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DONOR ACCEPTOR POLYMERIZATION CHEMISTRY AS A VEHICLE TO LOW ENERGY CURE MATRIX RESINS

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A recent study conducted by the National Materials Advisory Board has identified a need for matrix resins that can be prepared at ambient or near ambient room temperatures for on-site airfoil repair. This research project focuses on this problem through the synthesis of network polymers using donor/acceptor polymerization chemistry. The di and tetrafunctional donors used in this study are based on vinyl ether chemistry, and di and tetrafunctional maleimides are the acceptors.

Our first objective has been the synthesis of the necessary donor and acceptor monomers and so we have proceeded to study a variety of synthetic approaches to create these needed compounds. In the case of donor monomers we have selected a palladium-assisted vinyl exchange reaction as the best route. Using this chemistry we have been able to successfully prepare 15 monomers based on vinyl ether chemistry.

We have also synthesized an equal number of maleimides using a conventional synthetic

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19. ABSTRACT (Continues) chemistry, that being reaction of maletic anaydride with the amine, followed by condensation of the maleimic acid to the maleimide itself. This chemistry requires a great deal of patience, yet if done properly, yield the necessary monomers in high purity.

Our first polymerization studies have been done in solvents in order to prepare a series of "benchmark" polymers for thermal analysis work. We have examined all polymerization combinations, i.e., difunctional donors combined with difunctional acceptors, difunctional donors with tetrafunctional acceptors, tetrafunctional donors with difunctional acceptors, and finally, tetrafunctional donors and tetrafunctional acceptors. DSC and TGA analysis of these polymers indicates they possess the thermal stability necessary for performance in their required application.

Our research work is turning toward bulk polymerizations using room temperature initiator systems based on benzoylperoxide and diethylaniline.

FOREWORD

This report covers research performed by the University of Florida, Gainsville, Florida 32611, on Contract F33615-85-C-5093, "New Cure Chemistry for Low Energy Cure of Matrix Resins". The period of research covered was from February 1986 to April 1987. The report was submitted in June 1987.

The research was performed in the Department of Chemistry by Choon H. Do, Mike Johnson, and Mark A. Smith under the direction of Dr. Kenneth B. Wagener, the principal investigator.

This effort was sponsored by the Polymer Branch (AFWAL/MLBP), Nonmetallic Materials Division of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright Patterson Air Force Base, Ohio. Bruce Reinhardt was the Project Engineer.

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I. INTRODUCTION AND STATEMENT OF THE PROBLEM

According to a recent study conducted by the National Materials Advisory Board, National Academy of Sciences[1], there exists a need for matrix resins that can be prepared at ambient or near ambient temperatures for "on site" airfoil repair. The low cure temperature thermoset polymers should possess excellent mechanical performance at temperatures around 350°F, rapid cure times, and easy formulation characteristics. Properties of interest include a high glass transition temperature, a high bending modulus, a low propensity towards fibrillation, a high degree of solvent resistance, essentially no creep, a high tear strength, significant puncture resistance, minimal flexural fatigue, and excellent adhesion to metal surfaces.

It is the goal of this research to synthesize such polymers by employing donor acceptor polymerization chemistry to create - at ambient temperatures - matrix resins that exhibit many, if not all, of the desirable mechanical properties mentioned above. Further, it is the goal of this work to demonstrate the mechanical performance of these polymers, thereby exhibiting their usefulness as matrix resins.

Donor acceptor polymerization is one type of addition polymerization of vinyl groups initiated by radicals. Figure 1 exemplifies donor acceptor polymerization. Two monomers are required, one possessing an electron donor group ("D" in Figure 1) and the other possessing an electron acceptor group, "A". As is shown in Figure 1, each monomer often is slow to polymerize by itself at room temperature, yet copolymerization is rapid yielding essentially alternating copolymers. For example, styrene copolymerizes with maleic anhydride (an excellent electron acceptor) one hundred times faster at 60°C than it undergoes homo-polymerization.[2]

