

Novel reagents for heat-activated polymer crosslinking

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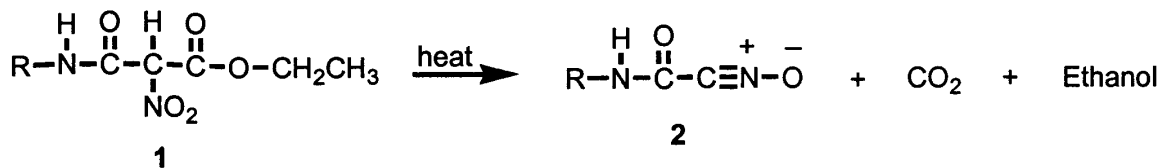
Summary

The dipolar cycloaddition of nitrile oxides with species containing unsaturation is a very attractive means of forming crosslinks in polymer systems, since the reaction is rapid and yields thermally stable links. Latent nitrile oxide precursors can be prepared by reaction of an isocyanate and an alkyl nitroacetate. These precursors release alkanol and carbon dioxide when heated to liberate the highly reactive nitrile oxide species. An improved synthetic procedure was developed to afford novel crosslinking agents based on difunctional, trifunctional and aliphatic precursors. Further, application of these agents to polymer crosslinking has been demonstrated.

Introduction

Nitrile oxides are very reactive species and several different methods for preparing them have been reported in the literature. Nitrile oxides can be generated *in situ* by the reaction of hydroxamoyl chloride with a tertiary amine or other base [1]. A drawback of this method is that it generates the Cl⁻ ion as a byproduct, which is corrosive and will attack metal surfaces. In addition, this method of generating nitrile oxide occurs at room temperature, which may cause a problem for process stability. Alternatively, furoxans can thermally decompose *in situ* to produce two nitrile oxide moieties, which can then be used to crosslink polymers [2]. The dinitrile oxides produced by this method react very rapidly at temperatures in the range of 80 to 110 °C. Finally, a special class of sterically hindered nitrile oxides [3,4,5,6] can also be used to crosslink unsaturated polymers.

More recently, nitrile oxides have been generated from heat-activated latent precursor compounds.



These latent precursors, **1**, are produced by a method which involves the generation of the

potassium enolate of ethyl nitroacetate *in situ* using K_2CO_3 [7,8,9]. The enolate then reacts with an isocyanate in toluene generating the salt form of the precursor. The salt form of the precursor is stable at elevated temperatures (180°C) and will not decompose to nitrile oxide. The salt is then acidified at low temperature ($\sim 40^\circ\text{C}$) to yield the protonated precursor. This type of precursor is attractive, since it is stable at low temperatures ($<100^\circ\text{C}$) and decomposes rapidly to the nitrile oxide species at elevated temperatures ($>150^\circ\text{C}$). At the decomposition temperature, nitrile oxide precursors (generically represented as **1**) will decompose into nitrile oxides (generically represented as **2**). At the same time, CO_2 and alcohol are evolved as by-products as illustrated in Figure 1.

