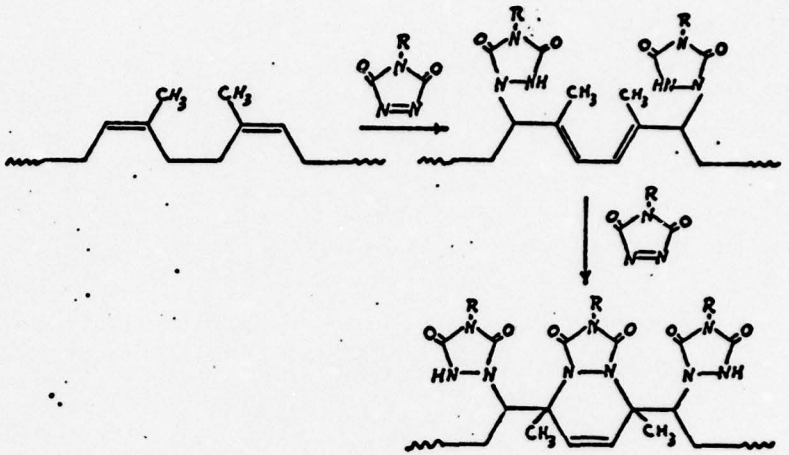


Figure 5: Possible Structures in Modified Poly(cis-isoprene) Containing Head-to head Isoprene Units.

Fig 5

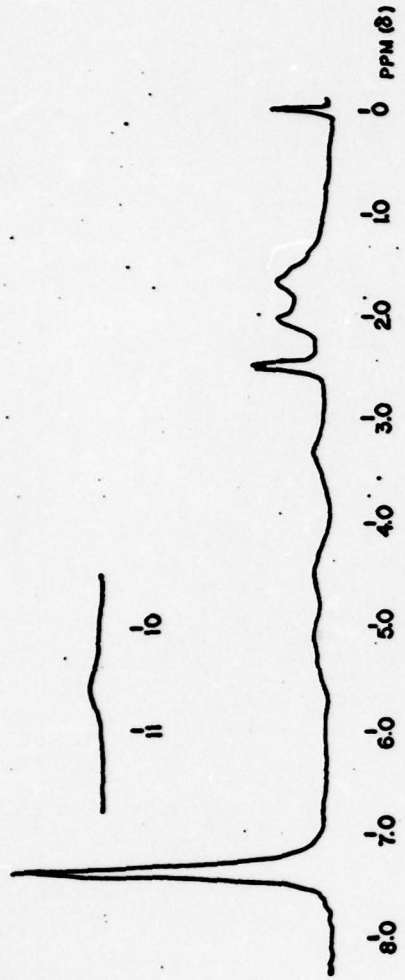
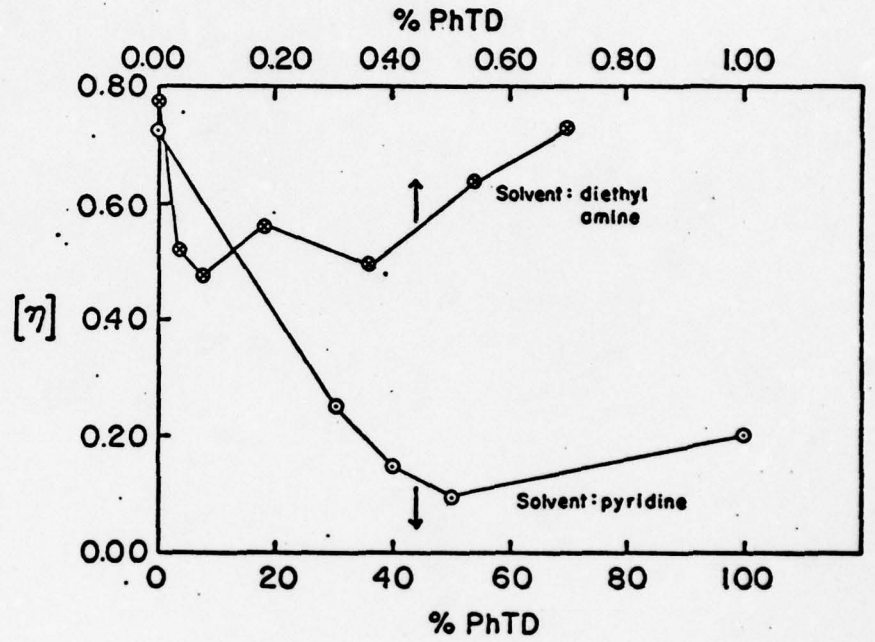


Figure 6: NMR Spectrum of I 100% Modified with PhTD
Solvent: (DMSO d_6)



STYRENE/BUTADIENE ABA BLOCK COPOLYMER MODIFIED WITH PhTD
(31.2°C)

