Metathesis Polymerization of *N*-Phenylnorbornenedicarboximide

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ABSTRACT: This paper describes the ring-opening metathesis polymerization (ROMP) of *N*-phenylnorbornenedicarboximide (NDI). The exo isomer of NDI is found to polymerize into a high molecular weight straight-chain polymer with high conversion. Under similar conditions, the polymerization of the endo isomer leads to a low molecular weight polymer with low conversion. In the polymerization of isomer mixtures the molecular weight and molecular weight distribution and the total conversion decrease with an increase in the endo concentration in the monomer feed; the maximum amount of endo isomer incorporated in the polymer chain is found to be about 28%. The glass transition temperatures of polymers produced using ruthenium and osmium catalysts, having predominantly a trans structure of the double bond, are about 15 °C higher than the polymers produced using tungsten catalysts, having a mixture of cis and trans double bonds. Copolymerization of NDI with 5-norbornene-2-carbonitrile (NN) produces random copolymers; the glass transition temperature increases linearly with an increase in the imide content in the copolymer.

Introduction

Metathesis polymerization is a very versatile reaction. Materials ranging in properties from soft rubber to hard and tough thermoplastics and highly cross-linked thermosets can be prepared by this chemistry. Metathesis polymerization, depending on the ring strain of the cycloolefin, is fast, can be carried out in bulk without any major byproducts, and can be driven to complete conversion. These characteristics lead to the possibility of producing the finished polymer from the monomer in one step without a need to use solvents or remove unpolymerized monomers. Fast polymerization of dicyclopentadiene has led to the commercialization of reaction injection-molded parts of poly(dicyclopentadiene) by Hercules Inc.[1,2] Several patents issued to B.F. Goodrich report the bulk polymerization of methyltetracyclododecene.[3,4]

The activity of a metathesis catalyst system is generally adversely affected by the presence of polar functionalities on the metathesizing moiety. However, when the functionally substituted substrate is norbornene, several catalyst systems show a remarkable tolerance to a variety of functional groups, because the norbornene is a highly strained ring. The release of ring strain during the ring-opening polymerization makes the free energy of the reaction highly negative. A greater tolerance toward different functionalities has led to the polymerization of a variety of functionally substituted norbornenes.[5-9] The discovery of novel catalysts for living metathesis polymerization has led to the synthesis of several interesting block copolymers.[9-11]

This paper describes the synthesis and properties of a high-heat polymer based on *N*-phenylnorbornenedicarboximide (NDI). The polymerization of exo and endo isomers, *exo*-NDI and *endo*-NDI, has been investigated. The endo isomer is found to have very poor reactivity toward metathesis, whereas the exo isomer polymerizes to a high molecular weight straight-chain polymer.[12]

Experimental Section

Tungsten hexachloride, acetal, diethylaluminum chloride, and 5-norbornene-2-carbonitrile (NN) were purchased from Aldrich Chemical Co. NN was distilled before use. The isomer ratio in NN, as analyzed by ^{13}C NMR, was found to be 55/45 exo/endo.

The *exo*-norbornene-5,6-dicarboxylic anhydride, *exo*-NDA, was prepared by the thermal isomerization of the corresponding endo isomer as described by Kastner and Calderon.[8]

Synthesis of *exo-N*-Phenylnorbornene-5,6-dicarboximide. A total of 229.8 g (1.3 mol) of *exo*-NDA was dissolved in 1400 mL of toluene. An amount of 130.4 g of aniline is added dropwise to the stirred solution of NDA, resulting in a slurry of amic acid. This was maintained at 100 °C for 1 h and then cooled to room temperature, filtered, and dried to give 327 g of the amic acid.

A total of 290 g of amic acid, 43.6 g of anhydrous sodium acetate, and 850 g of acetic anhydride were heated at reflux for 1$^1/_2$ h and then cooled. The solid that crystallized out on cooling was filtered, washed several times with water, and dried in a vacuum oven at 60 °C overnight. Analysis by NMR shows pure *exo*-NDI, mp 200–202 °C.

Polymerization Procedure Using WCl_6/Aluminum Alkyl. To a solution of 3.45 g of NDI in 21 mL of 1,2-dichloroethane was added 0.15 mL of 0.5 M tungsten hexachloride/acetal solution in toluene (mole ratio of WCl_6/acetal was 1/2) followed by 0.22 mL of 2.05 M diethylaluminum chloride in heptane. The reaction was carried out at 70 °C for 4 h. The polymer was precipitated in methanol. The precipitated polymer was again dissolved in methylene chloride and reprecipitated in methanol, filtered, and dried in a vacuum oven at 60 °C overnight. The inherent viscosity, as measured in chloroform, was found to be 1.03 dL/g.

Polymerization Procedure Using Mes·$W(CO)_3$/Et_2AlCl. In a vial containing 0.05 g of Mes·$W(CO)_3$ (where Mes = mesitylene) is added 0.015 g of norbornene epoxide. To this is then added 2 mL of chlorobenzene followed by 0.07 mL of Et_2AlCl.

To the catalyst solution prepared above is added 3 g of NDI. Reaction is carried out at 65 °C for 72 h. Polymer is recovered by precipitating the reaction mixture in methanol.

Polymerization Procedure Using Noble Metal Catalysts. A 1% solution of the catalyst ($RuCl_3{\cdot}3H_2O$, $IrCl_3{\cdot}3H_2O$, $OsCl_3$) is made in a mixture of ethanol and chlorobenzene (1/1 ethanol/chlorobenzene).