This chemistry can be used to synthesize matrix copolymers by using bis-donors and bis or tris-acceptors such that copolymerization will lead to matrix copolymer systems. Several vinyl ether based donor bis-comonomers are under investigation in combination with a variety of maleimide based, acceptor bis-comonomers. In each case a

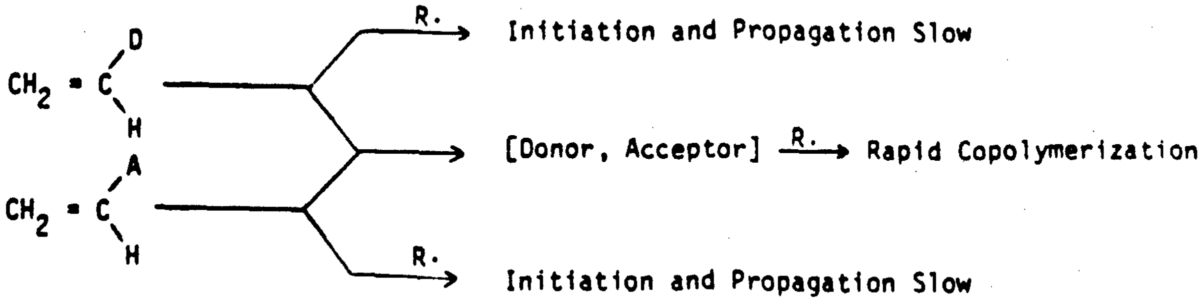


Fig. 1. The Donor Acceptor Polymerization Concept

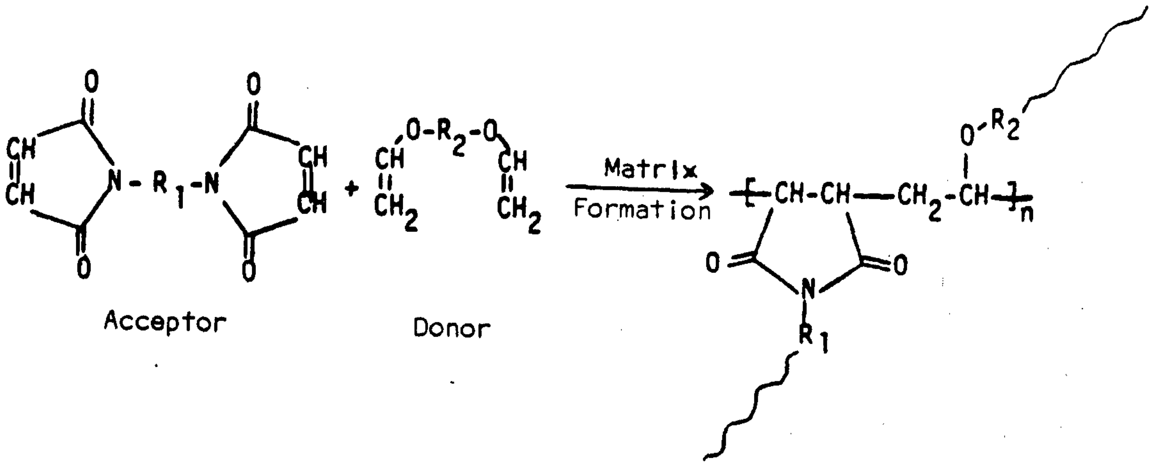


Fig. 2. An Example of Donor Acceptor Polymerization to Yield High Crosslink Density Matrix Polymers

two part radical initiator system will be used, one part dissolved in the donor and the other part in the acceptor, such that copolymerization (curing) will not occur prior to mixing the comonomers together.

Conventional cure chemistry is done at above-ambient temperatures to complete the chemical reaction needed to create thermoset resins. High tempearture curing also anneals the polymer; thus, the morphology of the polymer is established during high temperature cure, and consequently the polymer's properties do not change at these high use temperatures.

The problem at hand, then, is to identify reaction chemistry that proceeds to completion at ambient temperatures, and to specify the structure of multifunctional monomers such that the morphology of the network polymer - the matrix resin - remains insensitive to temperatures up to 350°F. High temperature curing would no longer be required. However, one of the challenges of the analytical technique to be employed is to show whether or not further reactivity of the matrix remains after this initial cure. Experimental techniques to make this determination are being designed.