Figure 7a: Intrinsic Viscosity Plot of SBS Modified with PhTD

Fig 7a

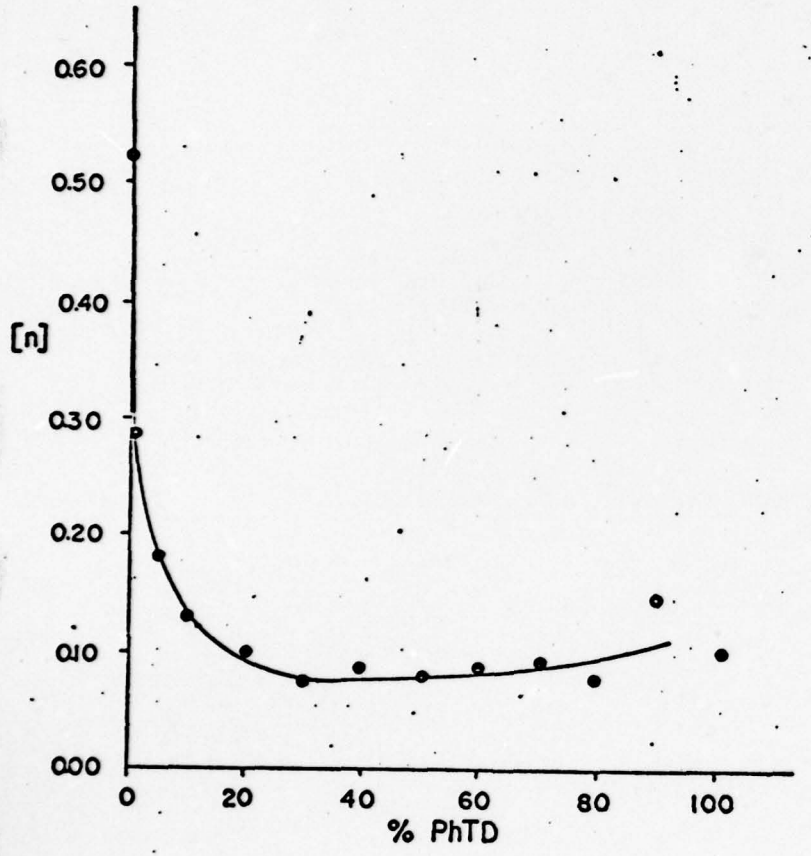


Figure 7b: Intrinsic Viscosity Plot of SI Modified with PhTD. Solvent: Pyridine

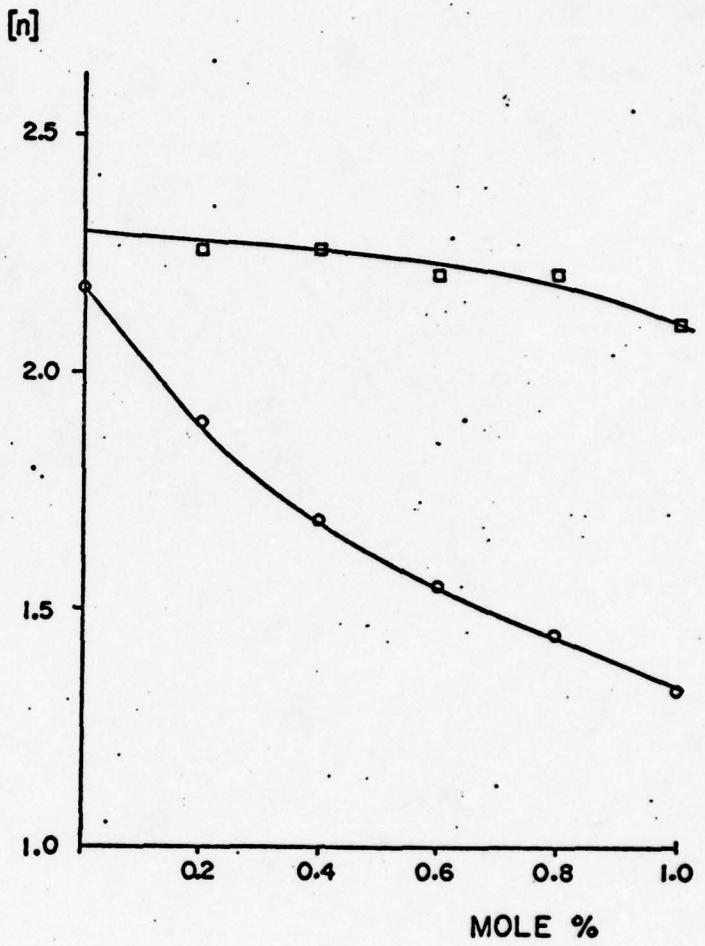


Figure 7c: Intrinsic Viscosity Plot of B Modified with PhTD and MeTD . Solvent: Benzene

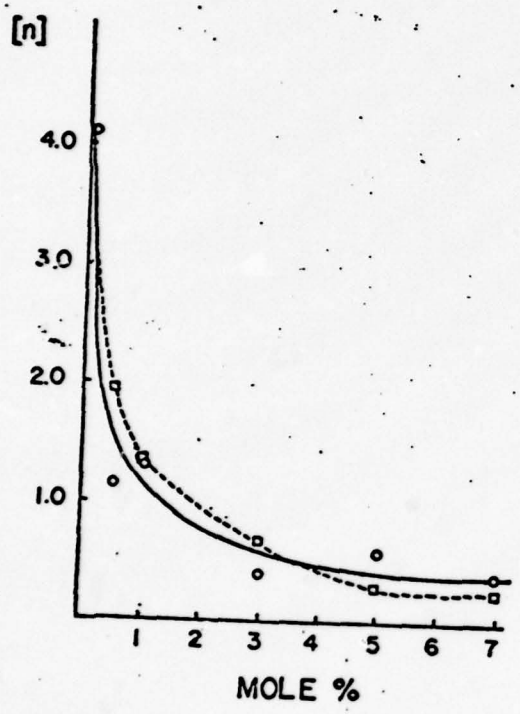


Figure 7d: Intrinsic Viscosity Plot of I modified with PhTD —— and MeTD ----. Solvent: $CHCl_3$

Fig 7d

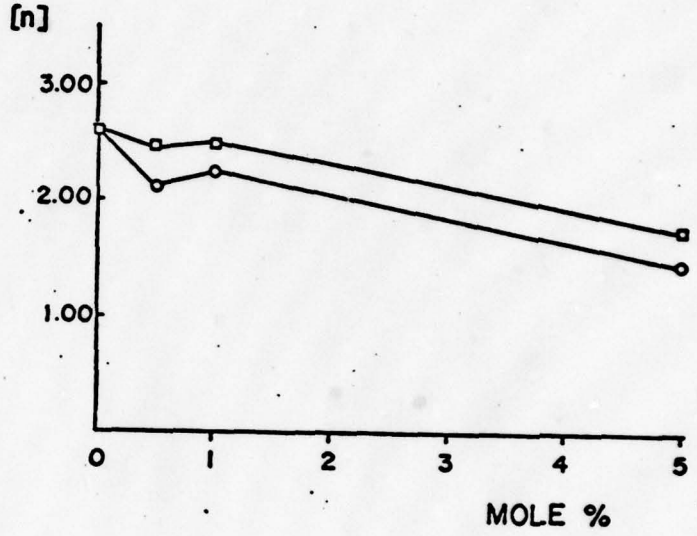


Figure 7e: Intrinsic Viscosity Plot of S/B Modified with PhTD and MeTD . Solvent: Benzene.

Fig 7e

Table V

Intrinsic Viscosity Data of Various Modified Polymers at 5% Modification

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

modified polymer should have a higher intrinsic viscosity value due to the increase in molecular weight. The experimental results shown in Table V 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 % 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 methyl urazole groups can be observed through the [η] data. In general, the phenyl urazole groups cause slightly larger decreases in [η] than the methyl groups. This implies that the hydrogen bonding tendency is stronger in phenyl urazole than methyl urazole. 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:

$$\phi_0 V_n = [\eta]M = KV_r$$

where V_n = hydrodynamic volume

ϕ_0 = universal constant, 2.8×10^{21}

$[\eta]$ = intrinsic viscosity

M = molecular weight

V_r = retention volume or elution volume

K = constant

Since V_n is proportional to V_r, any change in the hydrodynamic volume due to intramolecular interaction would result in increase or decrease of retention volume in GPC. As the urazole pendant groups form H-bonding within the polymer molecule, the hydrodynamic volume in non-protic 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 VI 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 VII. 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.

Table VI[a]

GPC Data of Modified Polymers Expressed in 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 using polystyrene standards of narrow MWD.

Table VII

GPC Data of Modified Polymers Expressed in V_n, (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

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

Differential Scanning Calorimetry: Any changes in the molecular association forces would be reflected in the glass transition temperature, Tg, and melting temperature, Tm 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 Tg value. In general, this is true among the polymer samples modified with PhTD and MeTD. Specifically, the Tg of the olefinic polymer segments increases with the amount of urazole pendant groups present in the segments. Some of the data are shown in Figure 8.

There are several interesting features among the Tg data. First of all, the Tg of S/B copolymer modified with PhTD and MeTD is split into two values when the extent of modification exceeds 5%. Secondly, the Tg of A/B copolymer decreases instead of increases with % 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 non-homogeneous. 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 occurrance of two separate Tg values on the DSC thermogram. The upper value accounts for the modified segments whereas the lower one, the unmodified segments as shown in Figure 8e.

In the case of A/B copolymer system, the initial decrease in Tg can be explained in terms of changes in free volume of the polymer molecules. It is well known that the introduction of non-reactive branches or side chains would result in increase of free volume and subsequent decrease in Tg. Since at low

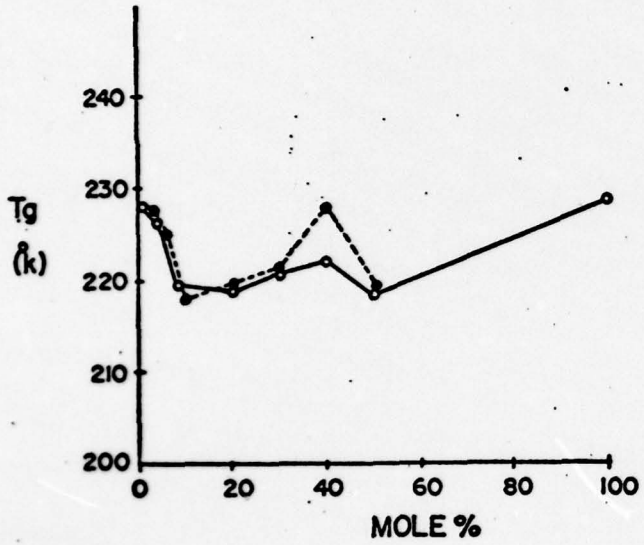


Figure 8a: Glass Transition Temperature Plot of SBS Modified with PhTD —— and MeTD ----.