Polymerization is carried out by addition of 1 mL of the catalyst solution to 1 g of NDI. Polymerization is carried out at 65 °C for 72 h.

DSC thermograms were obtained with a Perkin-Elmer DSC-2, using 20 °C min^{-1} heating and cooling rates. DMA data were obtained at a frequency of 11 Hz and a 3 °C min^{-1} heating rate.

All NMR spectra were obtained from a General Electric GN-300 operating at 300 MHz for ^1H and 75 MHz for ^{13}C. ^1H NMR spectra were acquired with a 2.132-kHz spectral width and a 1.054-kHz offset, which covered 0–7 ppm. All spectra were obtained with a 50% solution in $CDCl_3$ which decreased the viscosity and sharpened the lines. The $CDCl_3$ was also used as a lock signal.

Result and Discussion

Polymerization Behavior of Exo and Endo Isomers of NDI. Polymerization of *exo*-NDI and *endo*-NDI was

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Table I
Effect of Imide Stereochemistry on the Properties of the Monomer and the Polymer

	exo-NDI	*endo*-NDI	poly-(*exo*-NDI)	poly-(*endo*-NDI)
mp, °C	202	145		
convn, %	100	15		
inh visc,[a] dL/g			1.08	0.08
solubility[a]	low	high	high	low

[a] Solvent. (1) Monomers: acetone, 1,2-dichloroethane, chloroform. (2) Polymers: chloroform, DMSO, DMF, DMAC.

investigated using a metathesis catalyst system based on WCl_6/aluminum alkyl. The polymerization is carried out by dissolving the monomer in toluene or 1,2-dichloroethane and then injecting the catalyst into the monomer solution.

The viscosity of the polymerizing solution containing the exo isomer increases with time, whereas the solution containing *endo*-NDI and the catalyst does not show any change in viscosity. Polymers are recovered after precipitation in methanol. The solution containing poly(*exo*-NDI) precipitates in the form of a fibrous material, whereas the solution containing poly(*endo*-NDI) precipitates out in a powder form.

The melting and solubility behavior of the two isomers, *exo*- and *endo*-NDI, and their conversion in a metathesis reaction are listed in Table I. Table I also lists the viscosity of the polymers derived from the exo and endo isomers.

The melting point of *endo*-NDI is lower, and the solubility in organic solvents (acetone, chloroform, 1,2-dichloroethane) is much higher, compared to *exo*-NDI. Interestingly, polymers derived from them have the reverse solubility behavior.

Poly(*exo*-NDI) is soluble in organic solvents, whereas poly(*endo*-NDI) is soluble only in hot aprotic solvents. The lower melting point and high solubility of *endo*-NDI compared to the exo isomer is not surprising considering the spherical shape of the endo isomer. The effect of the conformation on bridge-substituted norbornene is so pronounced, in some cases, that the endo isomers exist in the form of plastic crystals much before complete melting.[13] In the plastic crystal state these materials behave like a liquid with a high degree of rotational freedom.

It is clear from Table I that *exo*-NDI can be polymerized, using a tungsten/aluminum alkyl catalyst system, into a high molecular weight polymer in high yields. However, polymerization of *endo*-NDI results in extremely low molecular weight oligomers with very low conversion. For all practical purposes *endo*-NDI does not really polymerize. Kastner and Calderon have described a similar difference in the polymerization behavior of *exo*- and *endo*-norbornenedicarboxylic anhydride.[8]

It is now well established that the active catalytic species in the metathesis polymerization is a metallacarbene. According to the carbene mechanism, the polymerization occurs by insertion of the monomer into the transition metal–carbene bond.

In the propagation reaction involving exo-substituted norbornenes the substituents and the metallacarbene are on the opposite side of the cyclopentane ring. Since the substituent group is disposed away from the growing polymer chain (metallacarbene), it does not sterically interfere in the propagation reaction. The same stereochemistry also eliminates any possibility of intramolecular interaction between the carbene and the substituents. The exo isomer, therefore, polymerizes readily to give a high molecular weight polymer in nearly complete conversion.

Table II
Effect of the Endo/Exo Ratio on the Polymerization of NDI (Catalyst, WCl_6/Aluminum Alkyl; Solvent, 1,2-Dichloroethane)

no.	*A*, % endo in the monomer feed	*B*, % convn of *endo*-NDI (NMR)	yield, % total convn	M_w (×1000)	MWD	T_g, °C
1	0	0	99	53.2	2.20	227.0
2	17	11	87	30.2	2.25	229.3
3	33	19	83	24.6	1.94	230.3
4	50	28	63	21.4	1.75	222.7
5	67	28	53	17.1	1.56	226.8
6	83	25	17	6.5	1.68	
7	100	15	15			225.8

In the propagation reaction involving endo-substituted norbornene, however, the substituent and the metallacarbene are on the same side of the cyclopentane ring. Cis disposition of the metallacarbene and the substituents creates both steric and electronic restrictions toward the propagation reaction.

Steric hindrance is created by the fact that four out of five carbons in the cyclopentane ring are cis substituted. The most important reason for the poor reactivity, however, appears to be the deactivation of the metallacarbene due to the intramolecular interaction (coordination) between the carbonyl oxygen and the transition metal, which becomes possible because of their proximity in the endo-isomer-derived metallacarbene.

