N86-11266

THE SYNTHESIS, CHARACTERIZATION AND THERMAL CHEMISTRY OF MODIFIED NORBORNENYL PMR ENDCAPS*

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As part of a program to further our understanding of the polymerization of Nadic-Endcapped PMR systems, we have synthesized a series of model Norbornenyl-Imides and explored their thermal behavior. We report herein their syntheses and characterizations as well as their rearrangement and polymerization chemistry. Monomer isomerization at temperatures as low as 125°C and oligomer formation at somewhat higher temperatures have been observed. Approximate relative rates for competing isomerization pathways have been established and some information has been obtained about the details of oligomer formation. The relationship of this data to current PMR systems is briefly discussed.

INTRODUCTION

While there are already many successful applications of polyimides in high temperature polymer matrix composites, the search still continues for materials with better performance and/or processing properties. The specific focus of our work is on understanding and ultimately improving the current PMR-15 polyimide system. This thermally cured resin consists of a mixture of 2-carbomethoxy-3-carboxy-5-norbornene (NE), 4,4'-methylene dianaline (MDA), and 3,3'-dicarbomethoxy-4,4'-dicarboxybenzophenone (BTDE). It has been modeled effectively by monoimide I, diimide II, and polyimide III. This is consistent with the notion that thermal imide formation dominates the early stages of the curing process.

Interestingly, the later stages in the curing of PMR systems remain a mystery. It is assumed that the heavily crosslinked polymer products result from a thermal vinyl polymerization of species like II and III. However, neither the mechanism of this polymerization nor the structural details of the crosslink network have been established. It is this aspect of PMR-15 that we intend to probe.

The plan of our research has been to design new, modified, model PMR monomers by making appropriate changes in the structure of I (the "parent" model compound). These modified monomers are chosen with an eye toward their potential for elucidating the mechanism of the PMR cure. The new model monomers are then studied

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* This work was supported by NAG 3-163.

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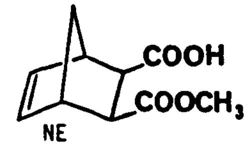
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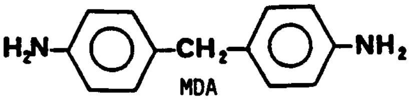
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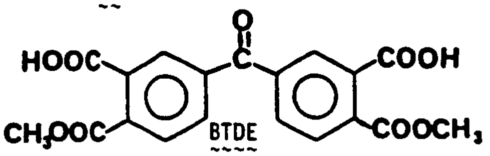
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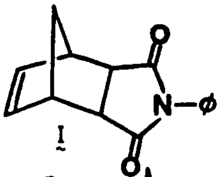
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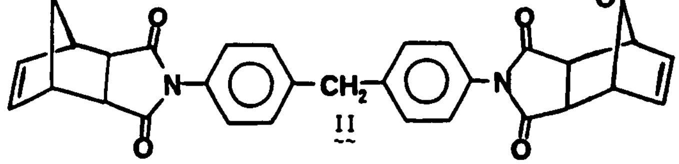
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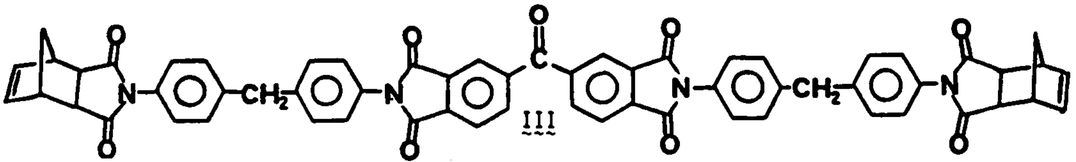
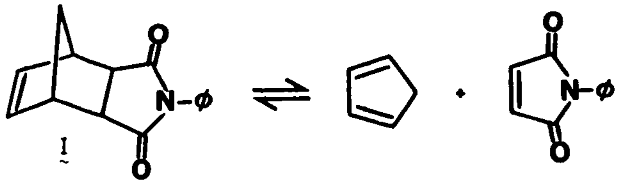

III

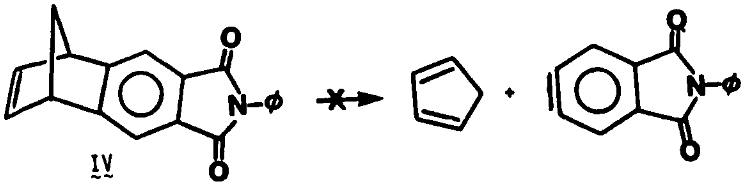
under cure-like conditions. It is hoped that these studies will provide a better understanding of PMR chemistry and will also lead to the development of new PMR resins with lower curing temperatures than are required by current PMR. Ideally, these new resins would also have improved structural and oxidative integrity.