Fig 8a

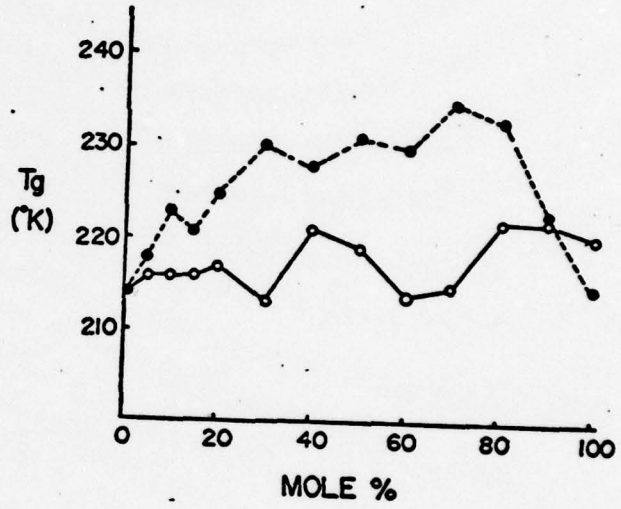


Figure 8b: Glass Transition Temperature Plot of SI Modified with PhTD —— and MeTD ----.

Fig 8b

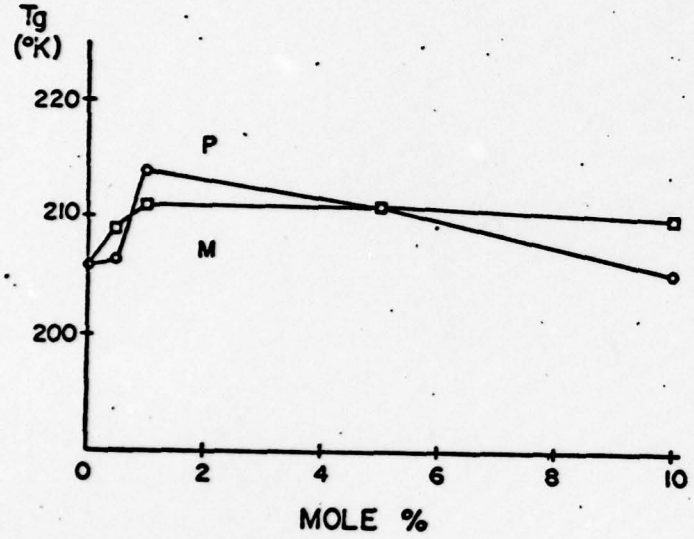


Figure 8c: Glass Transition Temperature Plot of B Modified with PhTD and MeTD.

Fig 8c

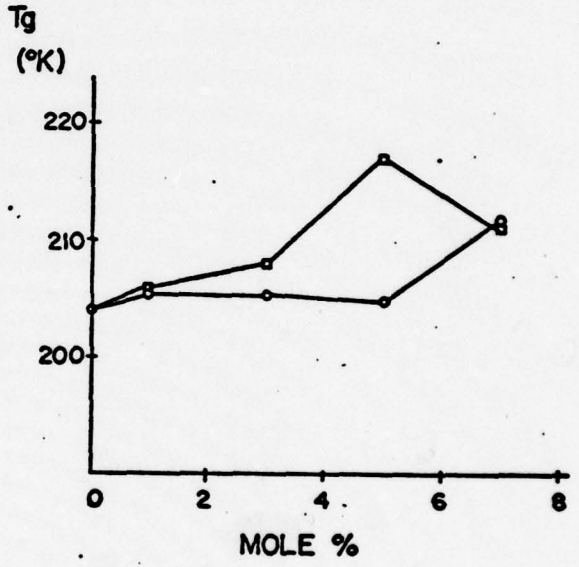


Figure 8d: Glass Transition Temperature Plot of I Modified with PhTD and MeTD.

Fig 8d

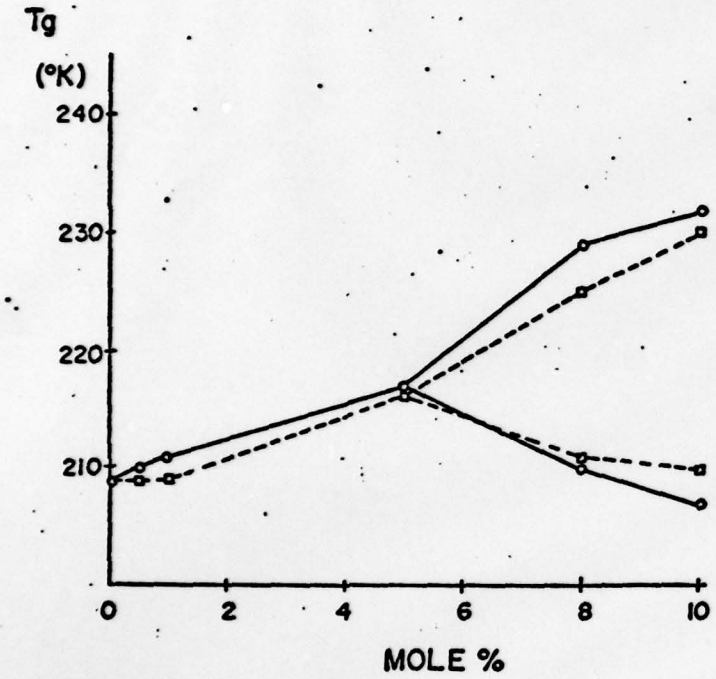


Figure 8e: Glass Transition Temperature Plot of S/B Modified with PhTD —— and MeTD ----.

Fig 8e

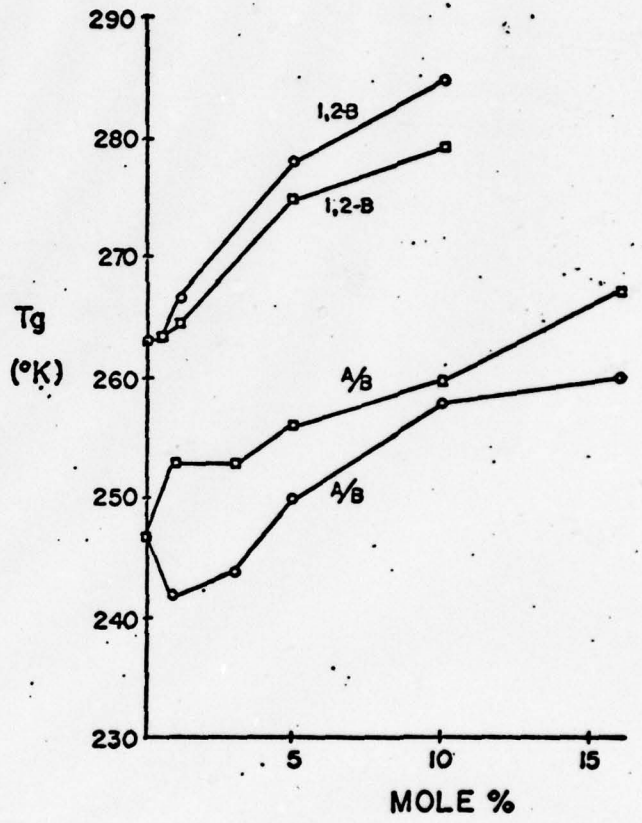


Figure 8f: Glass Transition Temperature Plot of 1,2-B and A/B Modified with PhTD and MeTD

Fig 8f

% modification the probability of one urazole pendant group interacting with another one is very low, the intramolecular interaction due to H-bonding becomes negligible. Therefore, the increase in free volume due to the urazole side groups becomes significant, resulting in decrease in Tg 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 H-bonding exceeds the repulsive forces due to presence of pendant groups, the Tg value would increase again. This expansion and contraction of free volume might account for the fludtuation in Tg vlues among the modified SBS and SI polymers shown in Figure 8a and 8b, respectively.

