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Crosslinking of Diene Polymers via 'ENE' Reaction with Bistriazolinediones

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Dedicated to Prof. C.I. Simionescu in honor of his 60th birthday

SUMMARY

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 crossliked 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 triazoline-diones, and the modification reaction was easily followed at room temperature because the characterisic pink color of the bistriazolinedione dissapeared 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 Multiple Internal Reflection Accesory (MIRA). They remained insoluble in a wide

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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 :

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

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 :

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

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 Rutkowska 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 traizoline 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-methyphenol (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 demonstrate 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, dimethysulfoxide, 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 streching 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 1 summarizes the data of modified copolymers of styrene-butadiene and styrene-isoprene.

TABLE 1

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	3200 cm^{-1}(m)	3200 cm^{-1}(m)	3200 cm^{-1}(m)
N-H bending	1500 cm^{-1}(m)	1500 cm^{-1}(m)	1500 cm^{-1}(m)
C=O stretching	1770 cm^{-1}(m)	1770 cm^{-1}(m)	1770 cm^{-1}(m)
	1700 cm^{-1}(s)	1700 cm^{-1}(s)	1700 cm^{-1}(m)

w = weak, m = medium, s = strong

Table 2 summarizes the data of modified poly(butadiene) cis and trans.

TABLE 2

IR Data From Modified PB Polymer

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

A signal at 3500 cm^{-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 1680 cm^{-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, $\overline{M}_c$ 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 $\overline{M}_c$, that is to a highly 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 (8).

Table 3 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 3

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 χ	Crosslink Density ν/V 10^{-4} mole/cm^3 at 25°C	Average Molecular Weight Between Crosslinks $\overline{M}_c$ 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

TABLE 3 - continued

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.

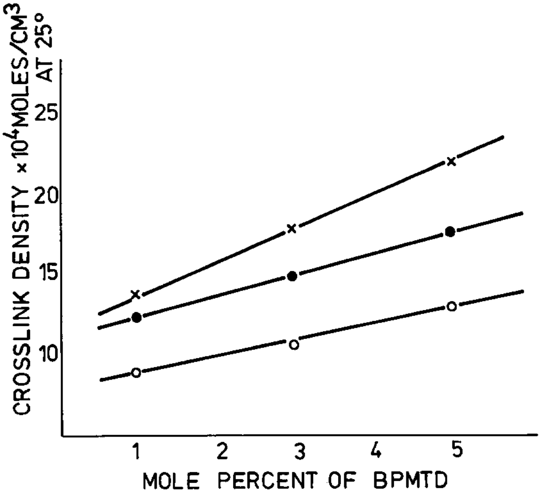

Figure 1. Plot of crosslink density of modified PI (o), PB (•) and S/B (×) with mole percentage of BPMTD incorporated

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, $\overline{M}_c$ values, as illustrated in table 3.

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.

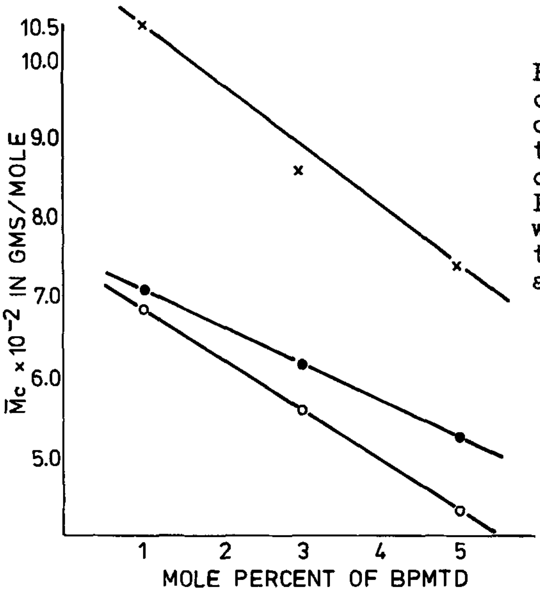

Figure 2. Plot of average molecular weight between crosslinks of modified PI (×) PB (●) and S/B (o) with mole percentage of BPMTD added

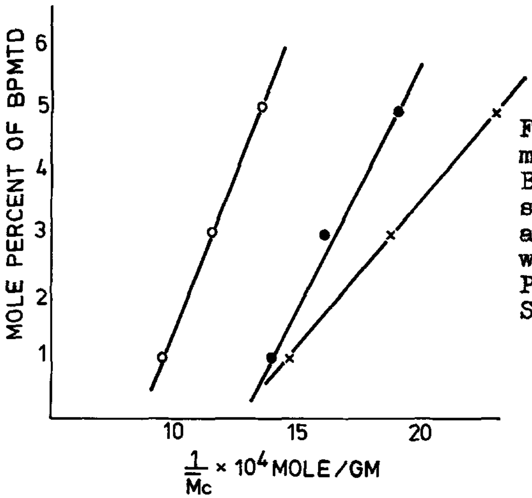

Figure 3. Plot of mole percentage of BPMTD content versus reciprocal of average molecular weight of modified PI (o), PB (●) and S/B (×)

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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