The specific mechanistic questions that we are considering require that we first establish the relevance of any retro Diels Alder reaction of the norbornene to the polymerization process. We would then be able to begin to study the presumed vinyl polymerization of the double bond in the norbornene endcap. The fact that the kind of retro Diels Alder shown in equation (1) does occur in norbornene derivatives and even for imide I itself has been demonstrated (vide infra). However, the significance of this process to the thermal polymerization is as yet unclear.



(1)

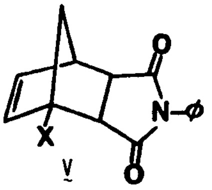
We therefore designed two kinds of modified monomers. The benzonorbornadiene imide, IV, was suggested as a compound with a vinyl group comparable to that in I, II and III but which cannot undergo retro Diels Alder reaction (equation 2). If the polymerization of I were occurring by a simple addition type vinyl polymerization, then IV should behave similarly. Furthermore, the possibility that IV might polymerize to yield a new resin type with higher aromatic content might add an interesting dimension to its performance properties. If, however, the cyclo-



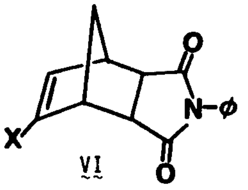
(2)

pentadiene or maleimide generated by equation (1) are crucial to the polymerization of I, then IV might not polymerize at all.

The second kind of modified monomer involved selective functionalization of I with various X groups at either a bridgehead (V) or vinyl (VI) position. This would allow an investigation of the effect of various X groups on both the ease of polymer formation and the properties of the new resins. The specific X groups that we initially chose were X = Ø and X = COOMe. These were suggested based on the known thermal polymerization of both styrene and methyl methacrylate and the analogy between the vinyl substituted norbornenes (VI) and these materials.



V

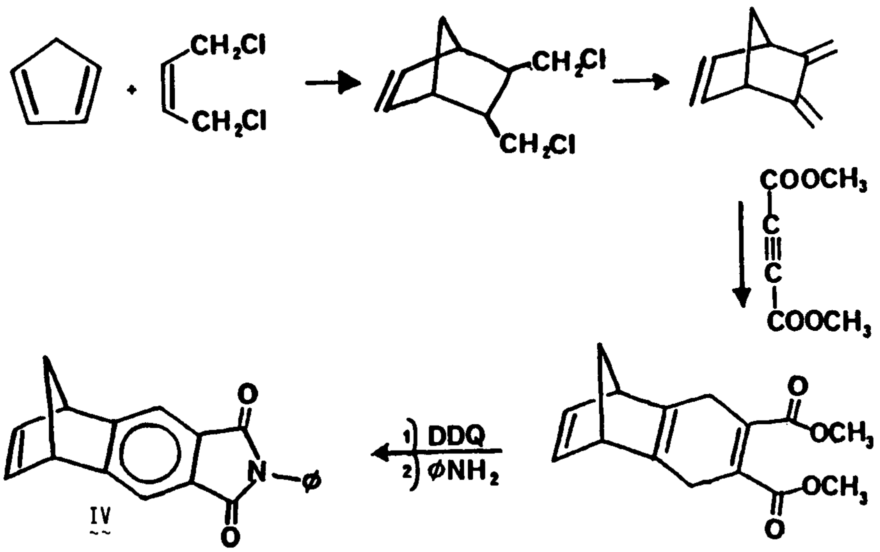


VI

MONOMER SYNTHESIS

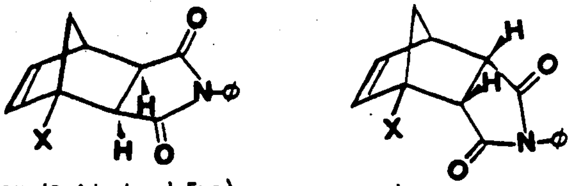
The synthesis of IV was modeled after the route to related benzonorbornadienes used by Paquette et al (ref. 1). This route, which is shown in Scheme I, has been used to produce gram quantities of IV. This compound is a pale yellow crystalline substance with M.P. = 149°-150°C. It has been thoroughly characterized by H^1NMR, C^{13}NMR, MS and IR.