As we have mentioned before, Tm is not sensitive to molecular changes in amorphous polymer systems. But, we noticed some effect on the decomposition temperature, Td (an exotherm) of the polymer samples as PhTD or MeTD was added. Some representative data are shown in Figure 9. The decomposition pattern does not seem to follow any trend. At high % 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 methyl urazole groups appear to stabilize the I polymer but destabilize the B and 1,2-B polymers towards thermal decomposition. At low % modification, the phenyl urazole groups have destabilizing effects, whereas at high % modification, they appear to stabilize the polymer. This peculiar behavior about the phenyl urazole 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 H-bondings of the phenyl urazole groups can be overcome easily, since the strength of H-bonding is only about 5 Kcal/mole. At high concentration, the H-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 the mode of action of the modifying groups because thermal

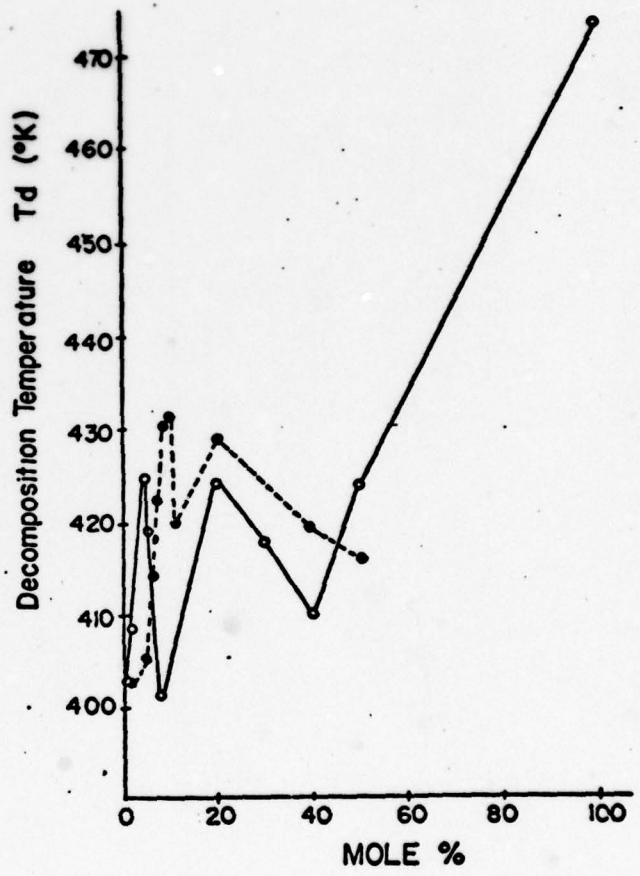


Figure 9a: Plot of Decomposition Temperature (Td) for SBS Modified with PhTD —— and MeTD ----

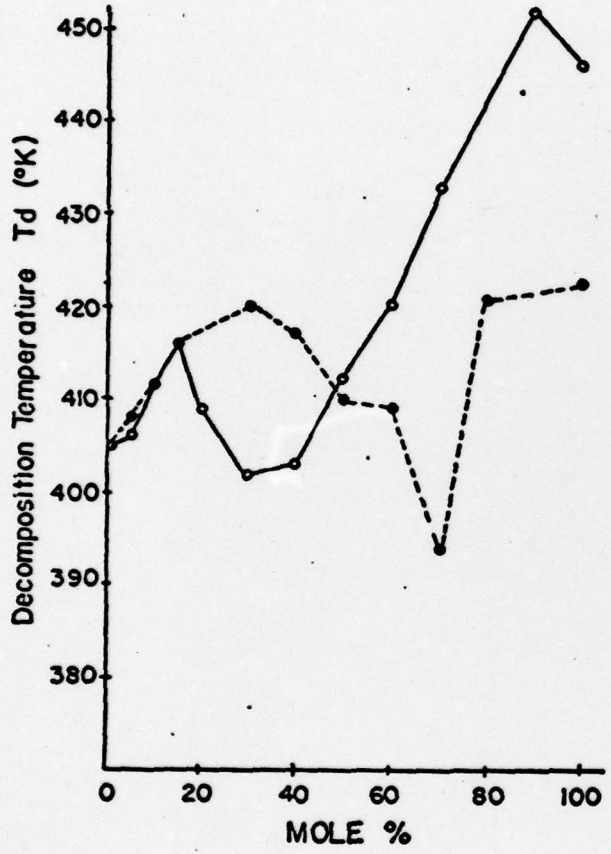


Figure 9b: Plot of Decomposition Temperature (Td) for SI Modified with PhTD —— and MeTD ----

Fig 9b

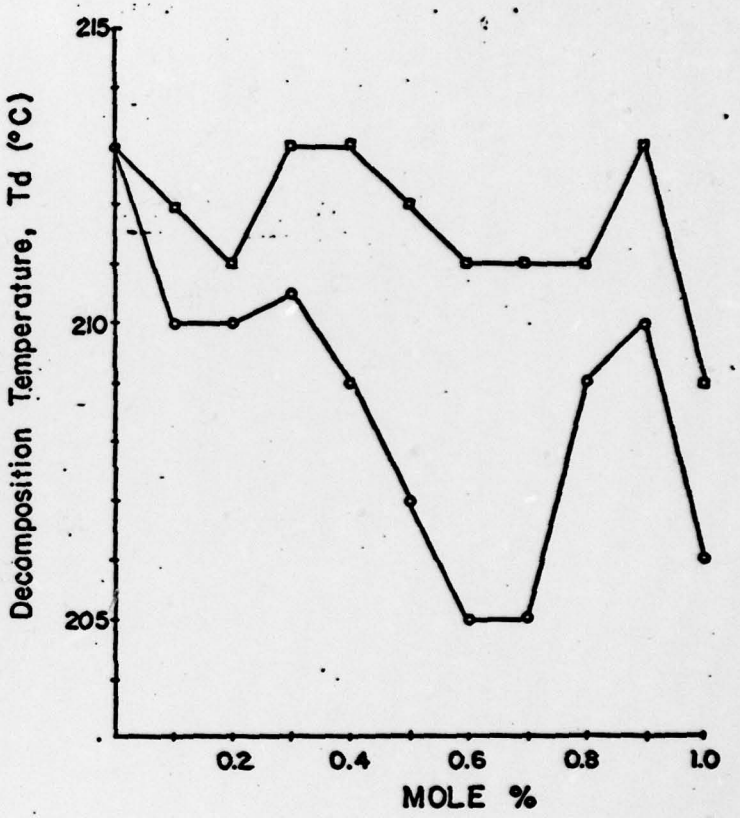


Figure 9c: Plot of Decomposition Temperature (Td) for B Modified with PhTD and MeTD

