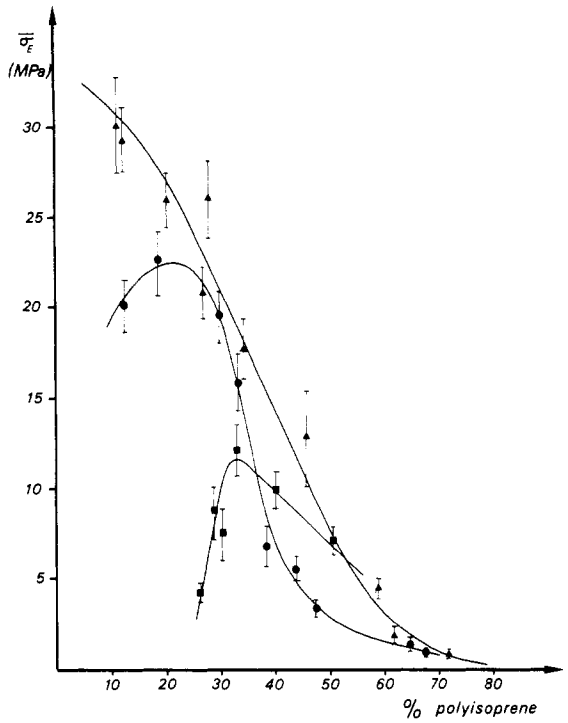

Figure 3. Average tensile strength $\bar{\sigma}_E$ as a function of polyisoprene content: (■) M_{tot} = 30000; (●) M_{tot} = 50000; (▲) M_{tot} = 90000.

PS), below which the cohesive strength decreases, as chain entanglement is no longer realized.[9] That limit may be lowered by addition of low-modulus particles such as a polydiene.[10] But a reinforcement by this method is only observed when the elastomer is able to form discrete phases. When both phases are chemically bound, as in block copolymers, the reinforcing effect is even enhanced. Thus, for SIS copolymers with low M_{tot} or low content in one phase, there is no phase separation and the corresponding films are not very cohesive and difficult to handle.

We now consider the two curves in Figure 3 presenting a maximum. For a M_{tot} of 30000, the polyisoprene content at the maximum is 30%, hence corresponding to a central block of 10000; for SIS with an M_{tot} of 50000, where the maximum is located at 20%, we also find 10000. This value is precisely the molecular weight predicted by several authors,[11] above which styrene–isoprene block copolymers exhibit phase separation.

For SIS copolymers of still higher molecular weight, around and over 90000 (corresponding to the upper curve in Figure 3), a maximum in $\bar{\sigma}_E$ would be expected to appear at less than 10% polyisoprene content. This is difficult to verify, as there are insufficient experimental points in this range. Nevertheless, for homopolystyrene, we have obtained approximately the same value as for the SIS film with the lowest elastomer content. This seems to favor our assertion that, for a given M_{tot}, $\bar{\sigma}_E$ increases up to a point where the % I becomes too low for a good film to form. Beyond this limit, films show microscopic defects, especially crazes, and $\bar{\sigma}_E$ decreases rapidly.

Conclusion

Our experiments show that the total molecular weight influences the tensile strength of thin SIS films, but not their Young's modulus. Classically, $\bar{\sigma}_E$ and $\bar{E}$ are expected to increase continuously with increasing hard-phase content. The observed maximum in $\bar{\sigma}_E$ corresponds to the point from which film formation is no longer possible due to a decrease in cohesive strength of the polymer material.

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Nuclear Magnetic Resonance Study of Norbornene End-Capped Polyimides. 1. Polymerization of *N*-Phenylnadimide

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ABSTRACT: Carbon-13 and high-field proton NMR were used to study the thermally induced polymerization of *N*-phenylnadimide. In addition to the exo–endo isomerization, *N*-phenylnadimide undergoes a retro-Diels–Alder reaction to produce cyclopentadiene and *N*-phenylmaleimide. Two major isomers are found via Diels–Alder reaction from cyclopentadiene and *exo*-*N*-phenylnadimide. Their isomeric forms are determined by empirical calculation of the ^{13}C chemical shifts. These products and the two phenylnadimide isomers polymerize with *N*-phenylmaleimide to give stereochemically and sequentially irregular polymer chains which contain no olefinic functional groups.

Introduction

Thermal polymerization is one of the areas of polymer science that is still not well understood. While many monomers appear to undergo spontaneous polymerization when heated in the absence of catalysts, on careful investigation, such polymerization is often initiated by homolysis of the impurities present in the reaction mixture.[1]

A group of oligomers which appear to undergo spontaneous polymerization when heated thermally are the aro-

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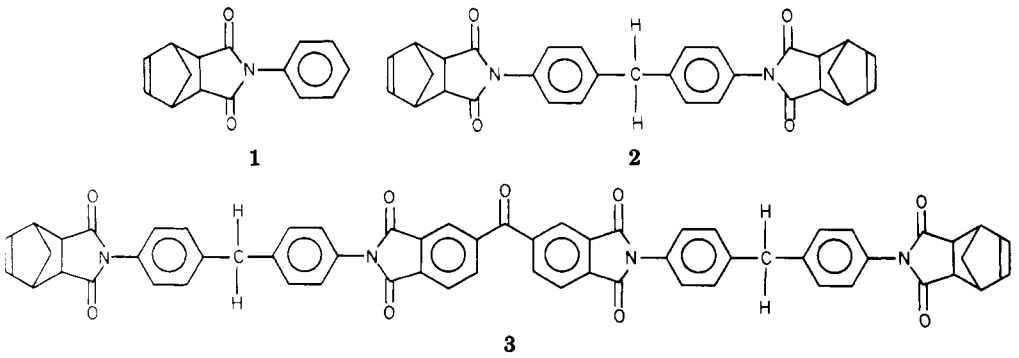
Chart I



matic imide oligomers end capped with strained norbornene rings.[2,3] While such cross-linked polyimides show excellent high-temperature properties,[4] the actual mechanism of polymerization is not well understood due to the intractability and the insolubility of the cured polymers.