SCHEME I

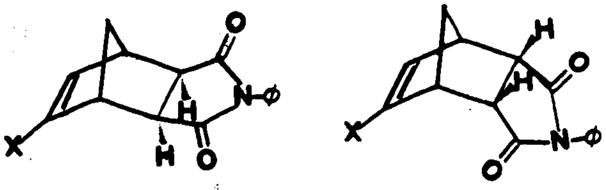


The selective synthesis of V and VI is complicated by the fact that V and VI each represent two compounds, i.e. each of them can exist with the imide ring either exo or endo to the norbornene skeleton (as is also the case for I itself). This means that, for each X group, we must prepare and characterize four distinct compounds (Scheme II).

SCHEME II



BX (Bridgehead-Exo) BN (Bridgehead-Endo)



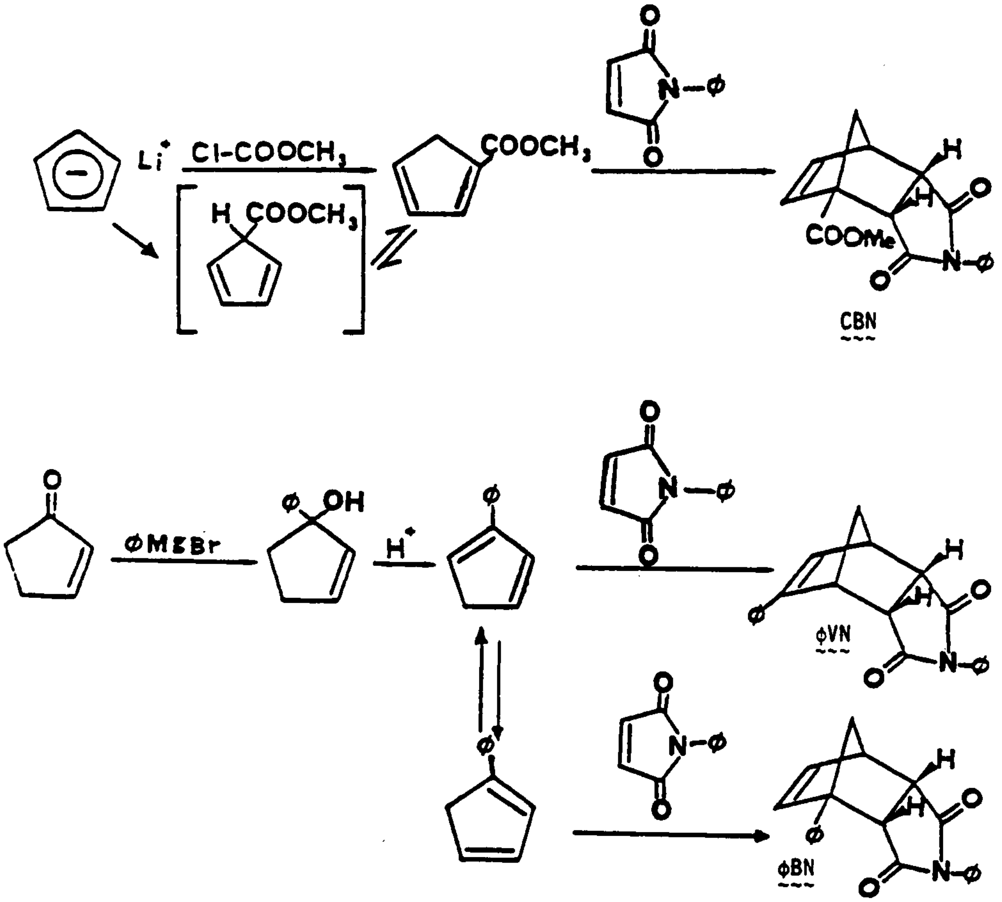
VX (Vinyl-Exo) VN (Vinyl-Endo)

X = ϕ, COOMe

While a number of attempts were made to functionalize either exo or endo I and specifically obtain one of the isomers of V or VI, these were all unsuccessful. We instead chose an approach which made our functionalized monomer in much the same way as I itself is made, the Diels Alder reaction of cyclopentadiene with N-phenylmaleimide. We used either phenylcyclopentadiene (ref. 2) or carbomethoxycyclopentadiene (ref. 3) and allowed it to react with N-phenyl-maleimide. The synthetic routes and the specific isomers that were produced are shown in Scheme III. The notation used to identify these compounds is based on a three-letter code where the carbomethoxy derivatives of V are called CBN (Carbomethoxy-Bridgehead-Endo) and CBX (Carbomethoxy-Bridgehead-Exo) and the derivatives of VI are labeled as CVN and CVX, respectively, to identify the vinyl substituent. Phenyl compounds are similarly named ϕBN, ϕBX, ϕVN, and ϕVX. The two isomers of the parent model compound I will also be refered to by the same convention as PN (parent-endo) and PX (parent-exo).