Fig 9c

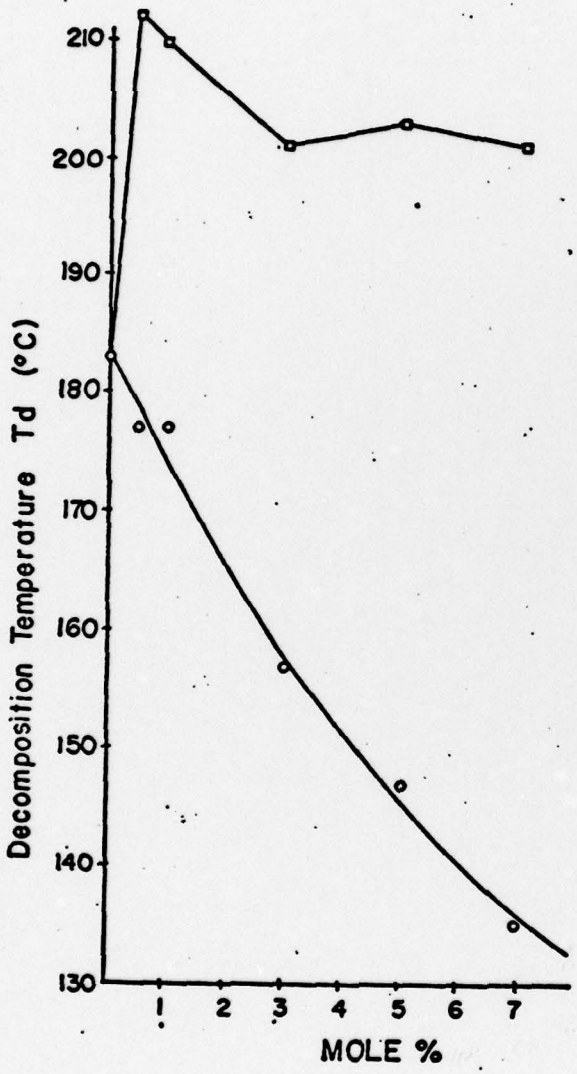


Figure 9d: Plot of Decomposition Temperature (Td) for I Modified with PhTD and MeTD

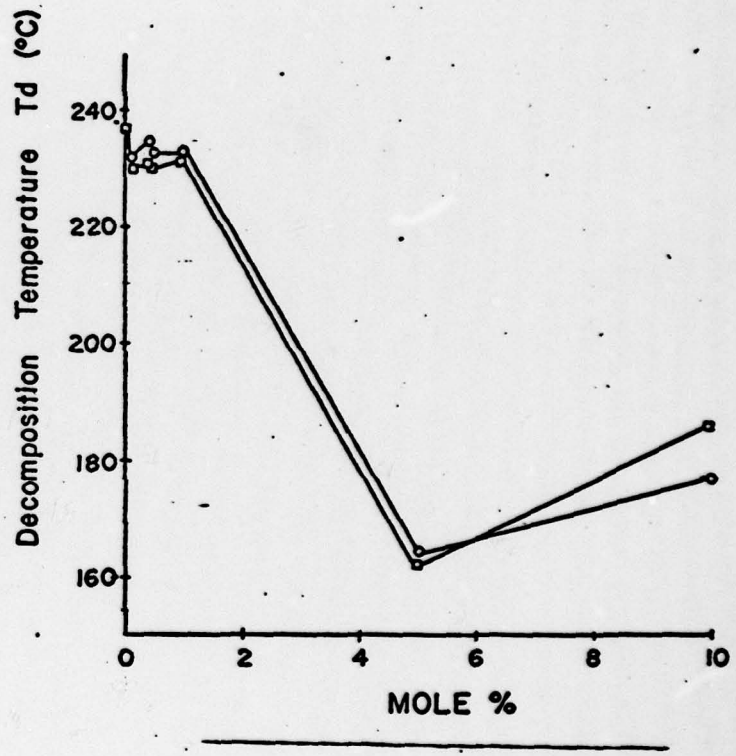


Figure 9e: Plot of Decomposition Temperature (Td) for 1,2-B Modified with PhTD and MeTD

Fig 9e

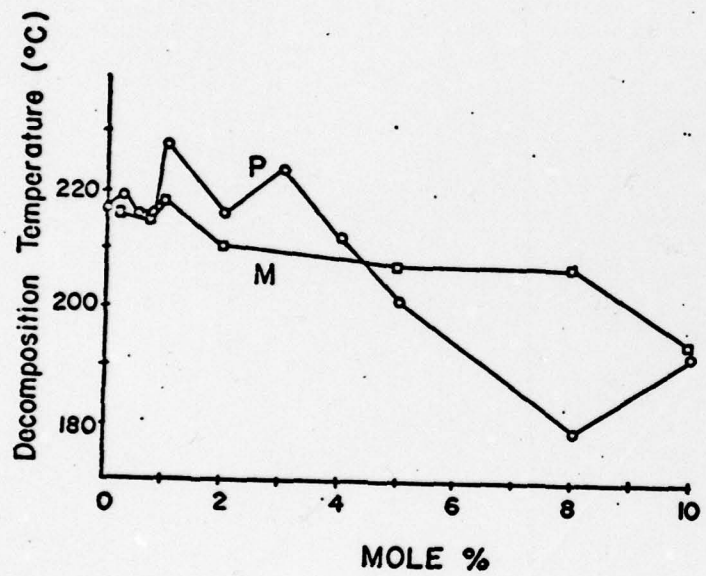


Figure 9f: Plot of Decomposition Temperature (Td) for S/B Modified with PhTD and MeTD.

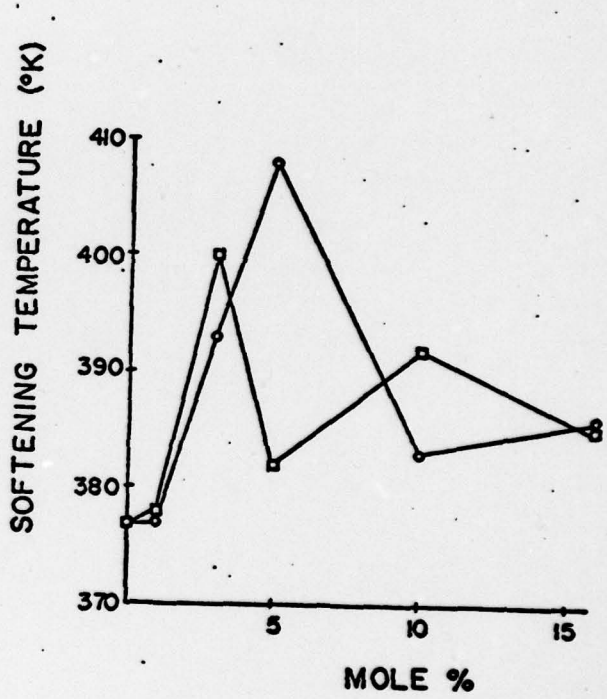


Figure 9g: Plot of Softening Temperature (Ts) for A/B Modified with PhTD and MeTD.

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 VIII. It appears that MeTD can adversely affect the thermoplasticity to a greater degree than PhTD.

Table VIII

Maximum % of 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

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 H-bondings formed by the urazole groups prevent the hydrating solvent molecules 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 IX. A sample of poly(butadiene), B was modified to 75% PhTD incorporation and converted to

Table IX

Data Showing Maximum % Modification for Polymer to Remain or Become Soluble in Various Solvents

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 A.G. Williams,[5] Ph.D. Dissertation, University of Florida, 1976.
[b] 0.8 M KOH used; and when the modification >60%, the samples are soluble in 1.0 M $NaHCO_3$.