Poor solubility of poly(*endo*-NDI) is the reflection of its rigidity. The cis substitution of the four carbon atoms of the cyclopentane ring in poly(*endo*-NDI) gives rise to strong steric hindrance and makes the chain motion difficult. This is reflected by the high glass transition temperature of this very low molecular weight (inherent viscosity = 0.08) polymer. The low molecular weight poly(*endo*-NDI) has the same T_g as the high molecular weight polymer from *exo*-NDI. The molecular weight of poly(*endo*-NDI) is significantly below the critical molecular weight. If high molecular weight poly(*endo*-NDI) could be synthesized, it should have a glass transition temperature significantly higher than poly(*exo*-NDI).

On the basis of the discussion above, it can be concluded that the stereochemistry of the imide which is responsible for high solubility and low melting in the case of the *endo*-NDI results in a polymer with poor solubility and a high glass transition temperature. The disposition of the imide group toward the double bond in the case of the endo monomer results in poor reactivity and lower conversion.

Polymerization of the Isomer Mixture of NDI. The effect of endo isomer concentration on conversion, polymer structure, molecular weight and molecular weight distribution, and glass transition temperature was investigated.

To study the effect of endo isomer concentration on the polymerizability of the isomer mixture, *endo*- and *exo*-NDI were mixed in different proportions and then polymerized under identical reaction conditions (see Table II). All the polymers were analyzed by ^{13}C NMR. Because the difference in the chemical shift of the carbonyl carbon derived from the *endo*- and *exo*-NDI is significant, the amount of *endo*-NDI which participated in the polymerization could be easily investigated.

Table II shows the amount of endo isomer in the monomer feed and the concentration of endo-monomer-derived units in the polymer chain as analyzed by ^{13}C NMR. Increasing the endo isomer concentration in the monomer charge results in higher amounts of endo-monomer-derived units incorporated in the polymer chain,

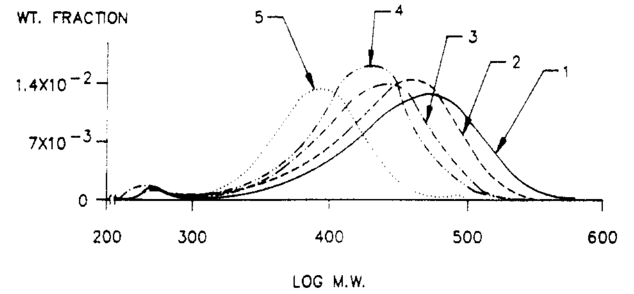

Figure 1. Molecular weight profile for poly(*N*-phenylnorbornenedicarboximide) prepared from the monomer containing (1) 17%, (2) 33%, (3) 50%, (4) 67%, and (5) 85% endo isomers.

but the maximum amount of endo isomer which participates in the polymerization is only 28%.

Evidence from solubility studies indicates that, in spite of the vast difference in the reactivity of the two isomers, they have copolymerized and the product is not a mixture of two homopolymers. Poly(*endo*-NDI), as reported in the previous section, is soluble only in hot aprotic solvents and is insoluble in chlorinated solvents, whereas poly(*exo*-NDI) readily dissolves in all chlorinated solvents. All the polymers derived from the polymerization of the isomer mixtures are soluble in methylene chloride. Mixtures of the two homopolymers, poly(*endo*-NDI) and poly(*exo*-NDI), on the other hand, do not influence each other's solubility behavior.

The effect of the endo isomer concentration on the molecular weight and molecular weight distribution was studied by size-exclusion chromatography (SEC). Figure 1 shows the SEC curves of the polymers derived from the polymerization of NDI containing different exo/endo ratios. As the concentration of the endo isomer in the monomer feed increases, the weight fraction of the high molecular weight polymer decreases. The molecular weight (M_w) and the molecular weight (MWD) are given in Table II. It is interesting to note that it is not only the molecular weight that is reduced with the increase in the endo isomer but also the molecular weight distribution. This suggests that chain transfer does not increase because of the presence of higher amounts of endo monomer units. This is also indicative of the inability to form the metallacyclobutane transition state by the endo-monomer-derived carbene. *endo*-NDI-derived carbenes may be less reactive because the metal can coordinate with the carbonyl group of the imide to give a stable six-membered ring.

Figure 2 shows the effect of the endo isomer in the monomer feed on the total conversion and the molecular weight (M_w) of the polymer. Conversion and the molecular weight both decrease linearly with an increase of the endo isomer concentration. With the present reaction conditions it seems that an exo isomer concentration of ~80% or higher will be needed for the synthesis of high molecular weight poly(NDI) in high yield.

The glass transition temperature of the polymers containing different amounts of *endo*-NDI-derived units was investigated by DSC and the glass transition temperature (T_g) are reported in Table II. If the T_gs of poly(*exo*-NDI) and poly(*endo*-NDI) were the same, then a decrease in the T_g will be expected with an increase in the endo concentration, since low molecular weight polymers are formed from a monomer mixture with an increasing endo isomer concentration. The T_gs of all the polymers in Table II are not significantly different. This suggests that the T_gs of poly(*endo*-NDI) and poly(*exo*-NDI) of similar molecular weight may not be the same and that the T_g of poly(*endo*-NDI) is higher than that of poly(*exo*-NDI). In summary, increasing the endo isomer concentration leads to two effects: (1) a decrease in the T_g due to lower molecular weight, and (2) an increase in the T_g due to the higher concentration of endo units in the polymer. The two effects nearly cancel each other, resulting in substantially no change in T_g with a change in the isomer content in the polymer.