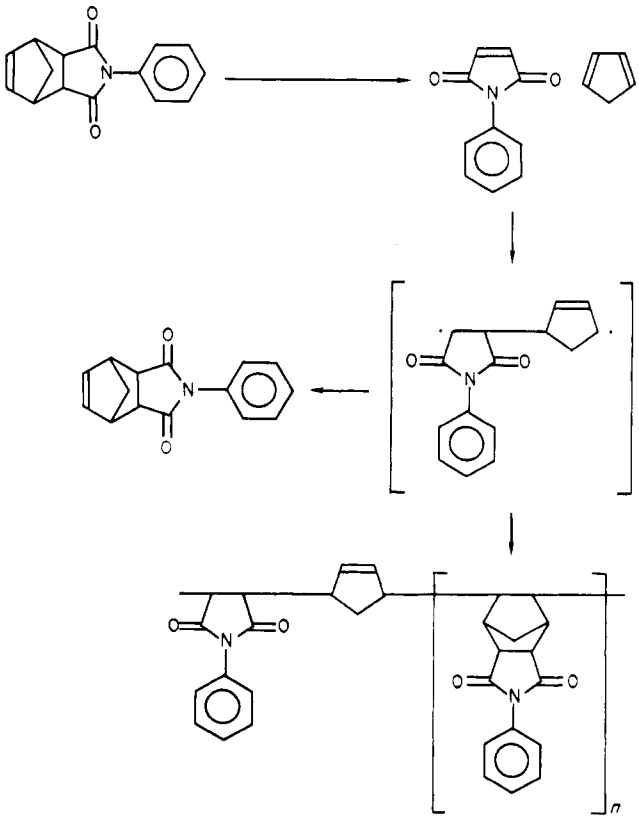
To facilitate the study of the thermal polymerization of these imide oligomers, we recently synthesized *N*-phenylnadimide (1) as a model compound for prepolymers 2 (2NE/MDA) and 3 (2NE/2MDA/BTDE) (Chart I). The thermally induced polymerization of *N*-phenylnadimide was studied by both proton and carbon-13 NMR spectroscopy.

The advantages of using *N*-phenylnadimide as a model compound are its low molecular weight relative to other nadic end-capped imides and its similarity to the reaction course of the more complex nadic end-capped imide oligomers.[5] In particular, the partially and fully cured product can easily be dissolved in common NMR solvents, thus facilitating a mechanistic study by NMR.

Thermal polymerization of *N*-phenylnadimide was studied some years ago,[2,3] with elemental analysis, IR spectroscopy, and continuous-wave, low-field proton NMR as the primary analytical tools. On the basis of the results of these studies, it was proposed that during thermal polymerization, *N*-phenylnadimide undergoes a reverse Diels–Alder reaction, producing cyclopentadiene and maleic imides (or their radicals). These, in turn, act as the initiators of chain polymerization (Scheme I).[6]

Our recent studies of *N*-phenylnadimide showed that at temperatures below the retro-Diels–Alder reaction, an endo–exo isomerization of the compound can take place.[7] DSC thermograms of the isomers show differences in both their melting point and polymerization temperature. The thermogram of the exo isomer displays an exotherm at ca. 25 °C lower than that of the endo isomer. With the advent of Fourier transform, multinuclear, and high-field NMR spectrometers, it is now possible to study the polymerization of the *endo*- and *exo*-*N*-phenylnadimides and gain new insight into their polymerization mechanism. In our current study, carbon-13 and high-field proton (270 MHz) NMR were used as the primary tools in the mechanistic investigation.

Scheme I

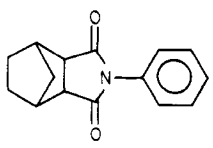


Experimental Section

***endo*-*N*-Phenylbicyclo[2.2.1]hept-2-ene-5,6-dicarboximide (*N*-Phenylnadimide or PN) (1).** *N*-Phenylmaleimide (17.3 g, 0.1 mol) was added to 60 mL of toluene. While this solution was stirred, 20 mL (0.3 mol) of freshly prepared cyclopentadiene was added dropwise and stirring was continued for an additional 0.5 h. The precipitate was then collected by filtration and recrystallized from 2:1 hexane/chloroform to yield 20.0 g (84%) of *endo*-*N*-phenylnadimide as white crystals, mp 140–141 °C.

***exo*-*N*-Phenylbicyclo[2.2.1]hept-2-ene-5,6-dicarboximide.** A solution of *endo*-PN (0.5 mol %) in diphenylmethane was placed in a sealed glass bottle and heated to 250 °C for 4 h. Most of the solvent was then distilled off under vacuum. Any polymeric materials formed were eliminated by running the products through a 3-in silica gel column, using methylene chloride as the solvent. The monomeric products were separated by using a Waters Prep LC 500 liquid chromatograph–spectrometer, using methylene chloride as the solvent. *exo*-PN has a higher R_f and was eluted prior to the endo monomer. Over 90% endo–exo conversion was found, and the exo product was obtained, after stripping off the solvent, as clear crystals, mp 198–199 °C.