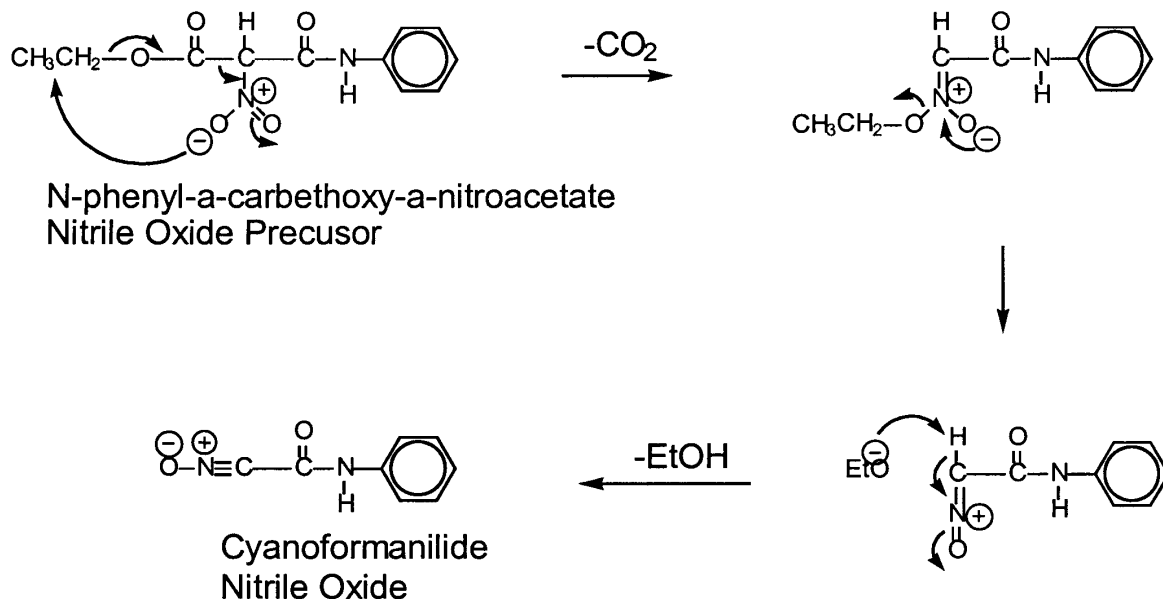
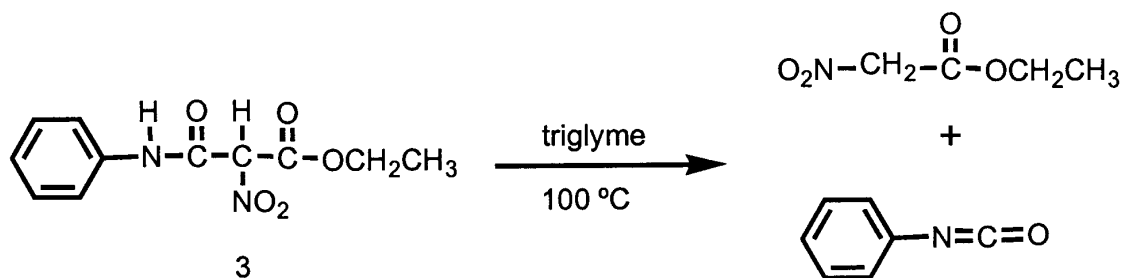


Figure 1. Proposed Mechanism of Decomposition

However, in our hands, the published preparative method that employed the *in situ* enolate provided low yields (30%) of the monofunctional aromatic precursor compound **3** and was ineffective on difunctional and aliphatic isocyanates. In addition, precursor **3** was found to revert to the original isocyanate in polar solvents (e.g. triglyme) at elevated temperature instead of generating the active nitrile oxide species. However, this reversion was not found to occur with aliphatic analogues under any conditions at elevated temperature. Under all thermal exposures, aliphatic analogues always generated nitrile oxides.



In order to utilize the latent nitrile oxide as a polymer crosslinking agent, we required a more

robust preparative method to provide a high yield of multifunctional agents. Herein, we report a modification to the procedure reported earlier [7,8,9] for synthesizing nitrile oxide precursors in order to afford difunctional, trifunctional and aliphatic analogues in high yield (90%). Further, application of these agents to polymer crosslinking has been demonstrated, as illustrated in Figure 2.