It should be noted that these routes lead only to endo ring-fused products, as expected for Diels Alder reactions. It is also important to point out that with carbomethoxycyclopentadiene only the 1-substituted isomer, the thermodynamically preferred isomer, could be trapped. Thus only CBN could be synthesized directly. However, in-situ trapping of phenylcyclopentadiene generated as the 2-substituted isomer was possible and allowed direct synthesis of ϕVN. As was the case with carbomethoxy, if the phenylcyclopentadiene is allowed to equilibrate to the 1-substituted isomer, only ϕBN is obtained.

SCHEME III

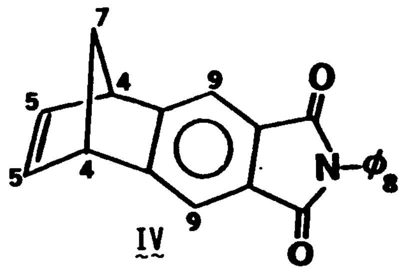


While the above routes led us directly to only three of our desired eight compounds (four phenyl and four carbomethoxy isomers), we found that low temperature thermolysis allows isomer interconversion within each substitutent set. It was this isomerization that was used to obtain most of the remaining compounds. The results and interpretation of these isomerization experiments are presented in the following section. At this point we need only note that CBN, CVN, CVX, ϕBN, ϕVN, and ϕVX have all been obtained as pure crystalline materials and have been fully characterized by H^{1}NMR, C^{13}NMR, MS and IR. A tabulation of physical and spectral data for these six compounds, as well as for the benzo model (IV), is shown in Tables I and II. Both CBX and ϕBX have been difficult to obtain in

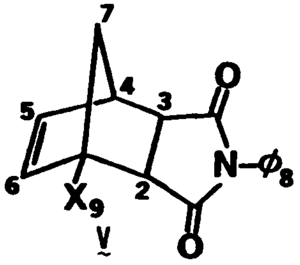
TABLE I: Melting Point, Infrared, and Ultraviolet Data

	M.P.(°C)	IR:C=O(cm^{-1})	UV(CH$_3$CN):log ε(λ254nm)
Benzo(IV)	149-150°	1710	4.11 (λ_{max}=240nm, log ε=4.60)
CBN	173-174°	1712	2.40
CVN	98-99°	1712	2.80
CVX	135-136°	1711	2.84
ϕBN	172-173°	1708	2.51
ϕVN	152-153°	1702	3.87 (λ_{max}=264nm, log ε=4.19)
ϕVX	195-197°	1706	3.91 (λ_{max}=264nm, log ε=4.05)

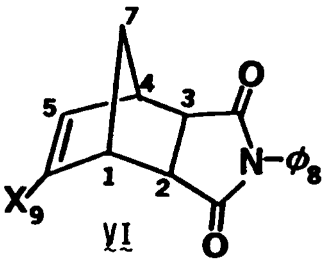
TABLE II. Nuclear Magnetic Resonance Data



IV



V



VI

a) H^1NMR:(200MHz; CDCl$_3$[*Benzene-d$_6$]; chemical shift in units δ; multiplicity:singlet(s), doublet(d), triplet(t), doublet of doublets(dd), doublet of triplets(dt), multiplet(m)).