***endo*-*N*-Phenylbicyclo[2.2.1]heptane-5,6-dicarboximide (4).** *endo*-*N*-Phenylnadimide (5 g) was dissolved in 300 mL of methanol and placed in a Parr bottle. Catalyst (0.5 g of Pd–Al_2O_3, Engelhard Industries, lot no. 11-101) was added to the solution and the bottle was shaken overnight under 45-psi hydrogen pressure. The solution was filtered and solvent rotovapped off to yield 4.8 g (95%) of protonated PN as white crystals, mp 145–146 °C.



Polymerization of *N*-Phenylnadimide. *N*-Phenylnadimide (1.0 g) was placed in a Pyrex tube (0.7-cm i.d. × 8-cm length) and the tube was sealed under nitrogen. The tube and contents were placed in a Thermolyne 2000 furnace at the desired temperature for 1 h, after which the tube was cooled and broken and the sample analyzed. Samples cured at 200, 250, 260, 275, 280, 285, 290, 300, and 315 °C (2-h curing) were prepared. For comparison purposes, samples with pure endo and pure exo monomers were used for each curing temperature study.

^{13}C NMR Measurements. All samples were examined in $CDCl_3$ and some in Me_2SO-d_6 as well. Most of the ^{13}C spectra were obtained on a Varian XL-100-15 equipped with a high-power amplifier and square-wave decoupler. A 60° (12 μs) flip angle was used and the time between pulses was generally 2 s. The spectral width was 5000 Hz and 8K data points were used to give a resolution of 1.25 Hz. Me_4Si was used as the internal standard for chemical shifts. Some of the off-resonance decoupling experiments were done on a Bruker WH-270 spectrometer for greater resolution. All experiments were carried out at 30 ± 2 °C.

^{1}H NMR Measurements. All samples were examined in 5-mm sample tubes on a Bruker WH-270 spectrometer, using $CDCl_3$ as solvent. Spectral width of 12 ppm (3240 Hz) and a 90° pulse (7 μs) were used. Recycle time was 5 s and 16K data points were used. Me_4Si was used as the internal standard for all samples and all experiments were carried out at 30 °C. All spectra were computer integrated.

Mass Spectrometry Measurements. The gaseous components in the 285 °C sample tube were analyzed on a Du Pont 21-490B mass spectrometer.

Liquid Chromatography Separation of PN285 (PN Cured at 285 °C for 1 h). A 10-in silica gel (particle size 15–25 μm) column was used to separate the various components of PN285. The products of the curing process were dissolved in the minimum amount of chloroform and eluted through the column, using 30:70 ethyl acetate–hexane as the eluting solvent. Four major fractions were collected, using thin layer chromatography and ^{1}H NMR as determining methods. The materials that were not eluted were dissolved in tetrahydrofuran. All products were then stripped off the solvent and dried in a rotary evaporator.

Differential Scanning Thermograph. DSC thermograms of pure *endo*- and *exo*-*N*-phenylnadimides were taken on a Du Pont 990 differential scanning thermal analyzer. The temperature range from ambient to 400 °C was scanned at a rate of 10 °C/min.

Results and Discussion

In our earlier study of *N*-phenylnadimide, we found that endo–exo isomerization takes place at a temperature as low as 200 °C. The protons and carbons of both isomers give distinct NMR resonance signals and their chemical shifts have been reported previously.[7]

Similar to products formed by reacting cis-1,2-disubstituted olefins with cyclopentadiene, *endo*-*N*-phenylnadimide is the kinetically more favorable isomer, while the exo isomer is thermodynamically more favorable.[8] In addition to a significant difference in the isomers' melting points (198 °C for exo and 145 °C for endo), the DSC thermograms (Figure 1) show a distinct difference between the two isomers. The exo isomer shows an exotherm at ca. 250 °C, approximately 25 °C lower than that of the endo isomer. We show later that these exotherms are due to the polymerization reactions while the broad endotherms before these exotherms are probably a result of a reverse Diels–Alder reaction. NMR examination of PN samples treated at 200 °C for 1 h shows the presence of both endo and exo isomers. This is true whether the starting material is pure endo or pure exo isomer. However, because of the lower polymerization temperature exhibited by the exo isomer, it is polymerized to a greater extent than the endo isomer when both are cured under the same conditions, as shown later in the discussion. Since the polymerization products formed from both isomeric forms are essentially identical and since most of the imide oligomers are in the endo form, the following

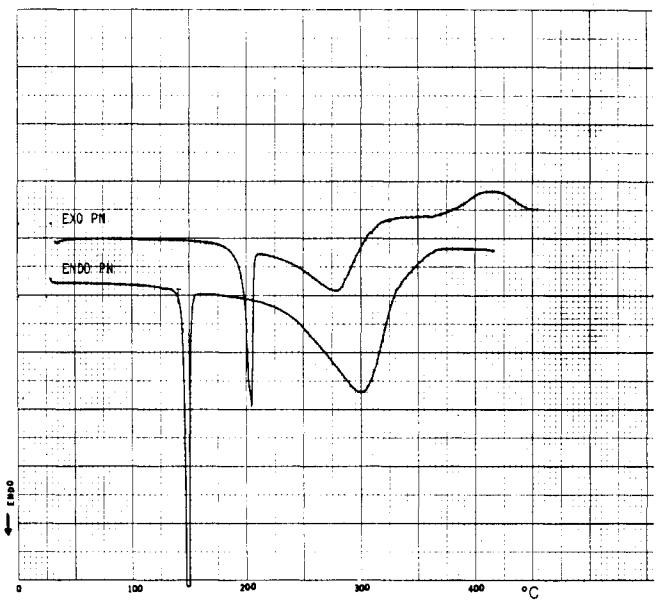


Figure 1. DSC thermograms of *endo*- and *exo*-*N*-phenylnadimides.