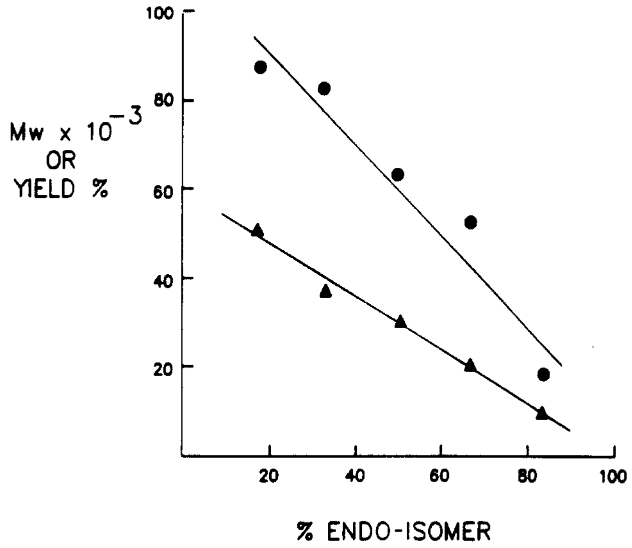

Figure 2. Effect of the endo isomer concentration on the conversion (●) and the molecular weight (▲) of poly(NDI).

Synthesis of Stereoregular Poly(NDI). Stereoregularity has a considerable effect on the properties of the polymer. Stereoregular polypropylene for example is a thermoplastic material with attractive properties and has applications in different areas, whereas polypropylene with a lack of stereoregularity (atactic) is soft and rubbery at room temperature. Control of the stereoregularity, therefore, increases the range of materials available from a particular monomer.

In an effort to synthesize stereoregular polymers of NDI, polymerization was investigated using several catalyst systems. The polymers were then analyzed by NMR to determine the microstructure. The effect of the microstructure on the polymer properties was studied by DSC and dynamic mechanical analysis.

Poly(*exo*-*N*-phenylnorbornenedicarboximide) prepared from a substantially pure exo isomer presented relatively simple ^{1}H and ^{13}C NMR spectra, apparently because NDI is a symmetrical molecule. As shown in Figure 3 there are only four possible modes in which the monomer units could be assembled. The polymers were analyzed primarily for the double bond structure. Tacticity was not examined because the polymer lacked fine structure. Polymers are prepared using catalyst systems based on $RuCl_3 \cdot 3H_2O$, $OsCl_3$, Mes·$W(CO)_3$, WCl_6/aluminum alkyl, $WCl_6/C(CH_3)_4$, $MoCl_5$, and $NbCl_5$. Because molybdenum- and niobium-based catalysts gave very poor polymer yields, the purification of the polymer, i.e., removal of the unpolymerized monomer, was difficult. The presence of cis and trans double bonds was determined by proton NMR. The trans content in the polymer prepared using a different catalyst system is shown in Table III. ^{1}H NMR analysis of ruthenium- and osmium-catalyzed polymers gave only one signal in the vinyl region, indicating only one type of double bond.

The ruthenium-catalyzed polymer exhibited the simplest spectrum and was investigated in detail. Vinylic, allylic, methylene, and the aromatic protons, present in polymer, were unambiguously identified by two-dimensional NMR (Figures 4 and 5). It is interesting to note that the two methylene protons at C-7 are not equivalent

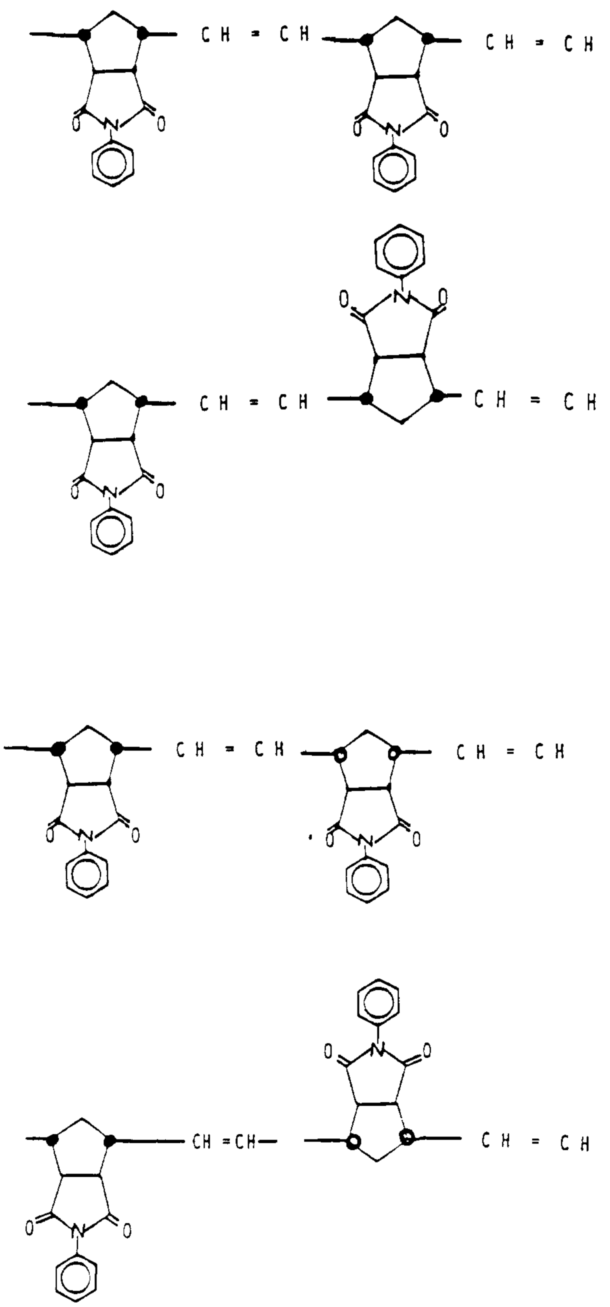

Figure 3. Possible assembly modes of poly(NDI).