Compound	H_1	H_2	H_3	H_4	H_5	H_6	H_{7a}	H_{7b}	H_8	H_9
Benzo IV	—	—	—	3.97(m)	5.74(t)	—	2.24(d)	2.38(d)	7.22-7.44	7.62(s)
				*3.22(m)	*6.25(d)		*1.72(d)	*1.93(d)	*6.86-7.34	*7.35(s)
CBN, V	—	3.86(d)	3.58(d)	3.52(m)	6.38(dd)	6.42(d)	1.96(s)	1.96(s)	7.06-7.44	3.79(s)
X=COOMe		*3.84(d)	*3.16(dd)	*3.30(m)	*6.22(dd)	*6.66(d)	*1.80(d)	*1.94(dd)	*7.24-7.72	*3.80(s)
CVN, VI	3.52(m)	3.88(m)	3.62(m)	3.52(m)	7.12(d)	—	1.70(d)	1.94(dt)	6.96-7.44	3.68(s)
X=COOMe	*3.00(m)	*4.00(m)	*3.28(m)	*3.00(m)	*7.24(d)		*1.06(d)	*1.58(dt)	*7.12-8.00	*3.70(s)
CVX, VI	3.72(s)	2.92(m)	2.92(m)	3.50(m)	7.14(d)	—	1.52(d)	1.72(dt)	7.18-7.38	3.74(s)
X=COOMe	*4.06(s)	*2.50(d)	*2.78(d)	*3.30(m)	*7.05(d)		*1.14(d)	*1.56(dd)	*7.30-7.66	*3.72(s)
φBN, V	—	3.65(m)	3.65(m)	3.65(m)	6.40(dd)	6.44(d)	2.09(m)	2.09(m)	7.16-7.64	7.16-7.64
X=φ		*2.97(d)	*2.87(dd)	*3.05(m)	*5.94(dd)	*6.07(d)	*1.29(dd)	*1.59(dd)	*7.01-7.56	*7.01-7.56
φVN, VI	3.99(m)	3.56(m)	3.56(m)	3.56(m)	6.50(d)	—	1.72(d)	1.95(dt)	6.63-7.52	6.63-7.52
X=φ	*3.02(m)	*2.30(m)	*2.30(m)	*2.65(m)	*5.71(d)		*0.45(d)	*0.92(dt)	*6.36-6.94	*6.36-6.94
φVX, VI	3.85(d)	3.01(d)	3.01(d)	3.56(dd)	6.57(d)	—	1.64(d)	1.82(dt)	7.26-7.54	7.26-7.54
X=φ	*3.60(m)	*2.38(m)	*2.38(m)	*3.16(m)	*5.97(d)		*1.30(s)	*1.30(s)	*7.08-7.37	*7.08-7.37

TABLE II (continued) Nuclear Magnetic Resonance Data

b) C^{13}NMR: (50 MHz, $CDCl_3$, Proton Decoupled, chemical shift δ (#attached H)).

Benzo(IV): 164.71(0), 160.05(0), 143.14(1), 132.16(0), 129.41(0), 128.63(1), 127.84(1), 127.06(1), 116.47(1), 70.20(1), 49.80(2).

CBN: 176.97(0), 175.93(0), 172.67(0), 136.17(1), 135.13(1), 132.73(0), 130.28(1), 129.89(1), 127.67(1), 62.19(0), 57.99(2), 53.84(3), 50.07(1), 48.17(1), 47.34(1).

CVN: 177.11(0), 176.58(0), 164.58(1), 146.02(1), 141.33(0), 132.80(0), 130.42(1), 130.01(1), 129.89(1), 53.85(1), 53.12(3), 47.75(2), 47.24(1), 46.74(1),46.69(1).

CVX: 173.73(0), 173.43(0), 161.57(0), 145.49(1), 141.18(0), 129.80(0), 127.06(1), 126.67(1), 124.71(1), 50.59(3), 46.51(1), 46.31(1), 46.27(1), 44.71(1),42.35(2).

ϕBN: 176.28(0), 175.78(0), 139.52(0), 138.23(1), 134.34(1), 131.77(0), 129.01(1), 128.54(1), 128.51(1), 127.32(1), 126.26(1), 126.55(1), 62.1(0), 57.93(2), 49.51(1), 47.96(1), 45.25(1).

ϕVN: 176.66(0), 176.09(0), 146.98(0), 133.29(0), 131.55(0), 128.86(1),128.54(1), 128.30(1), 128.10(1), 126.69(1), 126.38(1), 125.55(1), 51.86(2), 47.76(1), 46.98(1), 46.09(1), 45.80(1).

ϕVX: 176.92(0), 176.74(0), 150.29(0), 133.56(0), 131.82(0), 130.50(1), 129.20(1), 128.78(1), 128.71(1), 128.11(1), 126.38(1), 125.07(1), 49.42(1), 47.59(1), 47.18(1), 47.03(1), 42.26(2).

significant quantities from either direct synthesis or isomerization studies. While this has been a disappointment, the discussion of the thermal chemistry of our model monomers will suggest that both of these compounds are of little consequence for our polymerization work.