It will be necessary to create copolymers at room temperature having a very high crosslink density using bis- comonomers capable of participating in donor acceptor polymerization. The high density of crosslinks will reduce the mobility of the network as a whole, thus leading to high glass transition temperatures. It may also be necessary to create multiphase matrix polymers wherein one phase permits the other to achieve a maximum degree of order during polymerization. This represents a form of self annealing. Multiphase matrix resins also will reduce the brittleness often associated with high crosslink density.

Donor acceptor polymerization at ambient temperatures will yield matrix polymers possessing a high density of crosslinks. By choosing bis- (and/or tris-) donor and acceptor monomers exemplified in Figure 2, it will be possible to achieve the high crosslink density in relatively short reaction times. The actual mechanical performance of these polymers will depend upon the nature of R_1 and R_2 in the comonomers. Thus, it should be possible to synthesize a variety of tailor-made crosslinked polymers in this manner. Properties like high temperature stability (low hydrogen content in R_1 and R_2), high dimensional stability (high crosslink density), dry processability (no solvent), high electrical resistance (saturated R_1 and R_2), and moisture resistance (hydrophobic R_1 and R_2) should be possible, properties that escape conventional crosslinking technology. A combination of more than two types of R groups within a given polymerization is also possible to enhance the control of properties. Choice of IMMISCIBLE fragments within R_1 and R_2 will permit molecular phase separation to occur, leading to self annealing, wherein the actual glass transition temperature of these molecular composites, then, will depend upon the molar ratio of each phase.

2. RESEARCH RESULTS TO DATE

Monomer Synthesis. During this first phase we have focused our attention on the synthesis of di and tetra functional vinyl ether monomers and maleimide monomers. Due to the lack of availability of monomers of this nature in both cases, it has been necessary for us to devise synthetic routes to monomers of both types. In the case of maleimide preparation, our synthetic work has revolved about the use of maleic anhydride chemistry wherein an appropriate amine or diamine has been chosen leading first to maleamic acid or bismaleamic acid followed by ring closing to the desired maleimide structure, and, with patience, this synthetic route has proven to be effective to create all of the di and tetra functional maleimides needed in this research.

The synthetic and di and tetra functional vinyl ethers has not been so straightforward and it has been necessary to explore a number of synthetic routes to create monomers of interest to us. Specifically, we have examined Williamson ether synthesis chemistry, phase transfer catalysis chemistry, mercuric acetatate catalyzed vinyl transetherification chemistry, including enzyme catalyzed routes for the removal of ethanol, and palladium II catalyzed vinyl transetherification reactions. Of these many approaches, the palladium catalyzed route appears to be the most effective and indeed gives high purity di and tetra functional ethers. This latter result is significant since it provides a low energy route for the synthesis of divinyl ethers in high purity. Figure 3 shows the synthetic route chosen for investigation in a typical Williamson ether synthesis. This is a reported procedure[3] wherein in this case bisphenol A is converted to its sodium salt in a toluene water mixture via refluxing. The sodium salt is then reacted with 2-chloroethylvinyl ether and DMSO at 60°, such that SN_2 chemistry occurs at the primary alkyl halide carbon thereby creating the divinyl ether. We found this to be an unacceptable procedure to prepare di and tetra functional vinyl ethers, mainly for experimental reasons. The reactions are slow, incomplete, solubility is difficult to predict, and since the reactions themselves are not complete, one ends up with a mixture and di and tetra functional monomers in the instances where tetra functional monomers are sought.