Table III
Effect of Stereoregularity on the Properties of Poly(NDI)

catalyst	trans/cis	T_g(DSC), °C	tan δ_{max}
$RuCl_3 \cdot 3H_2O$	100/0	240	263
$OsCl_3$	93/7	240	263
Mes·W(CO)$_3$	52/48	225	
WCl_6/aluminum alkyl	60/40	225	240
$WCl_6/(CH_3)_4Sn$	62/37		

and that they give two distinct signals at 1.74 and 2.23 ppm. The bridgehead protons at C-7 in the norbornene monomers are known to be nonequivalent because the chemical environment around the two protons is different. This is the first time, to the best of our knowledge, that the two methylene protons in a substituted norbornene polymer were found to give two distinct signals. The conclusion that chemical shifts at 1.74 and 2.23 ppm are due to the two protons on the same carbon was made in a selective decoupling experiment, shown in Figure 6.

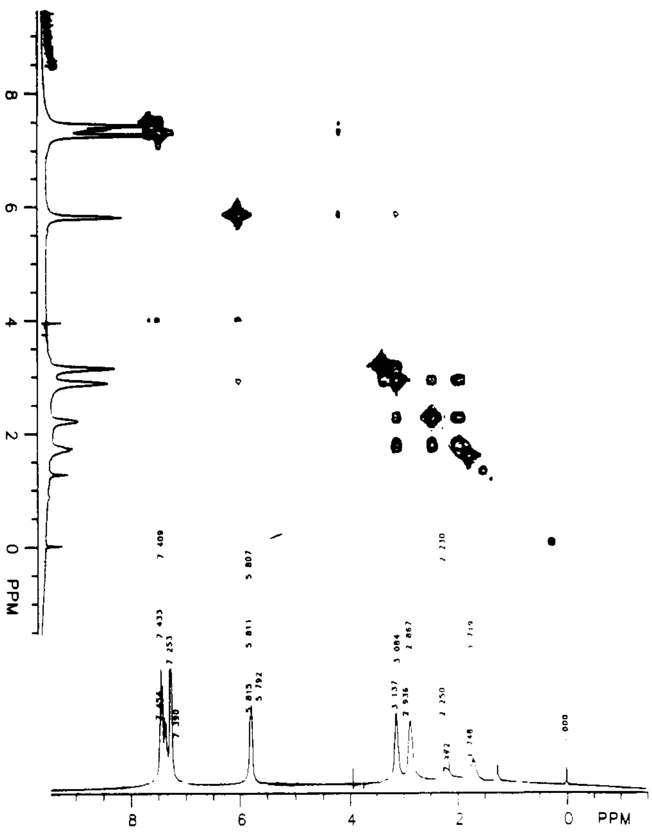

Figure 4. Two-dimensional proton NMR of ruthenium-catalyzed poly(*exo*-NDI).

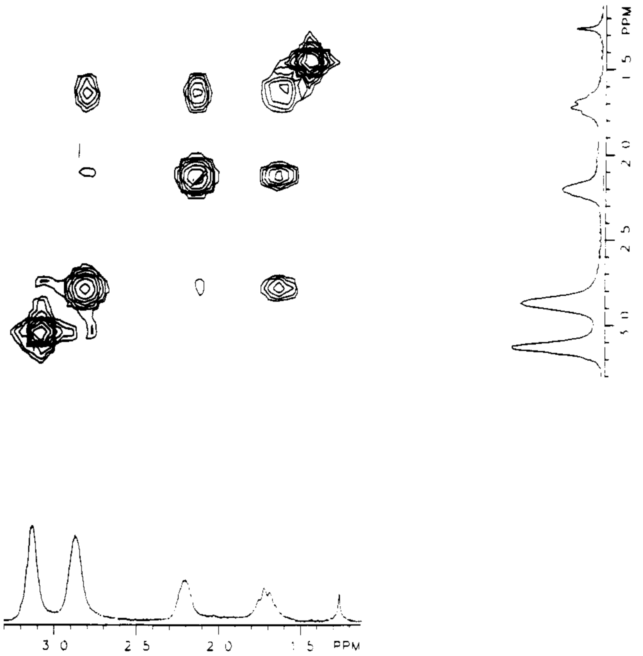

Figure 5. Two-dimensional proton NMR of ruthenium-catalyzed poly(*exo*-NDI) (high field).

The conclusion that the vinylic protons in the ruthenium-catalyzed polymer are trans comes from the fact that ruthenium catalysts provide predominantly trans double bonds in the metathesis of other norbornenes.[14] Trans selectivity in the ruthenium-catalyzed polymers is further confirmed from measurement of *J* coupling between the allylic and the vinylic protons in polymers containing both the cis and the trans double bonds. Polymer produced by using mesitylenetungsten tricarbonyl gives two signals in the vinylic region, one at 5.51 ppm and the other at 5.77 ppm (Figure 7). By measurement of the *J* coupling, the signal at 5.77 ppm was associated with the trans proton, and the signal at 5.51 ppm, with the cis proton. The *J* couplings with the allylic proton were 12 and 18 Hz, respectively. Typically, *J* values