THERMAL REARRANGEMENTS IN SOLUTION

As a means of first understanding any unimolecular thermal chemistry that might be occurring under pre-cure or cure conditions, we have looked at the behavior of all of our model monomers in solution between 100°-200°C. In general, we see no dependence of this chemistry on the choice of solvent (e.g. benzene, diphenylmethane, decalin). Since all of our reactions are done in sealed glass tubes, we have no problems with loss of material or solvent. And finally, since these reactions are done as dilute solutions of monomer in inert solvent, there is no problem with competing intermolecular (polymer forming) reactions. It was our intent to, first, clearly define the unimolecular thermal behavior of our substrates, and then be in a better position to deal with the behavior of neat samples and of polymer forming cures. These neat samples, presumably, have their intramolecular chemistry superimposed on the polymerization process itself.

The study of monomer isomerization in solution led to a number of conclusions. The benzo compound, **IV**, undergoes no unimolecular chemistry in solution up to 250°C and will thus not be considered any further in this section. Secondly, the parent compound **I** and its ϕ and COOMe derivatives each undergo isomerization in solution to a bonafide equilibrium mixture. This equilibrium mix may be reached at different rates depending on the starting isomer, but regardless of the isomer initially used, the final mixture is the same (± 2%; as measured by NMR). A summary of this equilibration data is given in Table III. Suffice it to say that dilute solutions of any of our monomers show no polymer formation even after a day at 200° and that such samples are fully equilibrated. The approach to equilibrium was , predictably, more rapid at higher temperatures, but this was not investigated in detail.

TABLE III: Isomer Composition at Equilibrium

Conditions: 200°±5°C/15±5 hr Solvents:ϕH,ϕ_2CH_2, decalin

Parent: 44% PN% 56% PX

ϕ: 1% BN/?% BX/37% VN/62% VX

COOMe: 2% BN/1% BX/27% VN/71% VX

To probe the isomerization threshold of the various monomers, we looked at the thermal reactivity of each monomer in solution at temperatures as low as 110° and for times up to 24 hrs. Due to their greater availability, the bulk of these studies were done on endo isomers only. However, adequate confirmation was obtained that nothing unusual occurred in the exo compounds of both the parent and vinyl substituted monomers. A representative set of data from isomerization experiments in benzene solution are shown in Table IV.

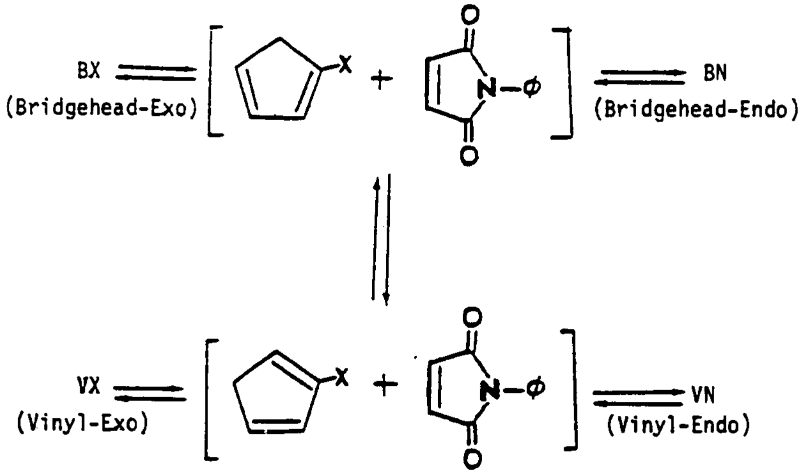
TABLE IV: Low Temperature Isomerization in Benzene Solution

Substrate	Temp (24 hr)	BN	BX	VN	VX
CBN	125°	49	4	44	4
CVN	155°	4	2	88	6
ϕBN	125°	17	-	74	9
ϕVN	155°	-	-	92	8
PN	155°	PN:88		PX:12	

Both the parent and vinyl substituted isomers are largely thermally stable at temperatures up to 150°C (10±2% isomerization after 24 hrs). However, those isomers with bridgehead substitution (either ϕ or COOMe) are substantially rearranged at even lower temperatures (125°C). In this context we also note that the activation provided for these bridgehead substituted monomers is somewhat greater for ϕ substituents than for COOMe. Lastly, we should point out that while 155°C for 24 hrs barely affects ϕVN, three hrs at 155°C (experiment not shown in Table IV) almost totally (>90%) isomerizes ϕBN.