We then turned our attention to phase transfer catalysis chemistry which appeared to be a more productive route to the synthesis of vinyl ether monomers. The conditions chosen for reaction are shown in Fig. 4. Catalyst A and catalyst B were investigated repeatedly, again choosing 2-chloroethylvinyl ether as the substrate for nucleophilic attack. There does appear to be a reaction occurring in the case of catalyst A but it is quite slow, and interestingly enough, once the vinyl ether is prepared it appears to polymerize probably via a cationic polymerization mechanism in the methylene chloride layer whereby the cationic polymerization possibly is induced by the phase transfer catalyst itself. This phenomenon is quite interesting and indeed may be the object of further study since phase transfer catalysis cationic polymerization has not been reported previously. We have not yet investigated this chemistry further, but a publication[4] that recently came to our attention reports that bis vinyl ethers of bis phenols can be produced under certain conditions using phase transfer catalysts. This may be the best synthetic route to these particular compounds. We then turned our attention to mercuric

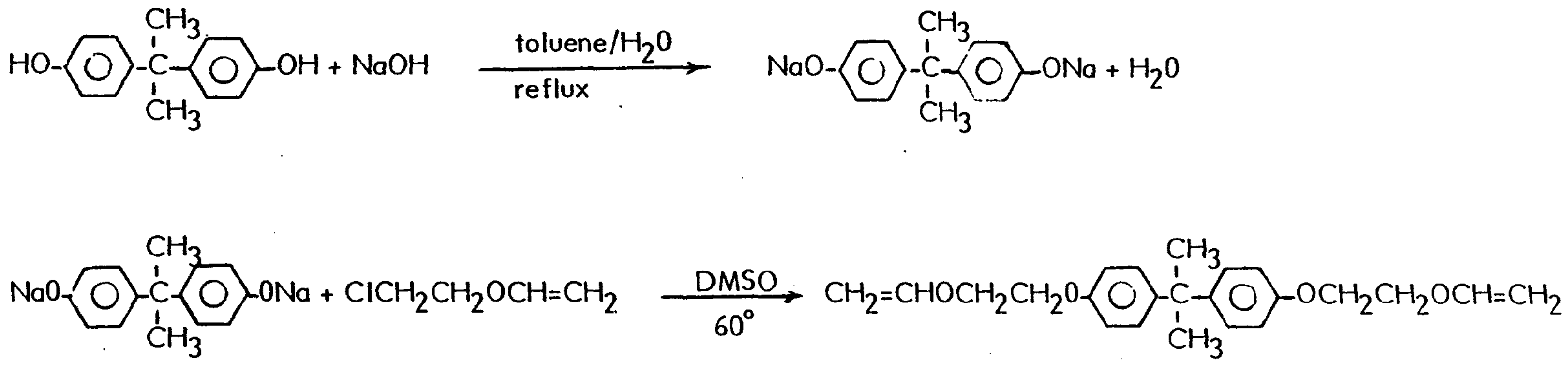
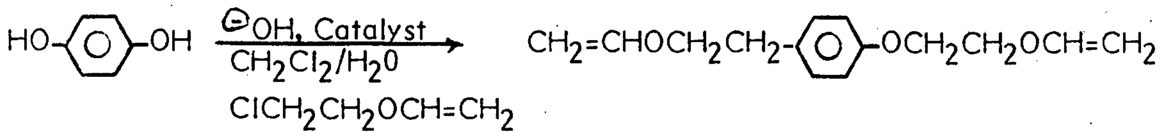


Fig. 3. Williamson Ether Synthesis



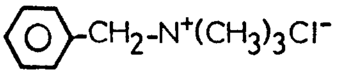
	Catalyst	Base
A.		NaOH
B.	15-Crown-5	NaOH
C.	18-Crown-6	KOH