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:[4] The Young's modulus data is not reliable, based on our methodology but gross differences do have significance. The tensile data is shown in Table X. The 1,2-B series (samples 20-24) best illustrates the effect of urazole pendant 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) are SI series (samples 4-6 and 25-27) are not particularly revealing as far as supplying evidence for intermolecular H-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 physicall associated by the styrene phase. Thus, a small increase in physical association by methyl urazole 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.

Table X
Tensile Data

Sample No.	Description	Casting Solvent[2]	Sample Thickness Mils	Elongation[3] to Break %	Young's Modulus Kg/cm²	Tensile[3] Strength Kg/cm²	Tensile Recovery %	Stress[4] Decay %
1	SBS	Toluene	4.2 (0.3)	648 (30)	218 (95)	138 (37)	95 (0.2)	20 (2.7)
2	SBS[5] 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----					

CONTINUED

Table X: Tensile Data - continued

Sample No.	Description	Casting Solvent[2]	Sample Thickness Mils	Elongation[3] to Break %	Young's Modulus Kg/cm²	Tensile[3] Strength Kg/cm²	Tensile Recovery %	Stress[4] Decay %
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)	-stress decay too high to measure tensile recovery- sample fractured in less than 1 minute	
21	1,2-B 0.5% MeTD	Chloroform	3.4 (0.3	126 (8)	45 (3.4)	107 (9.7)	-Same results as for sample 20.	
22	1,2-B 0.5% MeTD	Chloroform	3.2 (0.6)	150 (11)	40 (5.3)	111 (11)	-Same results as for sample 20.	
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)

CONTINUED

Table X: Tensile Data - continued

Sample No.	Description	Casting Solvent[2]	Sample Thickness Mils	Elongation[3] to Break %	Young's Modulus Kg/cm²	Tensile[3] Strength Kg/cm²	Tensile Recovery %	Stress[4] Decay %
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)
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

[1]Data in parentheses are standard deviations. Unless otherwise indicated, 5 measurements were made for sample thickness, elongations to break, Young's moduli, and tensile strengths. Three measurements were made for tensile recoveries and stress decays.

[2]Four gram samples were dissolved in 400 ml of solvent (800 ml for samples 7, 8, and 9).

[3]Samples were extended at a rate of 20 inches per minute.

[4]Samples were extended at 20 inches per minute to 1/2 their elongation to break and held there for 1 and 1/2 minutes to measure stress decay. The sample was then returned to a zero stress level to measure tensile recovery.

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

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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CROSSLINKING OF DIENE POLYMERS VIA 'ENE' REACTION WITH BISTRIAZOLINEDIONES

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SYNOPSIS

Bistriazolinediones (BTDs) have been used to synthesize a large number of highly crosslinked polydienes by the 'ene' reaction. BTDs have been found to be effective crosslinking agents at room temperature. The crosslinked polymers were swollen in benzene, and the crosslink density and the molecular weight between crosslinks were determined by the Flory-Rehner equation.

INTRODUCTION

Triazolinediones are among the most powerful dienophilic[1] and enophilic[2] reagents known. BTDs[3] were found to be much more reactive than triazolinediones, and the modification reaction was easily followed at room temperature because the characteristic pink color of the bistriazolinedione disappeared completely at the end of the reaction.

Saville[4] made an unsuccessful attempt to crosslink natural rubber with a BTD. However in the present study, polydienes were suitably crosslinked with BTDs. Modified polymers swelled in the original reaction medium (benzene), and the reaction proceeded instantaneously. The possibilities of unreacted N=N ends were ruled out because of the lack of colored polymers.

Butler, et.al. have synthesized copolymers of BTDs with α-substituted bisenol esters[5] and divinyl esters.[6] They have reported that depending on the solvent, temperature and appropriate ratio of comonomers, linear polymers of potential usefulness can be obtained.

The authors, in their future studies, contemplate using suitable preformed diene polymers having active terminal carboxyl and sulfonyl groups and crosslinking them with bistriazolinediones for potential applications in ion-exchange resins.

The present communication is a preliminary study in which the authors describe the novel crosslinking reaction of bistriazolinediones with various polydienes. The modified diene polymers were characterized by infrared spectroscopy using the Multiple Internal Reflection Accessory (MIRA). They remained insoluble in a wide range of organic solvents, implying that the modified polymers were crosslinked. A swelling equilibrium method was employed to evaluate the crosslink density and the molecular weight between crosslinks of the modified polymers by using the Flory-Rehner equation.[7]

Determination of Crosslink Density by Equilibrium Swelling Measurements:

Crosslinked polymers have a great variety of structures; and it is important to have techniques to characterize these structural parameters, such as crosslink density or the molecular weight of the chains between the crosslinks. The first step in the solution of a polymer is swelling and, in the case of a crosslinked polymer, it is the last step, since chains cannot be further separated because of the presence of crosslinks.

Swelling is accompanied by an increase in the volume of the polymer as it imbibes the solvent, and it is usual to assume, consistent with the Flory-Huggins theory of the thermodynamics of polymer solutions, that mixing occurs without change in the total volume of the system. A sample of crosslinked polymer placed in a solvent swells until the chemical potential of the solvent inside the gel is equal to that of the outside phase. During the process, solvents reduce or damage secondary bonds between chains, especially when the solvents are of remarkable polarity. Thus the number of crosslinks determined by this method depends on the nature of the solvent. This value was found by employing the Flory-Rehner equation[7] in the form:

$$\frac{\nu}{V} = \frac{-\ln(1-Vr) + Vr + \chi Vr^2}{Vo\left(Vr^{1/3} - \frac{Vr}{2}\right)}$$

where ν/V stands for effective crosslink density in moles/cm^3, Vr is the volume fraction of the polymer in the swollen sample, χ is the polymer-solvent interaction parameter of the Flory-Huggins theory, and Vo is the molar volume of the solvent.

Knowing the value of ν/V, one can then calculate the average molecular weight of the network chains:

$$\overline{M}_c = \frac{P}{\nu/V} \text{ gms/mole}$$

where P is the density of the polymer.

To calculate crosslink density and the molecular weight of chains between crosslinks, one has to know the values of the Flory-Huggins polymer-solvent interaction parameter. They were found by the method of Rútkowska and Kwiatkowski[8] by measuring the variation in swelling degrees from swelling measurements with temperatures using the Flory-Rehner equation for all samples.

$$\frac{-dVr}{dT} = \frac{\chi Vr/T}{\frac{5}{3}\chi Vr + \frac{2}{3} - [\frac{1}{1-Vr}] - [\frac{\ln(1-Vr)}{3Vr}]}$$

EXPERIMENTAL

Materials: Styrene-butadiene random copolymer (S/B) containing 23% styrene was obtained from Scientific Polymer Products, Inc. Styrene-isoprene block copolymer (S/I) containing 15% styrene was obtained from Cellomer Associates, Inc. Poly(isoprene)cis(I) and poly(butadiene)cis and trans(B) were obtained from Aldrich Chemical Co., Inc. Poly(acrylonitrile-co-butadiene) containing 45% acrylonitrile (A/B) was obtained from Polysciences, Inc. Poly(1,2 butadiene) containing 93.5 vinyl(1,2-B) was obtained from Firestone Tire and Rubber Company.