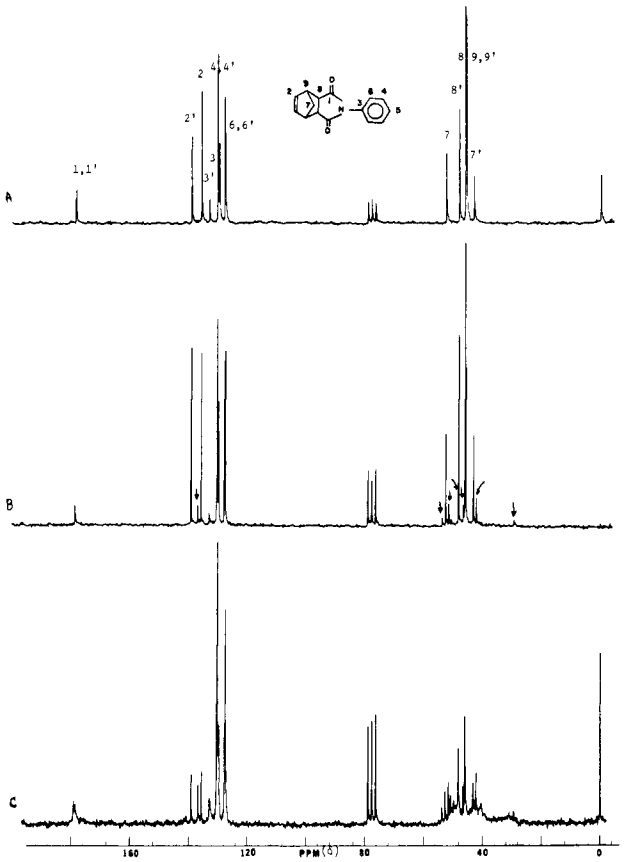


Figure 2. 25.2-MHz ^{13}C NMR spectra of PN cured for 1 h at (A) 200, (B) 275, and (C) 285 °C.

results are obtained using *endo,cis*-*N*-phenylnadimide as the only starting material, unless otherwise indicated.

Figures 2A and 3A show the ^{13}C and ^{1}H NMR spectrum of PN cured at 200 °C. Only endo and exo isomers are present. C-9 and C-9′ can be resolved if higher field NMR (180 or 270 MHz) is used or if Me_2SO-d_6 is used as a solvent. Figures 2B and 3B are spectra of PN cured at 275 °C. In addition to the resonances from the endo and exo monomers, eight new carbon resonances and several new proton resonances can be resolved (indicated by arrows).

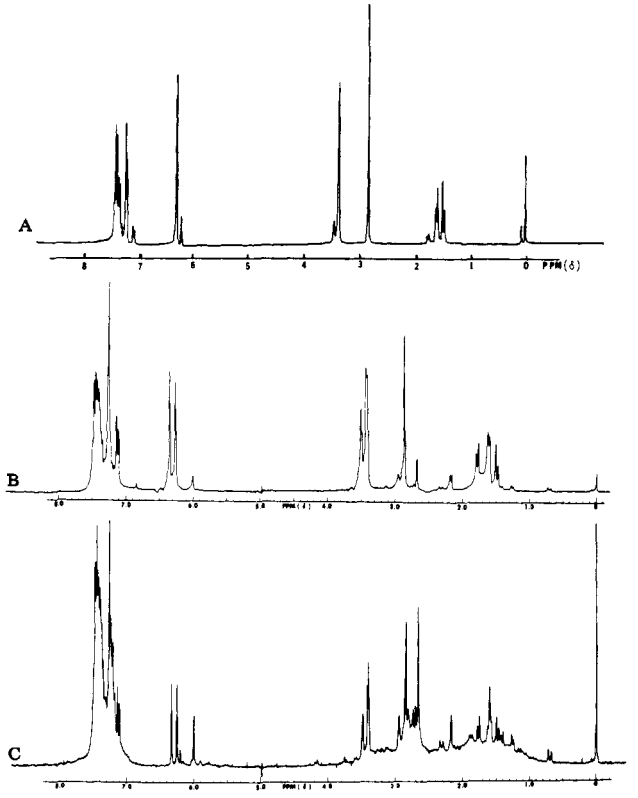


Figure 3. 270-MHz ^1H NMR spectra of PN: (A) endo (approximately 10%) and exo mixture; (B) cured at 275 °C for 1 h; (C) cured at 285 °C for 1 h.

The intensities of these new resonance signals increase rapidly as the curing temperature increases, as can be seen in Figures 2C and 3C. In addition to these resonances and those due to the two isomeric PN monomers, several new resonances are also observed in both ^{13}C and ^1H spectra. Broadening of the carbonyl and aromatic ^{13}C line widths and appearance of the broad "humps" in both the ^{13}C and ^1H aliphatic regions indicate the occurrence of polymer. In order to study the curing products in detail, we used column chromatographic methods to separate the sample cured at 285 °C into five major fractions. Each sample was examined in detail. The five fractions are numbered according to their elution order, with fraction 1 eluting first and fraction 5 not eluting at all. Carbon-13 and proton NMR spectra are shown in Figures 4 and 5. Fractions 3 and 4, being essentially exo and endo monomers, are not shown here.