Fig. 4. Phase Transfer Catalysis

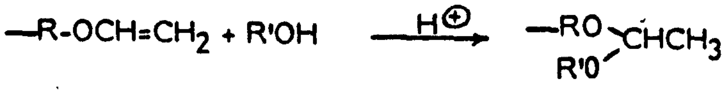
acetate catalyzed transetherification chemistry[5] as shown in Fig. 5. This reaction is done with excess ethyl vinyl ether being present and at the reflux which is less than 40°C. Only a catalytic amount of mercuric acetate is required. An equilibrium is established such that both di and tetra functional vinyl ethers are formed again in instances where tetra functional monomers are desired. The mechanism for such a reaction is shown in Fig. 6. Note that a biproduct, ethanol, is created in this reaction and in order for one to drive the reaction to completion, it becomes necessary to remove ethanol as it is being formed. This proves to be difficult since the boiling point is higher than ethyl vinyl ether. Consequently, in an attempt to distill ethanol, ethyl vinyl ether is removed instead, and equilibrium is then shifted in the direction of reactants rather than products. This holds true for all vinyl ethers and their respective alcohols that we considered for this reaction. This problem leads to only about 90% completion of the exchange. Thus one is left with 10% either difunctional vinyl ether or unreacted alcohol in the case of formation of difunctional monomers. When low boiling alcohols or diols are used as starting materials, pure products can be obtained by fractional distillation. When a poly(ethylene glycol) is used, however, separation of the product from the difunctional vinyl ether may not be possible. In this case a nearly quantitative conversion to product is necessary. In an attempt to avoid this problem two approaches were considered: 1) an adsorption or trapping of ethanol as it is being formed by a drying agent or molecular sieves, and 2) the enzyme catalytic conversion of alcohol to acid aldehyde which would have a lower boiling point than ethyl vinyl ether. The former approach proved to be completely unsuccessful in investigating the usual drying agents such as dry rite, etc. The use of molecular sieves also proved unsuccessful though it did appear as if the equilibrium was shifted slightly to the right, perhaps yielding 95% conversion. The enzyme approach remains under investigation.

Palladium II catalyzed vinyl transetherification[6] is by far the best route to the preparation of the desired monomers. Fig. 7 shows the reaction and mechanism

$$HO\text{-}R\text{-}OH + CH_3CH_2OCH{=}CH_2 \xrightleftharpoons{Hg(OAc)_2} CH_2{=}CHO\text{-}R\text{-}OCH{=}CH_2$$

$$HO\text{-}R\text{-}OH + CH_3CH_2OCH{=}CH_2 \xrightleftharpoons{Hg(OAc)_2} HO\text{-}R\text{-}OCH{=}CH_2$$

$$HO\text{-}R\text{-}OCH{=}CH_2 + CH_3CH_2OCH{=}CH_2 \xrightleftharpoons{Hg(OAc)_2} CH_2{=}CHO\text{-}R\text{-}OCH{=}CH_2$$



$$—R\text{-}OCH{=}CH_2 + R'OH \xrightarrow{H^{\oplus}} \left.\begin{matrix}—RO\\ R'O\end{matrix}\right\rangle CHCH_3$$