Synthesis: The synthesis of 4,4'(4,4'diphenylmethylene)bis-1,2,4 triazoline 3,5 dione (BPMTD) was accomplished by the method of Turner.[9]

Modification of Diene Polymers

General Procedure: A sample of 0.5 grams of polymer was dissolved in 20 ml of dry benzene. The mixture was stirred well until a clear solution was obtained. 4,4'(4,4'-diphenylmethylene)bis,1,2,4 triazoline 3,5 dione (BPMTD) was dissolved in 20 ml of benzene, and was added very rapidly to the polymer solution at room temperature. The reaction mixture was stirred well and allowed to stand overnight (~12 hrs.) after the pink color had completely faded. Modified polymers were recovered by precipitation into 100 ml of 95% ethanol containing 0.5% 2,6-di-tert-butyl-4-methylphenol (BHT), and then dried in a vacuum disiccator for 24 hours. For acrylonitrile-butadiene copolymer, dichloromethane was used as the reaction solvent. The amount of BTD used in the reaction was expressed as a certain percentage of the total unsaturation in the diene polymer or actually simply in terms of butadiene or isoprene content in the polymer.

Characterization of Modified Polymers: Modified polymers were characterized by infrared spectroscopy, solubility tests and the equilibrium swelling method. Due to the insolubility of the modified polymers in a wide range of organic solvents, conventional techniques of polymer characterization like gel permeation chromatography, viscosity, vapor phase osmometry and NMR measurements could not be performed.

Infrared Spectroscopy (IR): IR was primarily used as a qualitative tool to emonstrate the molecular association through hydrogen bonding. Solid polymer samples were used by employing the Multiple Internal Reflection Accessory (MIRA).

Solubility Tests: A few milligrams of the modified polymers were added to 1 ml of the solvent. The mixture was agitated periodically for about 30 minutes at room temperature. When a clear solution resulted after 30 minutes, 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 then re-examined. Appearance of swollen fragments was taken as insolubility. The solvents used in the solubility tests were benzene, chloroform, acetone, dioxane, toluene, dichloromethane, dimethylformamide, dimethylsulfoxide, ethanol, pyridine and 10% aqueous sodium hydroxide.

Swelling Measurements: Samples of about 50 milligrams of modified polymers were equilibriated with benzene for 48 hours at temperatures of 298°, 303° and 312°K, keeping the temperatures constant during equilibration. Then the samples were blotted using filter paper and subsequently immersed in diethyl ether for awhile. Thirty seconds after removing the samples from ether, their weights were determined with an accuracy of 0.5 milligrams. Then the swollen samples were dried to constant weight under vacuum at 333°K.

RESULTS AND DISCUSSION

Evidence of Intra- and Intermolecular Association in Polymers Modified By Bistriazolinediones

IR Spectroscopy: IR spectra for the modified BTD diene polymers throws light on the absorption bands associated with urazole substituents. The presence of urazole groups in the modified polymers was confirmed by the carbonyl stretching frequencies which appear as bands around 1770 cm^{-1} and 1700 cm^{-1}. The evidence of hydrogen bonding was confirmed by the bonded N-H stretching band around 3200 cm^{-1} and N-H bending band around 1500 cm^{-1}.

Table I summarizes the data of modified copolymers of styrene-butadiene and styrene-isoprene.

TABLE I

IR Data From Modified S/B and S/I Copolymers

	S/I - 1% BPMTD	S/I - 5% BPMTD	S/B - 5% BPMTD
N-H stretching	3200cm^{-1}(m)	3200cm^{-1}(m)	3200cm^{-1}(m)
N-H bending	1500cm^{-1}(m)	1500cm^{-1}(m)	1500cm^{-1}(m)
C=O stretching	1770cm^{-1}(m)	1770cm^{-1}(m)	1770cm^{-1}(m)
	1700cm^{-1}(s)	1700cm^{-1}(s)	1700cm^{-1}(m)

w = weak, m = medium, s = strong

Table II summarizes the data of modified poly(butadiene) cis and trans.

TABLE II

IR Data From Modified PB Polymer

	PB - 3% BPMTD	PB - 10% BPMTD
N-H stretching	3500cm^{-1}(m)	3500cm^{-1}(m)
N-H bending	1500cm^{-1}(s)	1500cm^{-1}(m)
C=O stretching	1680cm^{-1}(s)	1680cm^{-1}(m)

A signal at 3500cm^{-1} is present in the IR of modified poly(butadiene) cis and trans polymers indicating the presence of N-H bonding resulting from the ene reaction. Further, the presence of urazole groups in the modified polymers were confirmed by the presence of strong signals around 1680cm^{-1} for carbonyl groups.

Density of Crosslinking: There are several methods of studying network structures,[10] but the available techniques are not as good as those used conventionally to determine the molecular weights of linear soluble polymers. Among them, the chemical method is the most suitable and fairly accurate method of characterizing network structures. In a chemical method, it is observed that if the concentration of the crosslinking reagent is known, and if it reacts completely, then it is possible to estimate reasonably the average molecular weight, $\bar{M}_c$ of the polymer between the crosslinks.

In our system in the modification of diene polymers with bistriazolinediones, it was assumed that the reaction went to completion because the pink color of the BTD was discharged completely at the end of the reaction.

If an uncrosslinked polymer is soluble in a solvent, then the same polymer when crosslinked will swell in the same solvent. This fact has been taken advantage of to measure crosslink density and the average molecular weight between the crosslinks for the modified diene polymers. It was earlier shown by Hergenrother,[11] in the peroxide initiated crosslinking of poly(butadiene), that the Flory-Rehner equation is valid down to a value of 63 $\bar{M}_c$, that is to a highly crosslinked network. Recently, Gancarz and Kaskowski[12] have shown that the Flory-Rehner equation may also be used for crosslinked networks of low molecular weight polydienes.

In the present investigation, crosslink density was calculated by the Flory-Rehner equation.[7] Benzene was used as the swelling solvent for the crosslinked polymers and the Flory-Huggins polymer-solvent interaction parameter, χ, was determined by employing the method of Rutkowska and Kwiatkowski.[6]

Table III summarizes the crosslink density, the Flory-Huggins polymer solvent interaction parameter and the average molecular weight between the crosslinks of the BTD modified diene polymers.

TABLE III

Crosslink Density and Average Molecular Weight Between Crosslinks Of Modified Polymers Determined From Swelling-Equilibrium Method

Polymers	Mole Percentage of BPMTD Added	Flory-Huggins Polymer-Solvent Interaction Parameter X	Crosslink Density $\nu/V\ 10^{-4}$ mole/cm^3 at 25°C	Average Molecular Weight Between Crosslinks, $\bar{M}_c$ g/mole
Poly(isoprene) Cis	1	0.507	8.75	1038
	3	0.507	10.58	860
	5	0.507	12.34	737
Poly(butadiene) Cis and Trans	1	0.509	12.69	708
	3	0.509	14.63	615
	5	0.509	17.26	521
Copolymer of Styrene-Butadiene	1	0.512	13.63	684
	3	0.512	17.50	533
	5	0.512	21.58	432

Figure 1 represents the plots of crosslink density of modified polymers against the mole percentage of bistriazolinedione incorporated in the diene polymers. The plots are good straight lines and show that as the percentage of bistriazolinedione content in the diene polymer increases, then the crosslink density also increases in a linear fashion. Thus by increasing the extent of modification of polydienes with BTD, highly crosslinked networks are produced at room temperature.

From our experiments, it was observed that beyond 5% modification of the diene polymers with BTD results in immediate gelation. The reaction mixture becomes increasingly difficult to stir, and sometimes the magnetic stirring rod was entagled in the gelatinous mass. This proves, beyond doubt, that BTDs are good crosslinking agents at room temperature and, even with very low percentage incorporation of BTD in the polydienes, results in crosslinked networks. This is substantiated from the average molecular weight, $\bar{M}_c$ values, as illustrated in Table III.