It is obvious from the two figures that, except for fraction 5, complete separation of the components is not achieved. However, the major products of each fraction can be easily identified by comparing it with the fraction immediately prior and immediately after its elution order. The nonmajor products are then marked and are not taken into consideration in the specific fraction. If a more versatile computer system is used, the nonessential signals can be easily eliminated by an add–subtract routine. It is also apparent that by eluting prior to PN monomers, the compounds that yielded numerous distinctive resonances (observed after curing) arise from monomers rather than polymers. The major component of fraction 2 is produced in larger quantities than the major component in fraction 1. It is also observed earlier (at lower temperatures) in the curing process. Thus, it is important to characterize this component and its role in the polymerization mechanism; hopefully, knowledge of this component will give insight into the other products.

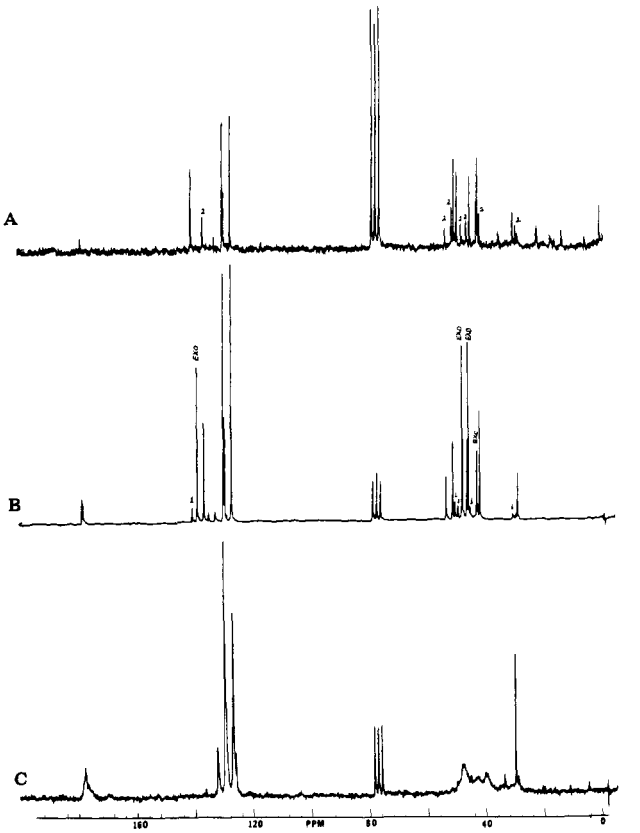


Figure 4. 25.2-MHz ^{13}C NMR spectra of column chromatography fractions of PN285: (A) fraction 1; (B) fraction 2; (C) fraction 5. Signals marked with "1", "2", or "exo" are due to products in fractions 1, 2, or *exo*-PN, respectively.

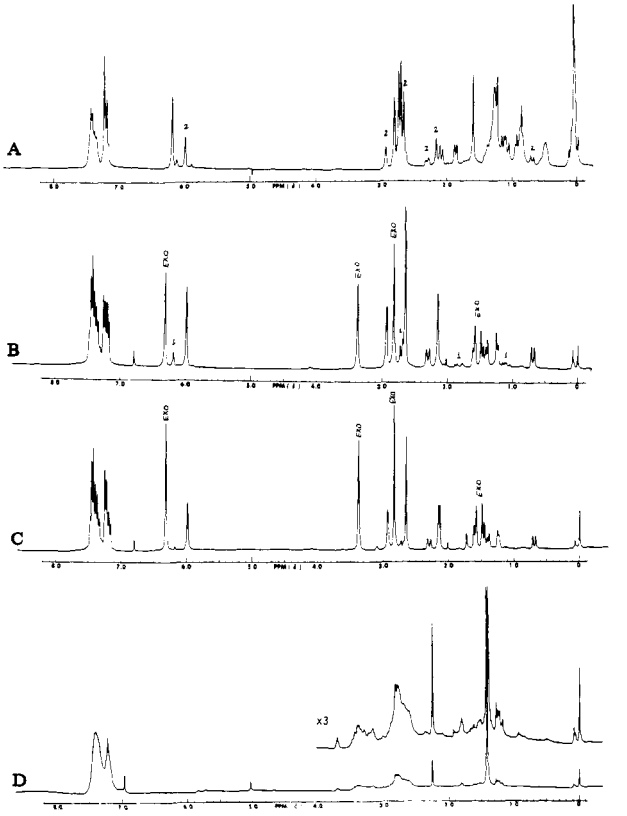
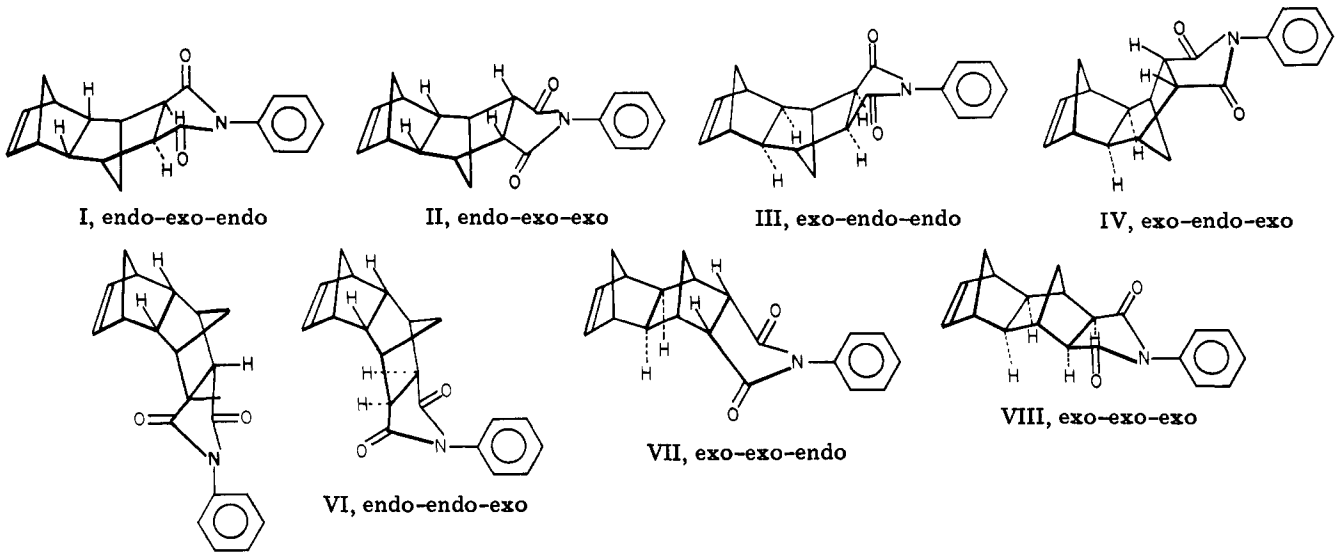