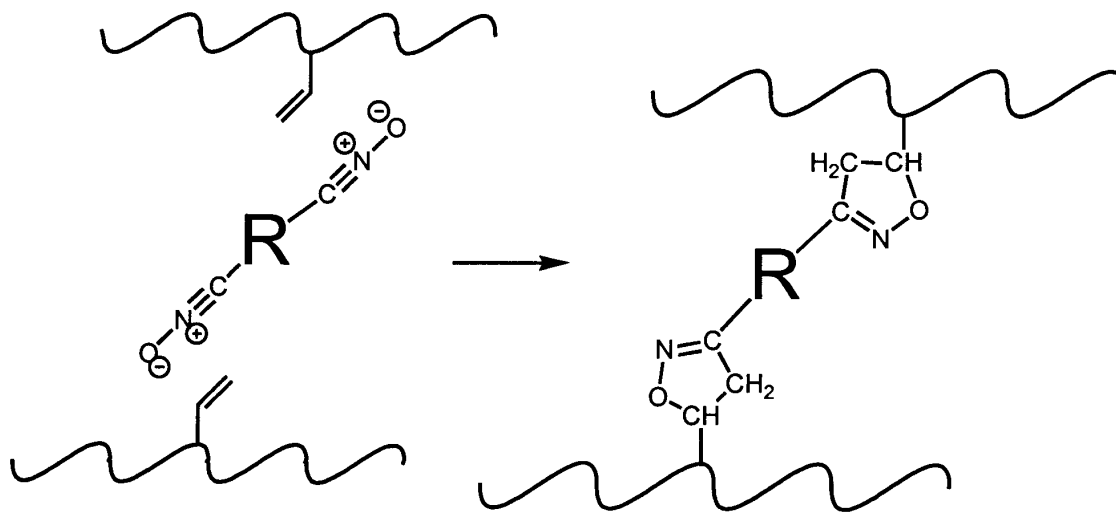


Figure 2. Polymer crosslinking through nitrile oxide

Experimental section

General

¹H NMR spectra were obtained with a BRUKER 300 MHz spectrometer: chemical shifts are expressed in ppm downfield from TMS as an internal standard. HPLC spectra were obtained using a Waters 996 photodiode array detector. GPC measurements were performed with a Waters 150-cv series equipped with Styragel HT 3, HT 6E (7.8 x 300 mm) columns calibrated with polystyrene standards, using THF as the eluent. Detection was made with a refractive-index detector. LC/MS spectra were acquired using a Finnigin MAT SSQ 7000 detector and the mode of ionization was APCI. Infrared Spectra were acquired on a Nicolet 560 Magna spectrometer.

Materials

Ethyl nitroacetate, ethanol, potassium hydroxide, isophorone diisocyanate, tetrahydrofuran, acidic amberlyst ion exchange resin, toluene, dichlorobenzene were obtained from Aldrich and used without further purification. Monoglyme and diglyme were obtained from Aldrich and dried over molecular sieves prior to use. ISOLENE 400 was bought from Hardman Chemicals and Hydrogenated MDI was bought from Bayer Corporation.

Nitrile oxide precursors

All glassware were dried and purged with nitrogen. Ethyl nitroacetate (45.3 g, 0.330 mol) and ethanol (30 mL) were added to the flask and the resulting solution was cooled to -78 °C.

Potassium hydroxide (155.9 mL (2.0 M), 0.315 mol) in ethanol was incrementally added using an addition funnel. The contents of the flask were then warmed to room temperature and the solvent was removed under vacuum. Dry diglyme (2-methoxy ethyl ether) (60 mL) was added to the solid enolate that remained. Desmodur W (0.1575 mol, 41.3 g) was dissolved in diglyme (200 mL) and added to the flask. The reaction contents were then heated to 100 °C for ~6 hours and the progress of the reaction was followed by infrared analysis. Once all isocyanate was consumed, the salt form of the precursor was isolated by vacuum filtration. The salt was washed with toluene and then air dried. In the salt form, the two carbonyl stretches due to the ester and amide were located at 1690, and 1630 cm^{-1} , respectively.

The salt was then dispersed in THF and strongly acidic amberlyst ion exchange resin (20 g) and then stirred overnight at 40 °C. Once the precursor was protonated, the reaction mixture was filtered to remove ion exchange resin and the filtrate was stripped under vacuum. The crude nitrile oxide precursor recovered was then purified by recrystallization. The purified nitrile oxide precursor was confirmed by IR, and NMR analysis.

IR (KBr) NH 3300 cm^{-1} , ester C=O 1760 cm^{-1} , amide C=O 1680 cm^{-1} , C-O 1020 cm^{-1} .

^1H NMR for precursor **4** (300 MHz in CDCl_3) δ NH 8.5; CH 6.5, 5.5; CH_2 4.5; CH_3 1-2.

Polymer crosslinking studies and analysis by GPC

ISOLENE 400, which is a 90,000 MW polyisoprene containing 92 mole percent unsaturation (X g) was added to a jar. Then the desired level of difunctional nitrile oxide precursor (Y g) was added. In order to achieve a more fluid mixture which allowed for easier stirring, a diluent (e.g. dichlorobenzene (5.0 g)) could be used in conjunction with the precursor and polymer. The jar containing the reagents was immersed into a 70 °C oil bath and thoroughly mixed (using a stir bar or an overhead mechanical stirrer) in order to dissolve the precursor in the polymer and obtain a homogeneous system.

Once fully dissolved, the jar was removed from the 70 °C oil bath and immersed into a 120, 150, or 180 °C oil bath with stirring resumed. Samples were withdrawn periodically and analyzed by Gel Permeation Chromatography (GPC) to observe increases in molecular weight. Crosslinking (gelation) was observed after a few hours with the time dependant on the level of nitrile oxide precursor used.

When the polymer was used alone as a control and subjected to the same conditions, no increase in molecular weight was observed.