Fig. 5. Mercuric Acetate Catalyzed Vinyl Transetherification

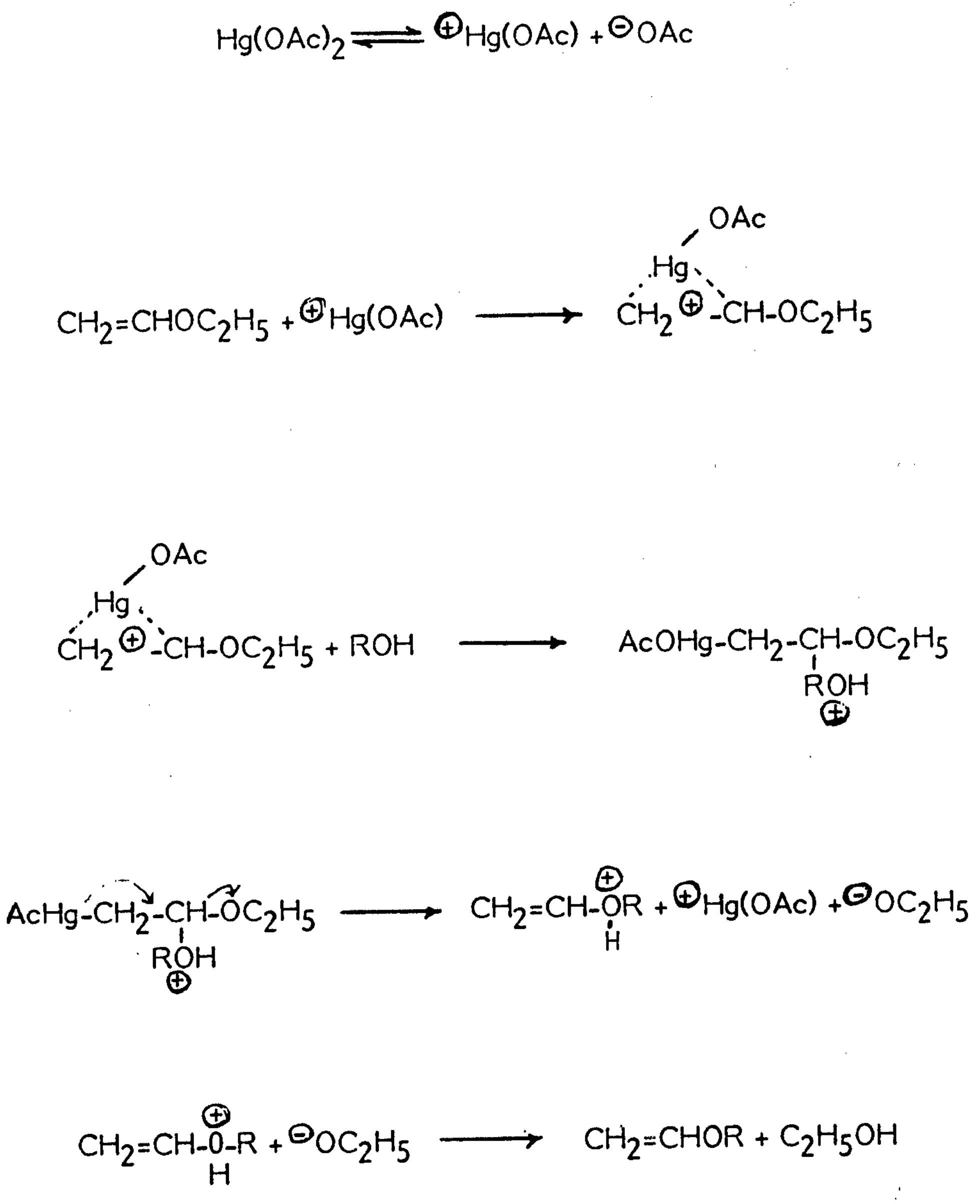
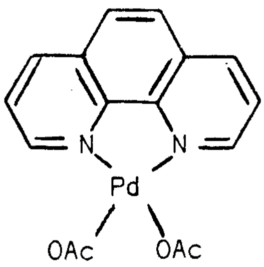


Fig. 6. Mechanism of Mercuric Acetate Catalyzed Vinyl Transetherification



$HO\text{-}R\text{-}OH + CH_2{=}CHOC_2H_5 \rightleftharpoons CH_2{=}CHO\text{-}R\text{-}OCH{=}CH_2$