Figure 5. 270-MHz ^1H NMR spectra of column chromatography fractions of PN285: (A) fraction 1; (B, C) these two portions combined to yield fraction 2 (shown here for comparative purposes); (D) fraction 5.

Chart II



I, endo-exo-endo

II, endo-exo-exo

III, exo-endo-endo

IV, exo-endo-exo

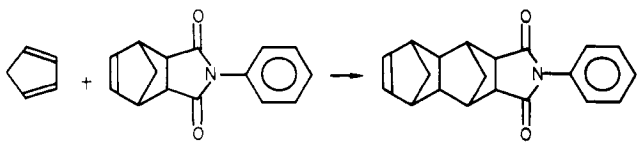
V, endo-endo-endo

VI, endo-endo-exo

VII, exo-exo-endo

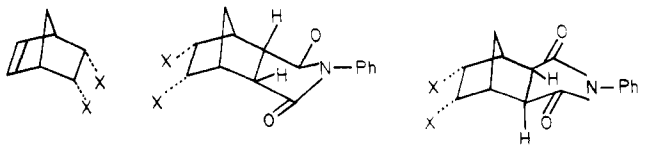
VIII, exo-exo-exo

In order to determine whether all major resonance signals in fraction 2 arise from one single compound, we measured the intensity variation of each signal at various curing temperatures for various fractions. The intensities of all of these resonances would vary proportionately from sample to sample if they were due to a single compound, and this was observed to be the case. By using selective decoupling and off-resonance techniques in ^{13}C NMR and homonuclear decoupling and computer integration in ^{1}H NMR, we established a one-to-one carbon–proton chemical shift relationship. Of the two methylene carbons, one (53.4 ppm) has an AB proton coupling pattern (^{1}H NMR, 1.44, 1.26 ppm) very similar to that observed for both *endo*- and *exo*-PN monomers. The other methylene carbon (29.1 ppm) shows an AX proton coupling pattern (^{1}H NMR, 2.32, 0.71 ppm). The two protons are coupled to each other and irradiation of either one in ^{13}C selective decoupling results in a doublet for the methylene carbon. Two of the aliphatic carbons (52.1 and 41.9 ppm) have protons whose chemical shifts are degenerate (2.66 ppm). By correlation of the ^{13}C and ^{1}H NMR data, it can be easily deduced that there are two identical olefinic carbons (^{13}C NMR, 135.7 ppm; ^{1}H NMR, 5.99 ppm), four methine carbons (^{13}C NMR, 52.1, 48.0, 46.3, 41.9 ppm; ^{1}H NMR, 2.66, 2.19, 2.97, 2.66 ppm, respectively), and two methylene carbons (^{13}C NMR, 53.4, 29.1 ppm). In addition, there are carbonyl and aromatic carbons which are very similar to those found in the PN monomers. Previous theories have proposed that retro-Diels–Alder reaction occurs at 275 °C.[3,7] Our mass spectroscopic study of the gaseous materials of samples cured at 285 °C supports this since a small amount of cyclopentadiene (*m/e* 65, 66, 67, 68) is the major gaseous product. However, instead of cyclopentadiene reacting to become part of the polymer backbone, as the previous theory suggested, the presence of PN, whose olefinic carbons can act as a dienophile, makes the following Diels–Alder reaction a likely possibility:



This reaction is strongly supported by our data. ^{13}C and ^{1}H data (i.e., both chemical shifts and intensities) strongly support that the above Diels–Alder products are present. Because there are two isomeric forms of *N*-phenylnadimide and because the norbornene's olefin and cyclopentadiene can both react with the other in either endo or exo form, there are eight possible products which could be formed as the result of the proposed Diels–Alder reaction. The eight possible products are shown in Chart II.