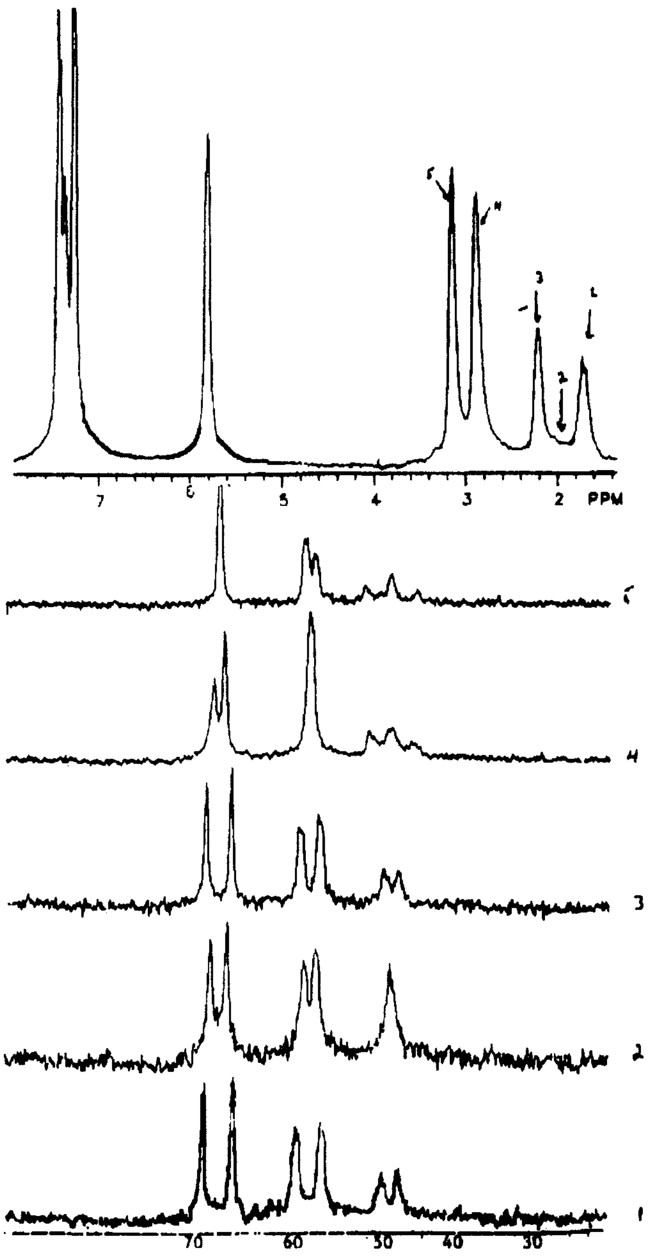

Figure 6. Selectively decoupled NMR spectra of poly(*exo*-NDI) prepared using a ruthenium-based catalyst.

for cis protons are larger (12–15 Hz) than with trans (6–15 Hz). Osmium-catalyzed polymer exhibited signals at 5.78 ppm which is identified with trans protons. Tungsten hexachloride-catalyzed polymer, on the other hand, exhibited a trans proton signal at 5.78 ppm and, additionally, a cis proton signal at 5.51 ppm. Integrated intensities indicated a trans/cis ratio of 60/40.

Effect of Stereoregularity on Polymer Properties. Polymers prepared using different catalysts, e.g., $RuCl_3 \cdot 3H_2O$, $OsCl_3$, $Mes \cdot W(CO)_3$, WCl_6/aluminum alkyl, $WCl_6/(Me)_4Sn$, having different cis/trans ratios of the double bond, were analyzed by DSC and the dynamic mechanical analysis.

Glass transition temperatures are shown in Table III. The glass transition temperatures of polymers produced using ruthenium and osmium catalysts, having predominantly a trans structure of the double bond, are about 15 °C higher than the polymers produced using tungsten catalysts, having a mixture of cis and trans double bonds (Figure 8).

The dynamic modulus vs temperature plot for ruthenium-, osmium-, and tungsten-catalyzed polymers is shown in Figure 9, and the tan δ vs temperature plot for the polymers is shown in Figure 10. Ruthenium- and osmium-catalyzed polymers, with predominantly a trans unsaturation, have a tan δ_{max} centered around 263 °C which is about 23 °C higher than the tan δ_{max} for the polymer containing a mixture of cis and trans double bonds,

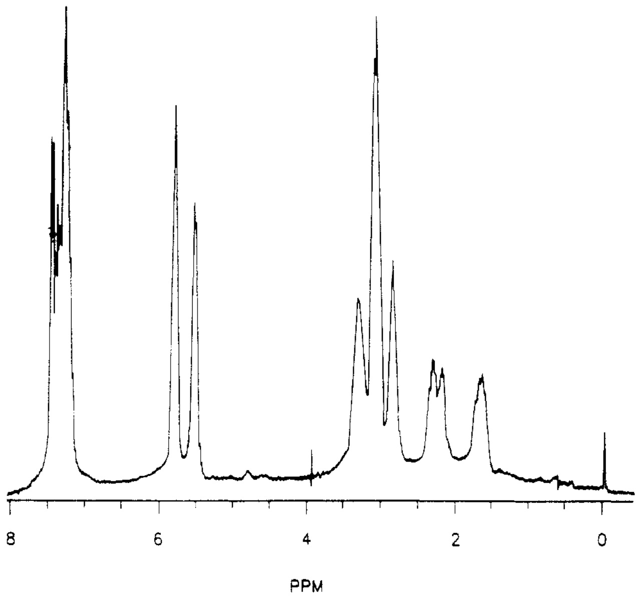

Figure 7. ^1H NMR of poly(*exo*-NDI) prepared using a mesitylene-based catalyst.