No acetal formation

MECHANISM

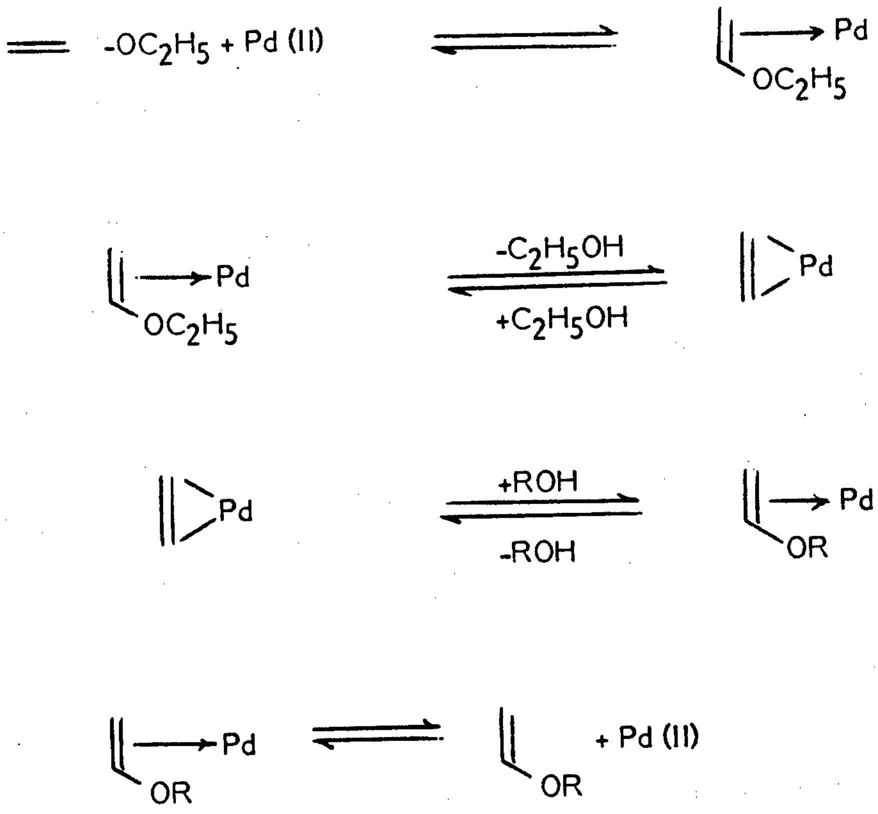


Fig. 7. Palladium (II) Catalyzed Vinyl Transetherification

responsible for conversion to di and tetra functional vinyl ethers. Reaction is done at room temperature and requires successive additions of ethyl vinyl ether in order for complete conversion to occur. Conversion is nearly quantitative as shown in Fig. 8 which displays an NMR spectrum of the divinyl ether of PEG 600. The extent of conversion in these reactions can best be determined by ^{13}C NMR spectroscopy. The reactions were also followed by ^{1}H NMR wherein the alcohol peak of polyoxyethylene was observed to disappear concurrent with the appearance of vinyl ether signals. Further quantification of this reaction has been done via a titration procedure and by mass spectral analysis which is currently underway.

Fig. 9 shows the vinyl ethers that have been synthesized by various techniques. It is clear that the procedure is general, high yielding, and is an important step in the achievement of the goals set forth in this project.

The preparation of di and tetra functional maleimides prove to be rather facile once reaction conditions were established to maintain the small percentage of side reactions that often accompany maleimic anhydride chemistry. Fig. 10 shows the reaction sequence that was chosen in the preparation of a typical maleimide compound.[7] In the first step nucleophilic ring opening of the anhydride link is accomplished at temperatures less than 20°C in either methylene chloride or chloroform to generate a maleimide acid. Malemide acid is purified at this step followed by ring closure to maleimide using the dehydrating system sodium acetate and acetic anhydride. Reaction is done between 70 and 80°C over a period of roughly an hour followed by pouring the solution into a beaker containing ice. The product then is extracted from the solution with ethyl ether and purified either by recrystallization or distillation, depending upon the state of matter for the compound.

While this procedure does appear facile, it has required a great deal of patience in preparing the necessary maleimides that are needed since side polymerizations can be induced at high temperatures. Fig. 11 shows the di and tetra functional maleimides that