However, when the average molecular weight between crosslinks was plotted against the percentage incorporation of BTD in the diene polymers, then in all cases, linear plots were obtained as shown in Figure 2. The linear plots demonstrate that as the extent of modification via BTD increases in the modified polymers, then the average molecular weight falls off steadily. This shows that the extent of incorporation of BTD into the diene polymers is inversely related to the average molecular weight between the crosslinks.

This was further confirmed from the plots of extent of modification via BTD versus the reciprocal of the average molecular weights, which were straight lines, as shown in Figure 3.

CONCLUSIONS

This is the first report of the crosslinking reaction of bistriazolinediones with polydienes. Crosslink parameters determined for the modified polymers were in good agreement with experimental observations.

An inverse relationship was found between the extent of modification and the average molecular weight between crosslinks in the modified polymers.

Further research is being carried out on the crosslinking of bistriazolinedione with suitable polydienes for useful applications.

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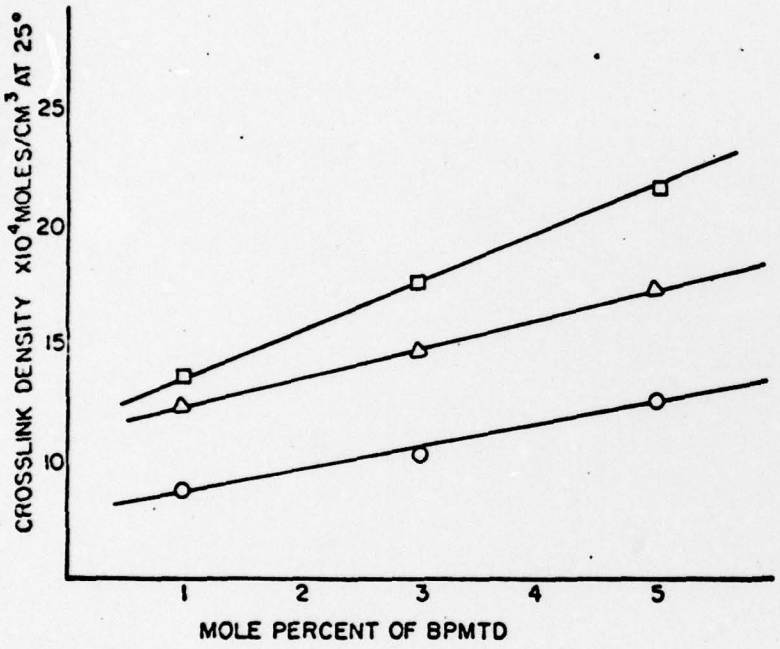


FIGURE 1: PLOT OF CROSSLINK DENSITY OF MODIFIED PI (○), PB (△) AND S/B (□) WITH MOLE PERCENTAGE OF BPMTD INCORPORATED.

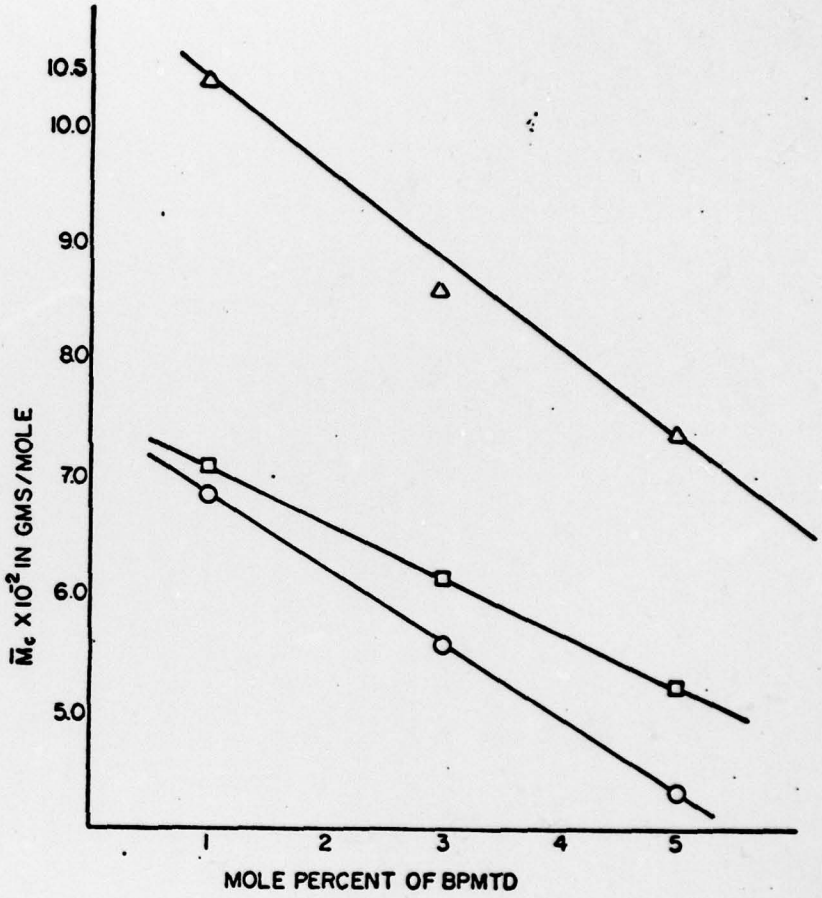


FIGURE 2: PLOT OF AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF MODIFIED PI (△), PB (□) AND S/B (○) WITH MOLE PERCENTAGE OF BPMTD ADDED.

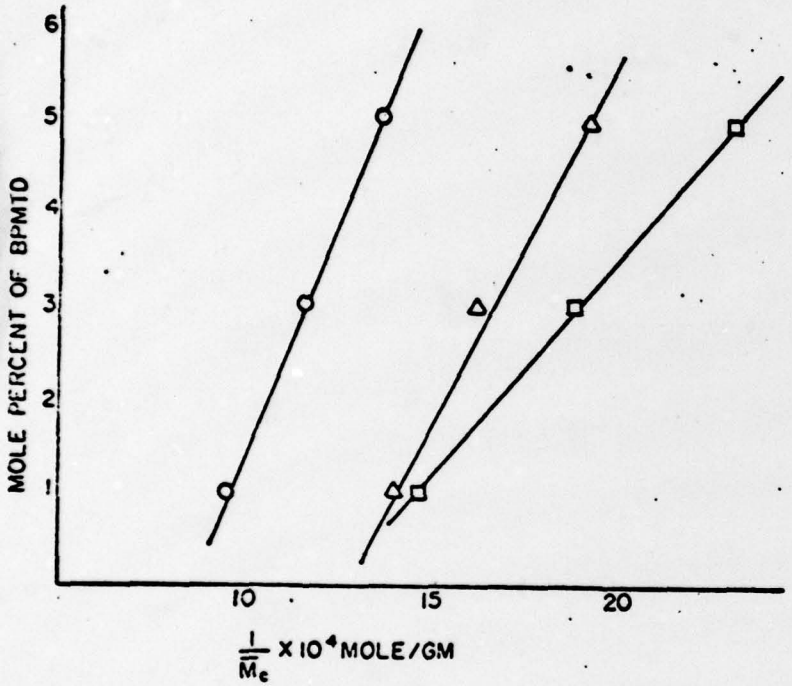


FIGURE 3: PLOT OF MOLE PERCENTAGE OF BPMTD CONTENT VERSUS RECIPROCAL OF AVERAGE MOLECULAR WEIGHT OF MODIFIED PI (○), PB (△) AND S/B (□).