In our previous study of the isomerization of *N*-phenylnadimide, we did an empirical calculation of the ^{13}C chemical shifts for the exo isomers and the results were very satisfactory.[7] By the same approach, determination of the stereochemistry of the product in fraction 2 can be carried out. Three compounds are used as the basic components whose ^{13}C chemical shifts after substitution can be calculated by using the available data.[9,10] The three compounds are norbornene, hydrogenated *endo*-PN and hydrogenated *exo*-PN:

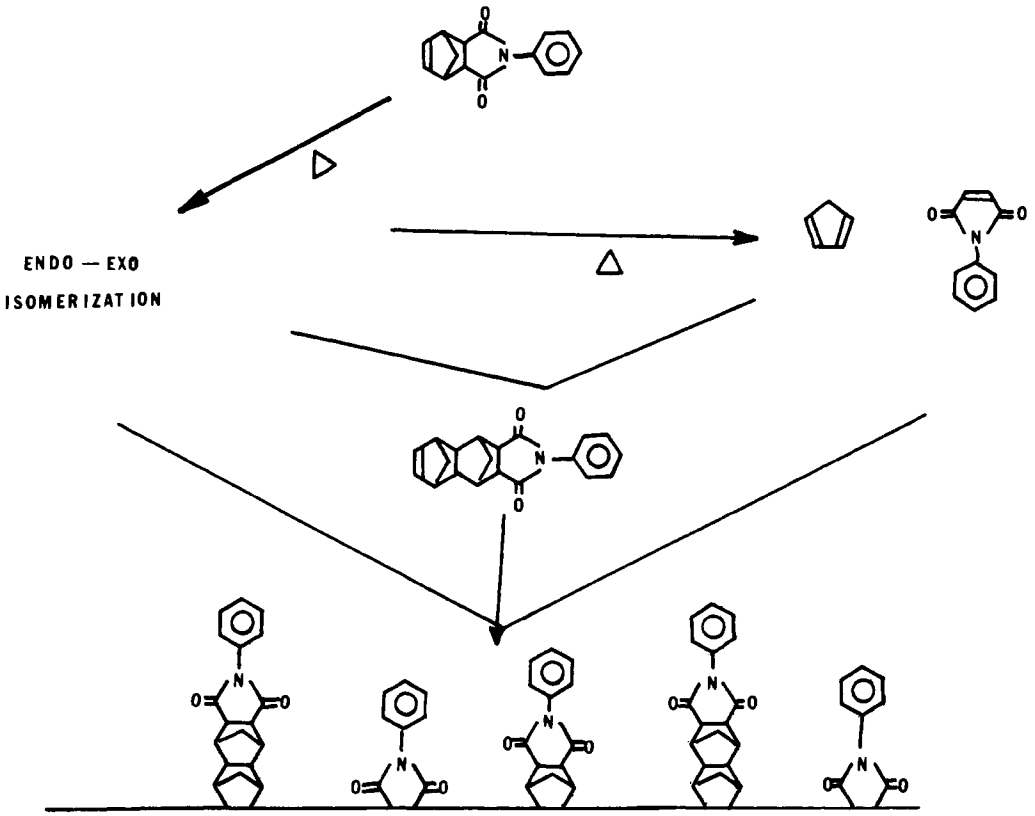


X = H in original compounds
X = CH_3 in empirical calculations (it can be in cis-endo or cis-exo conformation)

Although all available data we used are for monosubstituted compounds, we have found the calculated results to be very close to the observed chemical shifts if both substituents are taken into account. Most of the uncertainties in this calculation arise from two sources. First, the chemical shifts of hydrogenated *exo*-PN used in the following calculation is itself calculated based on the hydrogenated *endo*-PN data. A more significant uncertainty arises from using CH_3 as the substitution group while in fact the substituent is a CH group in a strained aliphatic ring. This second uncertainty is likely to shift most of the calculated carbons slightly upfield (1–3 ppm). The calculated results for the eight isomers are listed in Table I.

Comparison of the olefinic and the methylene ^{13}C chemical shifts of the compound in fraction 2 with those in Table I makes obvious that compound II (endo–exo–exo) is the compound observed. If the CH_3–CH substituent difference is taken into account, all seven carbon

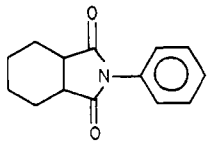
Scheme II



chemical shifts correlate well between the calculated and the observed values.

By the same analytical method, fraction 1 is found to have at least two major compounds. The ^{13}C chemical shifts of one of the compounds indicate that it probably is the Diels–Alder product similar to that found in fraction 2, but in isomeric form IV (exo–endo–exo). The other major compound gives several resonance signals in the very high field region (22 ppm in ^{13}C NMR spectrum and 1.5–0.4 ppm in the ^{1}H NMR spectrum) and probably does not contain any aromatic or carbonyl functional groups. Possibly it is some pyrolytic product in the form of small, strained rings. Since this compound does not appear in any significant amount in PN samples under more extensive curing, we did not investigate it further. The two minor olefinic resonances in Figure 5A are possibly due to other isomeric forms of the Diels–Alder products which occurred in very small fraction. The formation of isomers II and IV as the major products is consistent with the results of other studies. Both these isomers are formed by reaction of cyclopentadiene with the thermodynamically more stable form of PN, i.e., the exo isomer. Since the cis–endo product is kinetically more favorable, isomer II (endo–exo–exo) is formed first. As the reaction temperature increases, exo product IV (exo–endo–exo) is also formed. Being thermodynamically less stable, much of the *endo*-PN probably either converts to the exo form or undergoes a retro-Diels–Alder reaction to produce cyclopentadiene and *N*-phenylmaleimide during initial curing; thus very little *endo*-PN reacts with cyclopentadiene to form isomers I, III, V, and VII. It is also found that pure *exo*-PN samples polymerize to a greater extent than the endo isomers. *exo*-PN cured at 280 °C shows higher degrees of polymerization than *endo*-PN cured at 290 °C, as judged by the intensities of the base line "humps" and line broadenings. None of the LC fractions show dicyclopentadiene or monomeric maleimide as products.