Mole Ratio	Weight Ratio (X:Y)
(Olefin : Difunctional Precursor)	(Isolene 400 : Difunctional Precursor)
10 : 1	0.5 g : 0.35 g
100 : 1	5.2 g : 0.35 g
237 : 1	11.0 g : 0.35 g

The initial mole ratio of precursor to unsaturation was kept at 1:237 in order to eliminate any chance of gelation which would hinder analysis by GPC. The amount of precursor to unsaturation was small, but after six hours at 120 °C, a noticeable increase in molecular weight could be seen in the GPC curve due to crosslinking.

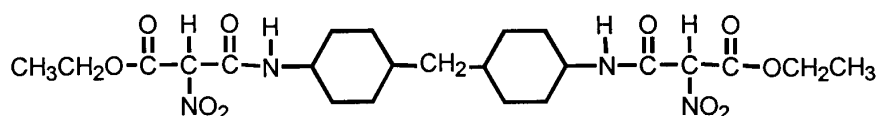
Since no gelation occurred using the ratio of 1:237, other experiments were conducted using higher levels of nitrile oxide precursor (e.g. 1:100, 1:10). With a 1:100 ratio it was determined that crosslinking took place after 3.5 hours at 120 °C resulting in gelation.

Polymer crosslinking studies by Rheological Dynamic Analysis

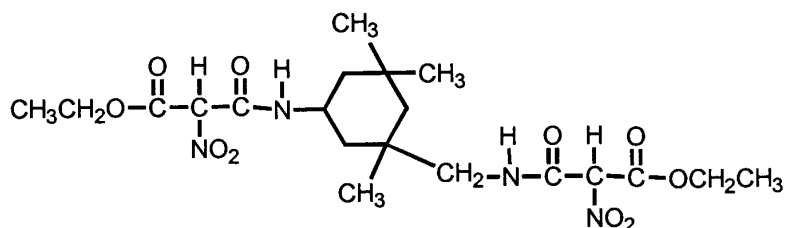
ISOLENE 400, an olefin polymer (0.499 g), was combined with a difunctional nitrile oxide precursor compound derived from Desmodur W (hydrogenated MDI) (0.368 g) and heated with stirring in an oil bath to 70 °C until homogeneous. The mole ratio of olefin to nitrile oxide precursor was 10:1. A small portion of the formulation was placed between two parallel steel plates and subjected to a temperature ramp study and evaluated by Rheological Dynamic Analysis. The temperature was increased 10 °C/minute to 150 °C and held isothermally at 150 °C for five hours. A sample of the polymer without precursor compound was also tested, as a control, and no increase in modulus was observed. As seen in Figure 4, the polymer with the nitrile oxide precursor crosslinking agent did decrease in modulus first as the viscosity was reduced at elevated temperature. However, a fairly rapid increase in modulus was observed reaching the plateau value at 2 hours into the experiment.

Results and discussion

There are two criteria that a nitrile oxide precursor must meet in order to be a suitable crosslinking agent: 1) a melt temperature in the polymeric system that is less than or equal to the decomposition temperature of the precursor and 2) solubility in the polymeric system to be crosslinked upon melting. The compatibility of the nitrile oxide precursor in the polymer and the level of crosslink density required to develop the properties for a particular application will dictate the choice of nitrile oxide precursor. The difunctional nitrile oxide precursors, **4** and **5**, served as irreversible chain extension or cross-linking agents in polymers having appropriate functionality to react with the nitrile oxide (e.g. alkene, alkyne, or nitrile).



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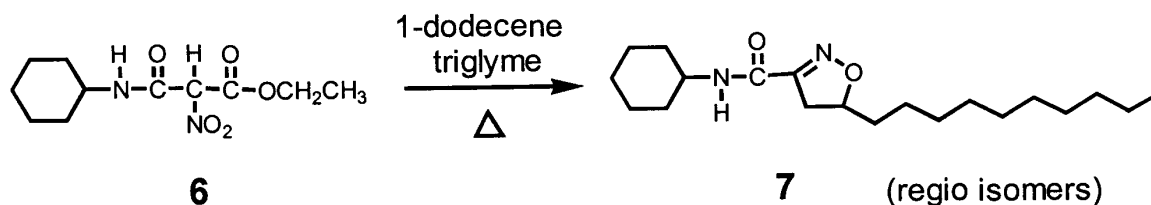


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The temperature at which these nitrile oxide precursors decomposed to form nitrile oxide was observed using Differential Scanning Calorimetry (DSC) analysis. When the difunctional nitrile oxide precursor **4** (derived from methylene bis (4-cyclohexyl isocyanate)) was heated at a rate of 10 °C/min., the precursor began to decompose at 160 °C. Thermal Gravimetric Analysis (TGA) confirmed weight loss at this temperature, which corresponded to the loss of CO_2 and ethanol.