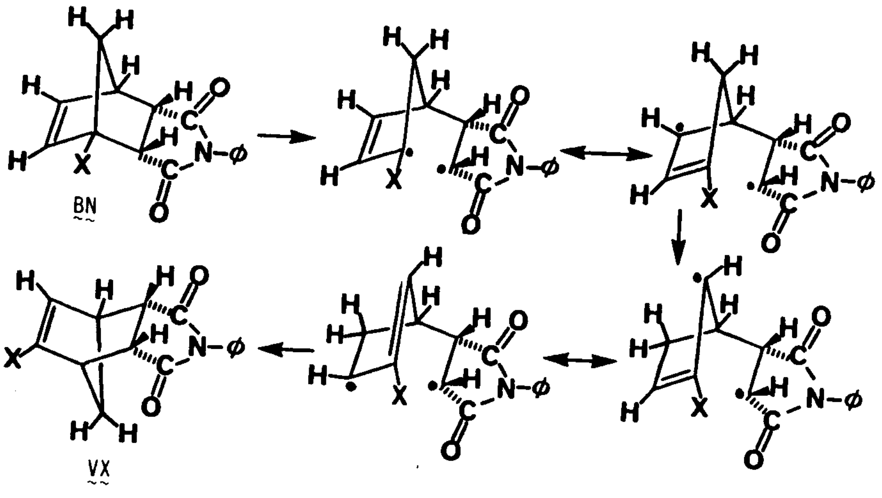
A second observation concerns the fate of these more labile bridgehead substituted compounds under conditions where little or no isomerization of vinyl substituted compounds is seen. Both ϕBN and CBN go to a mix of vinyl substituted isomers with very little bridgehead endo/exo isomerization. For the ϕ system the bridgehead-exo isomer has yet to be detected, while in carbomethoxy case it is seen by NMR, but never to an extent of greater than 10%. Interestingly, the vinyl-endo to vinyl-exo ratio formed on isomerization of either the ϕ or COOMe bridgehead compound heavily favors the vinyl-endo isomer. This preference for isomerization of the bridgehead-endo, preferentially, to the vinyl-endo is completely consistent with an isomerization process (Scheme IV) that proceeds via a) retro-Diels Alder of the bridgehead compound; b) isomerization of the substituted cyclopentadiene from the 1-substituted isomer to the 2-substituted cyclopentadiene; and c) Diels Alder cycloaddition of the 2-substituted cyclopentatiene with the N-phenyl maleimide that had been generated. This last Diels Alder would be expected to show the same, high, endo selectivity we observed in our initial syntheses. interestingly, this is precisely the opposite conclusion that one would expect to reach if the isomerization did not involve a bonafide retro Diels Alder. If the isomerization of either ϕBN or CBN were proceeding by a series of one-bond cleavage and H shift steps, then the expectation would be for BN to go selectively

SCHEME IV



to VX and not to VN at all. This is shown in an alternate hypothetical mechanism in Scheme V. Thus, our isomerization is clearly proceeding by a retro Diels Alder, consistent with literature precedent in related systems (ref. 4).

SCHEME V



An important conclusion from the above studies is that not only do all of our norbornenyl imides undergo retro Diels Alder reaction, but that this reaction pathway is greatly facilitated by bridgehead substitution. However, vinyl substitution has little or no effect on the ease of retro Diels Alder reaction as evidenced by its lack of effect on isomerization rates of VN and VX relative to parent, I.

POLYMERIZATION STUDIES

The first point to be addressed in our discussion of the polymerization of our model monomers is to consider the relevance of the "low temperature" isomerization to the actual polymerization process. That is, we must assess the extent to which isomerization of a substituted monomer has occurred relative to the degree of polymerization of monomer under comparable conditions of time and temperature. To answer this question, we took neat samples of each of our endo substrates (parent, vinyl, and bridgehead) and heated them in sealed glass tubes. At 195°C for 15 hrs, neither parent (I) nor the benzo analog (IV), showed any significant degree of polymerization. In fact, parent shows only small amounts of polymer even after 96 hrs at 195°C. It thus seems clear that, at moderate temperatures (≈200°C), parent (I) achieves exo/endo equilibration much more easily than it polymerizes. While we suggest that this will translate into our obtaining comparable polymer structures, at comparable rates, whether we start from pure PN or pure PX, this remains to be confirmed.