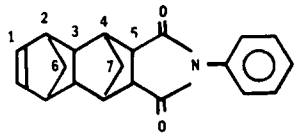
Fraction 5 consists mainly of polymeric products of thermal curing. The broad line widths in both carbon and proton NMR prevent any detailed interpretation. However, certain information can still be obtained from Figures 4C and 5D. It can be seen from both figures that no olefinic bonds remain in polymer. This suggests that few cyclopentadiene molecules are polymerized as suggested in Scheme I. The great amount of *N*-phenylmaleimide formed from the reverse Diels–Alder reaction should be the major reactant in thermal polymerization. The rather strong resonance peak at approximately 40 ppm is consistent with the proposed *N*-phenylmaleimide polymerization theory, after comparing it with the methine (40.1 ppm) chemical shift in compound **5**. ^{13}C resonance signals



5

at 30–32 and 40–50 ppm and ^{1}H resonances at 1.6, 2.5–2.8, and 3.25–3.3 ppm are consistent with the empirically calculated and the observed values for disubstituted hydrogenated PN. We have also found that when the olefinic group of PN is hydrogenated, most of the ^{13}C resonances shift upfield, while the chemical shifts of the bridge methylene protons are almost unaffected. In Figure 4C, the resonances due to bridge methylenes of isomer II (endo–exo–exo) (53 ppm) and *endo*-PN (52 ppm) are no longer observable; however, Figure 5D shows clearly that the bridge methylenes of II (endo–exo–exo; 1.26–1.44 ppm) are still present. On the basis of these results, we believe that in addition to the *N*-phenylmaleimide and PN, the polymer also consists of products from isomers of Diels–

Table I
Observed and Empirically Calculated ^{13}C Chemical Shifts for the Possible PN and Cyclopentadiene Diels-Alder Reaction Products[a]



^{13}C no.	compound								fraction 2 obsd	fraction 1 obsd
	I	II	III	IV	V	VI	VII	VIII		
1	134.2	134.2	137.9	137.9	134.2	134.2	137.9	137.9	135.7	139.8
2	49.2	49.2	49.2	49.2	49.2	49.2	49.2	49.2	52.1	50.5
3	41.8-41.6	41.8-38.4	42.5-39.9	42.5-36.7	41.8-49.9	41.8-36.7	42.5-41.6	42.5-38.4	41.9	42.7
4	47.0	47.0	46.6	46.6	46.6	46.6	47.0	47.0	48.0	49.5
5	47.9	45.4	41.6	39.1	41.6	39.1	47.9	45.4	46.3	45.4
6	52.2	52.2	41.2	41.2	52.2	52.2	41.2	52.2	53.4	43.0
7	34.6	27.0	42.4	34.8	42.4	34.8	34.6	27.0	29.1	30.8

[a] All shifts are in ppm from Me_4Si.

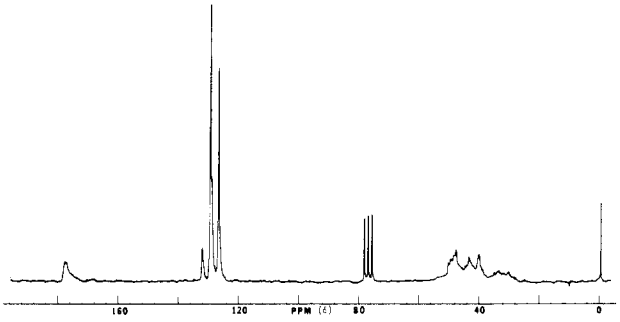


Figure 6. 25.2-MHz ^{13}C NMR spectrum of PN cured at 315 °C for 2 h.

Alder reactions (Scheme II).

The irregular sequential arrangement and the various stereoforms of the components contribute to the broadness of both ^{13}C and ^{1}H NMR resonances. Products proposed by other polymerization theories (all are catalytically polymerized[11,12]) may also be possible here; however, no concrete evidence is observed to support them.

The strong sharp resonance signals observed in both figures (30 ppm for ^{13}C and 1.5 ppm for ^{1}H) are possibly due to chemical reactions during extraction from the silica gel. These strong peaks are not observed in the nonseparated PN285 (Figures 2C and 3C) nor in the further cured phenylnadimides (Figure 6), indicating that they may not be part of the polymer system.

Conclusion

Using ^{13}C and high-field ^{1}H NMR as tools, we have shown that during the thermal polymerization of *N*-phenylnadimide, a retro-Diels–Alder reaction occurs in addition to endo–exo isomerization. Most of the cyclopentadiene formed reacts with *exo-N*-phenylnadimide to produce two isomers via a Diels–Alder mechanism, while the *N*-phenylmaleimide from the retro-Diels–Alder reaction polymerizes. The polymerization probably involves both *N*-phenylnadimide isomers and several isomeric compounds formed from cyclopentadiene and *N*-phenylnadimides. The polymer appears to be stereochemically and sequentially irregular and gives very broad unresolvable ^{13}C and ^{1}H NMR signals. The polymerization mechanisms of both *exo-* and *endo-N*-phenylnadimides appear to be identical. However, it is found that the exo isomer polymerizes to a greater extent than the endo isomer under the same curing conditions.

Unfortunately, the products from more complicated nadic end-capped imide oligomers are not soluble in any NMR solvents even under relatively mild curing conditions. Thus, we have carried out a solid-state ^{13}C NMR study of these materials; the results appear in the following paper.

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