The stability of these aliphatic precursors in polar environments was assessed. Precursor **6**,

derived from an aliphatic isocyanate (as opposed to the aromatic analogues), was found to react through 1,3-dipolar cycloaddition with unsaturation (i.e. 1-dodecene) in triglyme. In order to minimize any dimerization of nitrile oxide and maximize yield of adduct, the reaction was conducted under dilute conditions in 1-dodecene (1:100 molar ratio). The 1,3-dipolar cycloaddition product **7** was confirmed by LC/MS analysis ($m/e = 336$). In addition, ^1H NMR analysis confirmed the formation of the expected regioisomers.



The rate at which this reaction occurred was first illustrated using model compounds. Figure 3 illustrates the conversion rate from precursor **6** to 1,3-dipolar cycloaddition product **7** at several different temperatures. These conversions were determined by HPLC analysis of aliquots taken from the reaction vessel (consisting of nitrile oxide precursor and 1-dodecene) at several different time intervals. Precursor **6** and the 1,3-dipolar cycloaddition product **7** were resolved at different retention times and the rate was determined through the use of calibration curves. Since the rate determining step is the decomposition of the nitrile oxide precursor to nitrile oxide, analysis was based on conversion from precursor **6** to the 1,3-dipolar cycloaddition product **7**.

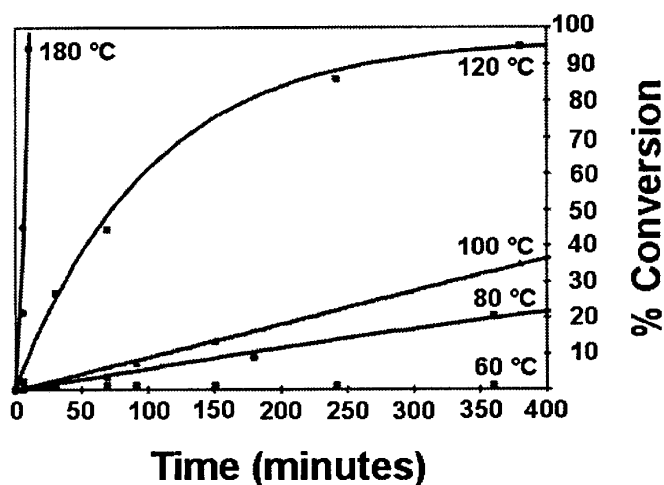
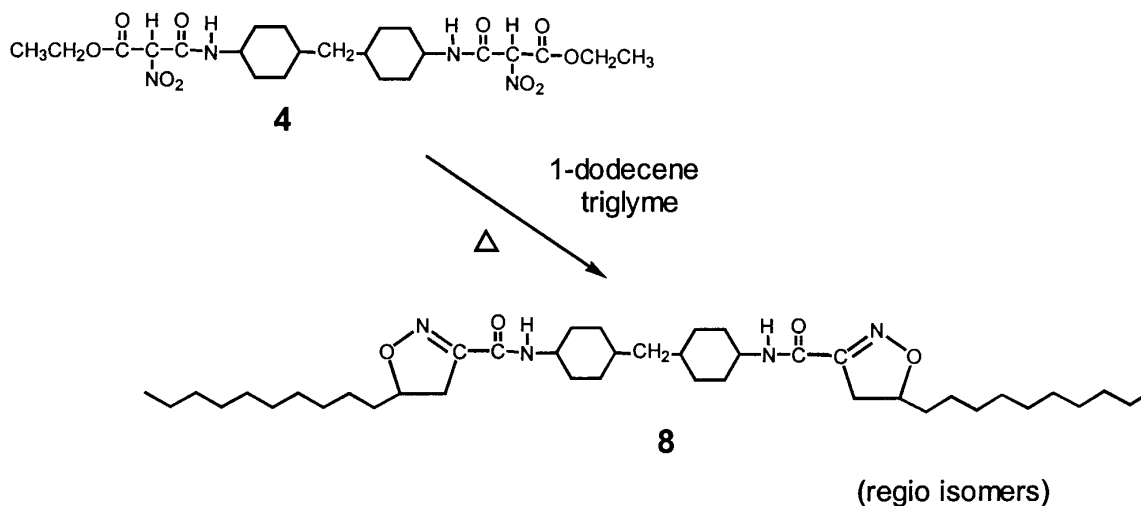