The isomerization of our substituted monomers (V and VI) under cure-like conditions leads to a somewhat more complicated situation. Some of the results obtained from the carbomethoxy substituted compounds are shown in Table V. This data provides convincing evidence that under conditions where only small amounts of polymer are detected by Gel Permeation Chromotography (GPC), the composition of neat samples of monomers are nearly the same whether they started as pure CBN or pure CVN.

TABLE V: Isomer Distribution During 195°C Cure (neat sample, sealed glass tube)

Substrate	1 hr	4 hr	15 hr
	VN:VX:BN+BX	VN:VX:BN+BX	VN:VX:BN+BX
CBN	71:21:7	34:57:9	30:68:2
CVN	72:24:4	33:59:6	25:74:1

When this isomerization data is combined with a measure of extent of polymerization that we have obtained by GPC analysis of these same samples the picture that emerges is as follows. If the thermal cure of a neat carbomethoxy sample is done at <200°C, isomer interconversion proceeds well ahead of polymerization. That is, there is less than 50% polymerization of the carbomethoxy sample even after 96 hrs, yet isomer equilibration is complete in less than a day. More specifically, in the approximately 15 hrs required for isomer equilibration at 195°C, there is ≤10% polymerization.

In a higher temperature cure, the situation is less clear. When neat samples of the carbomethoxy compounds were heated at 250°C they were 50%-80% polymerized even after 2 hrs. We therefore looked at isomer distribution after 0.5 hr and 1 hr at 250°C, full well realizing that our isomerizarion was proceeding in competition with polymerization. We now see evidence for two phenomena that still require further investigation. First of all, inspection of these samples at 0.5 hr and 1.0 hr suggests that complete isomer equilibration is not achieved before these higher temperature samples are polymerized. Secondly, we now start to see some evidence of different polymerization rates from our different substituted monomers. These observations suggest that polymer structure and properties may also vary as a function of starting isomer mix in these higher temperature cures, but this is yet to be studied.

The situation in the curing of the ϕ substituted versions of V and VI is even more complex than for the COOMe substitution, since the ϕ substituted compounds show appreciable polymerization even under our lower temperature cure conditions. Specifically, whereas 195°C for 15 hrs showed full COOMe equilibration and <10% polymer, the ϕ substituted monomers are all more than half polymerized after 15 hrs at 195° and were already showing significant amounts of polymer after only 8 hrs. Isomer equilibration seems to still run ahead of polymerization but the delineation is no longer as clear.

The higher temperature (250°C) cure for the ϕ isomers is also somewhat less tractable. After 2 hrs all of these samples showed no residual monomer, yet the approach to equilibrium after 1 hr was still incomplete. However, it is clear that the initial conversion of ϕBN to (largely) ϕVN has made samples arising from either of these two isomers have similar composition (analogous to Table V above). Other than this observation, there is still a great deal of ambiguity about the details of this polymerization vs isomerization question at 250°C.

The one point that does seem clear about our substituted monomers in general, is that both ϕ and COOMe substitution do substantially facilitate thermal polymerization. A qualitative summary of the data at 195°C indicates that after 15 hrs, parent(I) is less than 10% polymerized, while ϕ substitution results in greater than 2/3 polymer. At 250°C, parent is less than 1/3 polymerized in two hrs., while COOMe is 50%-80% polymer and ϕ is >90% polymer. These numbers are all very crude and are currently being refined, but they do represent clear trends.

While only preliminary results are available on the curing of the benzo compound (IV), a comment on those experiments is in order. Differential Scanning Calorimetry of IV (ref. 5) gives strong indication of significant thermal activity above 250°C. We find that our crude measures of polymerization activity both by NMR and GPC are consistent with the contention that IV polymerizes about as readily as I both in the 200°C and 250°C experiments. The nature of the polymers formed from IV in experiments at both 250°C and 282°C are currently under investigation.

It should be pointed out that while a great deal of current work reinforces the notion that the retro Diels Alder of norbornenyl endcaps is crucial to the behavior of PMR-15 (ref 6), our data seems not to require such chemistry for polymerization to occur. Two facts support this conclusion. Firstly, the benzo system (IV) which is incapable of retro Diels Alder chemistry seems to polymerize as readily as the parent model compound. Secondly, while we know that our vinyl substituted monomers undergo isomerization by retro Diels Alder with comparable ease to the isomerization of the parent compound, they still polymerize significantly more easily. Both these observations suggest that while retro Diels Alder is certainly occurring in PMR solutions, it may not be at the heart of the polymerization activity of these systems. We are continuing to explore this question.

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