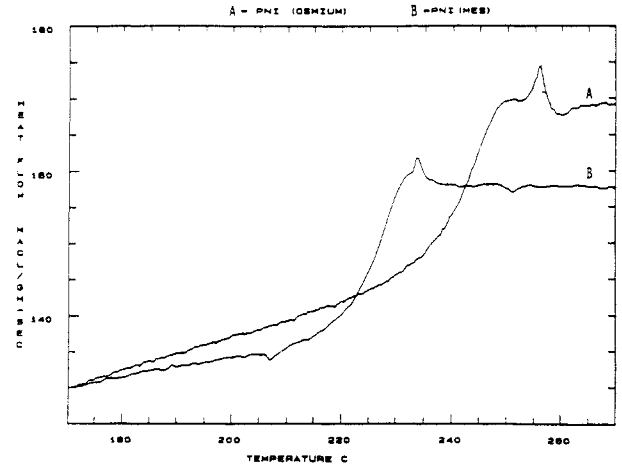

Figure 8. DSC thermograms of poly(*exo*-NDI) prepared using (A) osmium- and (B) tungsten-based catalysts.

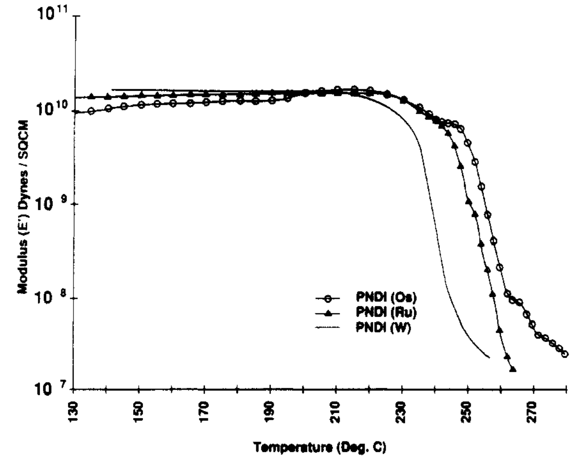

Figure 9. Dynamic modulus vs temperature plot for poly(*exo*-NDI) prepared using (a) ruthenium-, (b) osmium-, and (c) tungsten-based catalysts.

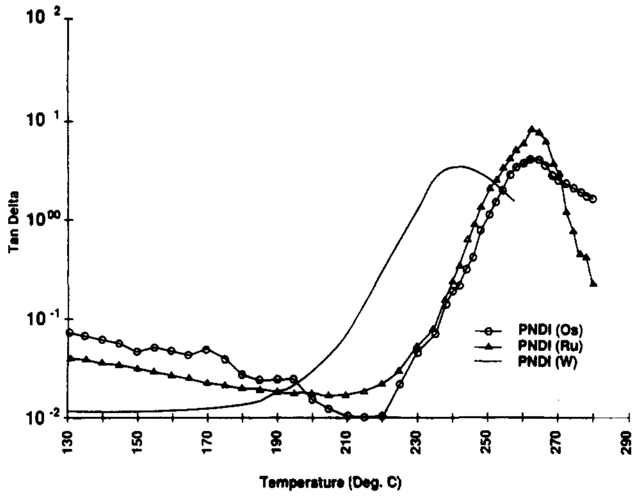

Figure 10. tan δ vs temperature plot of poly(*exo*-NDI) prepared using (a) ruthenium-, (b) osmium- and (c) tungsten-based catalysts.

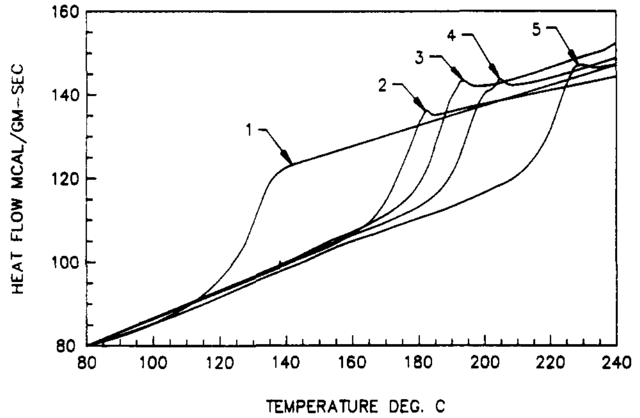

Figure 11. DSC thermogram of (1) poly(NN) and its copolymers with *exo*-NDI containing (2) 25%, (3) 40%, (4) 50%, and (5) poly(*exo*-NDI).

produced using a tungsten catalyst. A drop in the dynamic modulus is also observed at higher temperatures compared to the polymers containing mixtures of cis and trans double bonds.

It can be concluded that ruthenium and osmium catalysts polymerize *exo*-NDI to high molecular weight polymers, containing predominantly a trans double bond. The T_g and the tan δ_{max} of these polymers are about 15–20 °C higher than those of the polymer produced by a tungsten catalyst, such as WCl_6/aluminum alkyl, Mes·W[CO]$_3$, and $WCl_6/Sn(CH_3)_4$, which contain a mixture of cis and trans double bonds.

Copolymers of *exo*-NDI with 5-Norbornene-2-carbonitrile. Polymers containing different amounts of imide and nitrile groups were prepared by dissolving appropriate amounts of NDI and NN monomers in a solvent and carrying out the polymerization using tungsten/aluminum alkyl catalyst. The resulting copolymers were analyzed by ^{13}C NMR to determine the amounts of imide and nitrile groups in the copolymer. The imide/nitrile ratio in the copolymers was similar to the ratio in the monomer feed.

DSC thermograms for the homo- and copolymers of NDI and NN are shown in Figure 11. The glass transition temperature for poly(NDI) is considerably higher (220 °C) than that for poly(NN) (130 °C). This is because the bridgehead functionality, the *N*-phenyl imide group, substantially increases the rigidity of the polymer, making the segmental motion more difficult.