Figure 3. Rate of conversion from precursor to 1,3-dipolar cycloaddition product

As illustrated in Figure 3, the rate of decomposition from precursor **6** to 1,3-dipolar cycloaddition product **7** was very rapid at 180 °C. Further evaluation determined that a short temperature spike of only three minutes at 180 °C was sufficient to convert >90% of precursor **6** to 1,3-dipolar cycloaddition product **7**.

This same reactivity was also observed with difunctional precursors. A specific example was the reaction between precursor **4** and an alkene (i.e. 1-dodecene) in triglyme. The 1,3-dipolar cycloaddition product **8** was confirmed by LC/MS analysis ($m/e = 684$). In addition, ^1H NMR analysis confirmed the formation of regioisomers.



This chemistry has also been shown to be effective with unsaturated polymers. Nitrile oxides are very reactive and unstable species, and once a nitrile oxide is formed it reacts very rapidly with unsaturated functionality on the polymer (e.g. alkene, alkyne, or nitrile) as illustrated in figure 2. The ability of precursor **4** to crosslink a polyisoprene rubber (Isolene 400) was evaluated. Precursor **4** and polyisoprene were mixed in a stoichiometry of one precursor functionality for every 100 sites of unsaturation. The reaction contents were subjected to a heat treatment at 150 °C with continuous stirring and periodically analyzed by GPC. After the treatment, molecular weight increased as illustrated by the earlier eluting peak in Figure 4. When the polymer was used alone as a control and subjected to the same thermal conditions, no increase in molecular weight was observed.

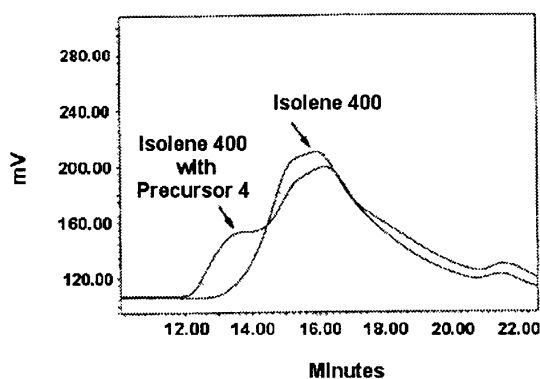


Figure 4. GPC showing increased M.W. of polyisoprene after reaction with precursor **4** at 150 °C

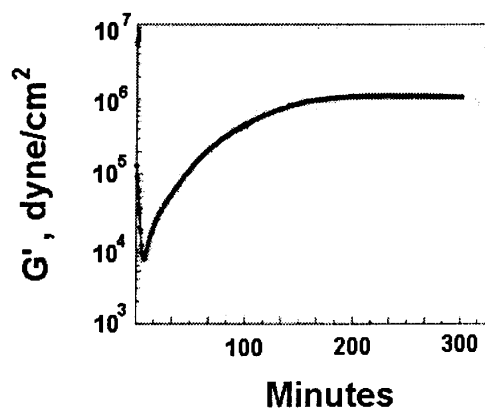


Figure 5. RDA showing modulus increase of polyisoprene after reaction with precursor **4** at 150 °C

This same system, consisting of precursor **4** and polyisoprene, was analyzed by Rheological Dynamic Analysis (RDA) and the modulus was monitored at 150 °C over time. As can be seen in Figure 5, the modulus was found to increase by two orders of magnitude after two hours, illustrating molecular weight increase through crosslinking. In a blank control test where nitrile oxide precursor was not added, we did not observe any increase in modulus of the isoprene polymer.

Conclusions

In conclusion, an improved synthetic method for the preparation of latent nitrile oxides in high yield and with increased structural versatility has been developed. Release of nitrile oxide and 1,3-dipolar cycloaddition reactivity has been demonstrated for these latent species. Thermal control over rate of reaction has also been shown. More specifically, the latent nitrile oxides can be stable at moderate temperatures (80 °C) for extended periods of time. Lastly, the utility of this chemistry as a new latent crosslinking system for polymers bearing olefinic unsaturation has been demonstrated.

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