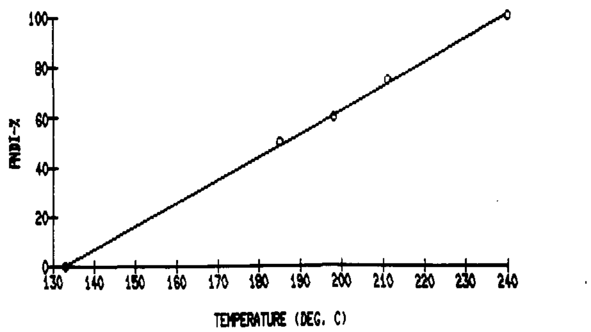

Figure 12. %poly(NDI) vs T_g for the copolymers of NDI and NN.

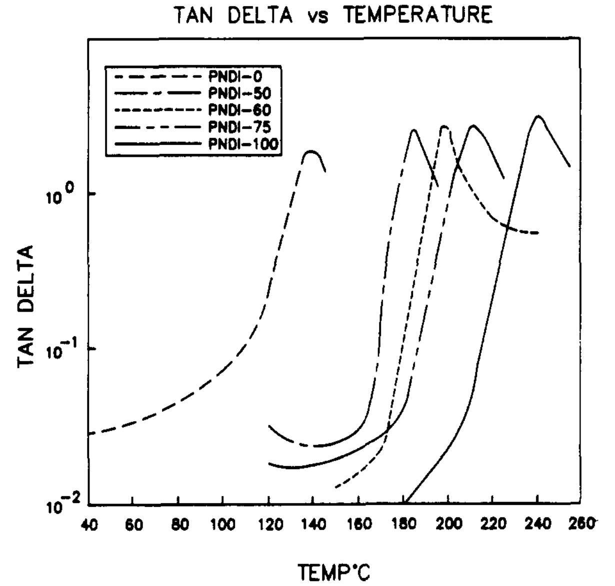

Figure 13. tan δ_{max} vs temperature plot for (1) poly(NDI) and its copolymers with NN containing (2) 25%, (3) 40%, and (4) 50% NN and (5) poly(NN).

Thermograms for all the copolymers of NN and NDI show a change in the specific heat only at one temperature, indicating that random copolymers are formed. The T_g of the copolymers are between the T_gs of the two homopolymers. Figure 12 shows the plot of the glass transition temperature vs % NDI in the copolymer. As can be seen, T_g increases linearly with an increase in the imide content in the copolymer.

Homopolymers of NDI and NN and their copolymers are amorphous and soluble in chlorinated solvents from which clear and tough films can be cast; such films were used for dynamic mechanical evaluation using a Rheovibron at a constant frequency (11 Hz).

The loss tangent as a function of temperature for the homopolymer and the copolymers containing different amounts of NDI and NN is shown in Figure 13. As can be seen, the tan δ_{max} is at a significantly higher temperature, 240 °C, for poly(NDI) compared to poly(NN), 132 °C. This shows that the substitution of the polynorbornene backbone by a polar bridgehead functionality, *N*-phenyl imide, has a much more pronounced effect on the rigidity than the monosubstitution by the nitrile group.

All the copolymers studied show only one α-dispersion peak, indicating that there are no separate phases of poly(NDI) and poly(NN), and the copolymers formed are random, giving a single-phase system. A single α-dispersion peak for the copolymers could also be obtained if the poly(NDI) and poly(NN) phases are miscible. tan δ_{max} shifts to higher temperatures as the amount of NDI increases in the copolymer, and the increase in the tan δ_{max} is linear just like the increase in T_g measured by DSC.

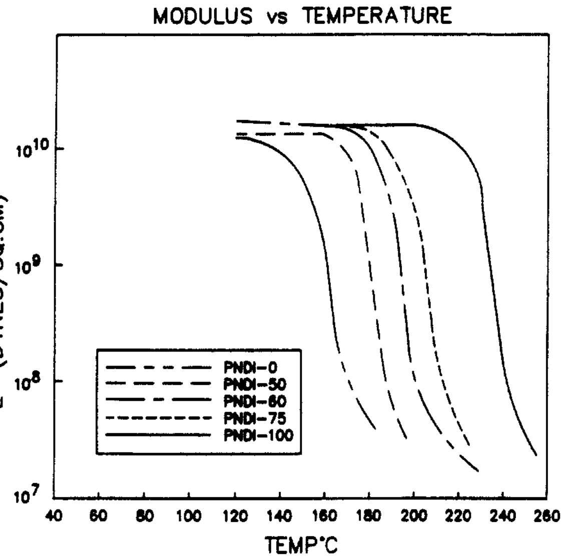

Figure 14. Dynamic modulus vs temperature for (1) poly(*exo*-NDI) and its copolymers with NN containing (2) 25%, (3) 40%, and (4) 50% NN and (5) poly(NN).

Dynamic modulus vs temperature for the homopolymers, poly(NDI) and poly(NN), and their copolymers is plotted in Figure 14. The dynamic modulus of poly(NDI) is considerably higher than that for poly(NN). This also is the reflection of the rigidity of the poly(NDI) backbone compared to poly(NN). Incorporation of imide units in the copolymers increases the dynamic modulus. Copolymers containing 60 and 70% imide units have dynamic modulus values very similar to poly(NDI). As the concentration of imide groups in the polymer increases, the drop in the dynamic modulus takes place at comparatively higher temperatures.

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