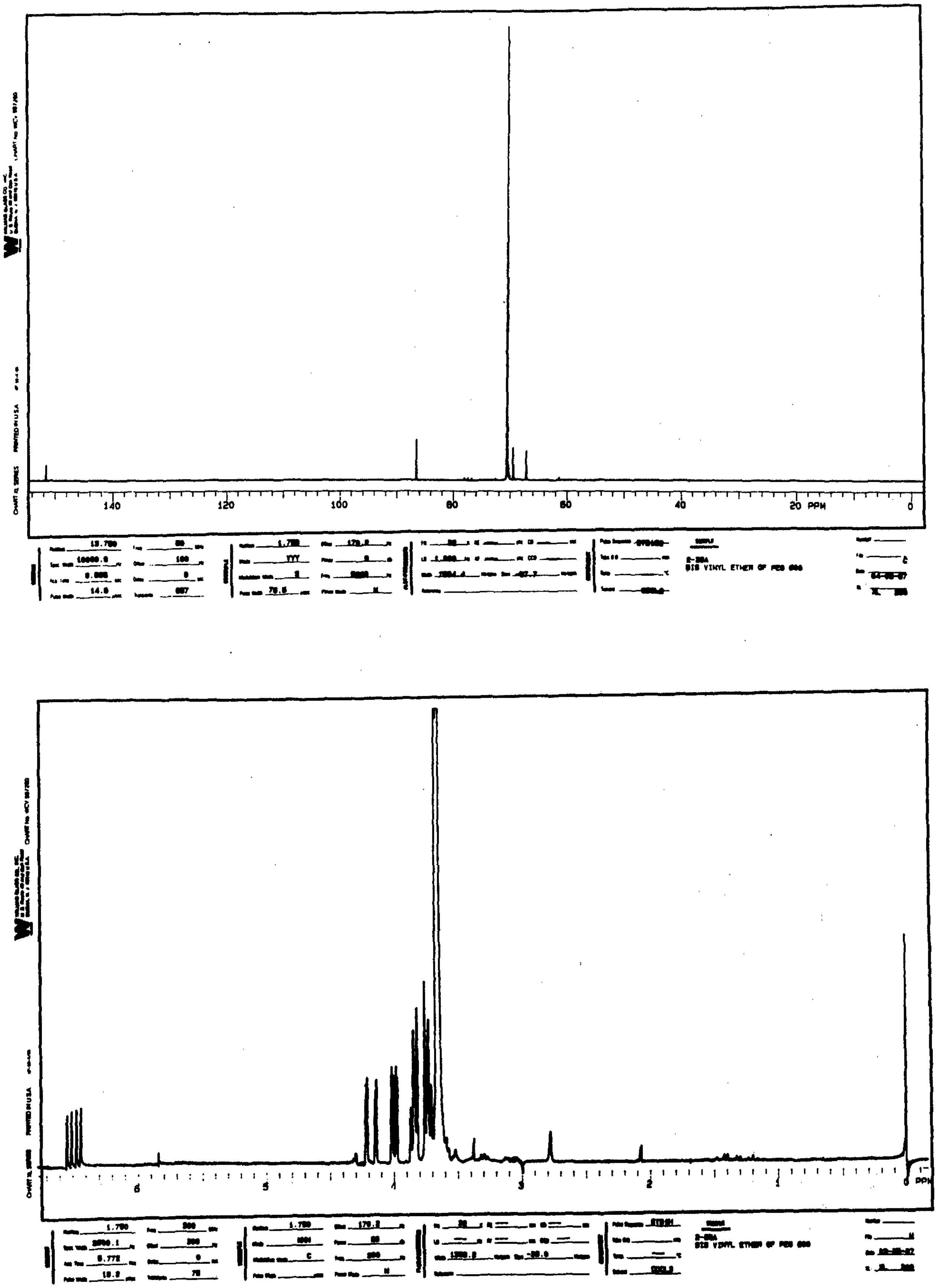
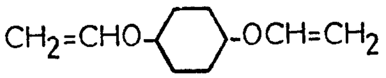


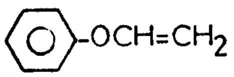
Fig 8. NMR Spectra of the Divinyl Ether of PEG 600

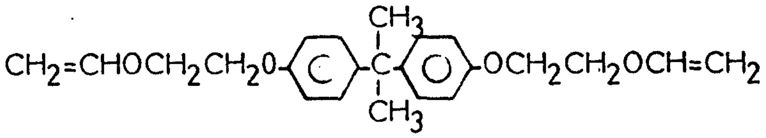
$CH_2{=}CHO\text{-}(CH_2)_n\text{-}OCH{=}CH_2$

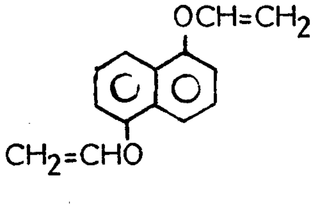
$n = 5, 7, 12$



$CH_3CH_2OCH_2CH_2OCH_2CH_2OCH{=}CH_2$







$CH_2{=}CHO(C_2H_5O)_nCH{=}CH_2$

$n = 13, 22, 44$

Fig. 9. Vinyl Ether Synthesis

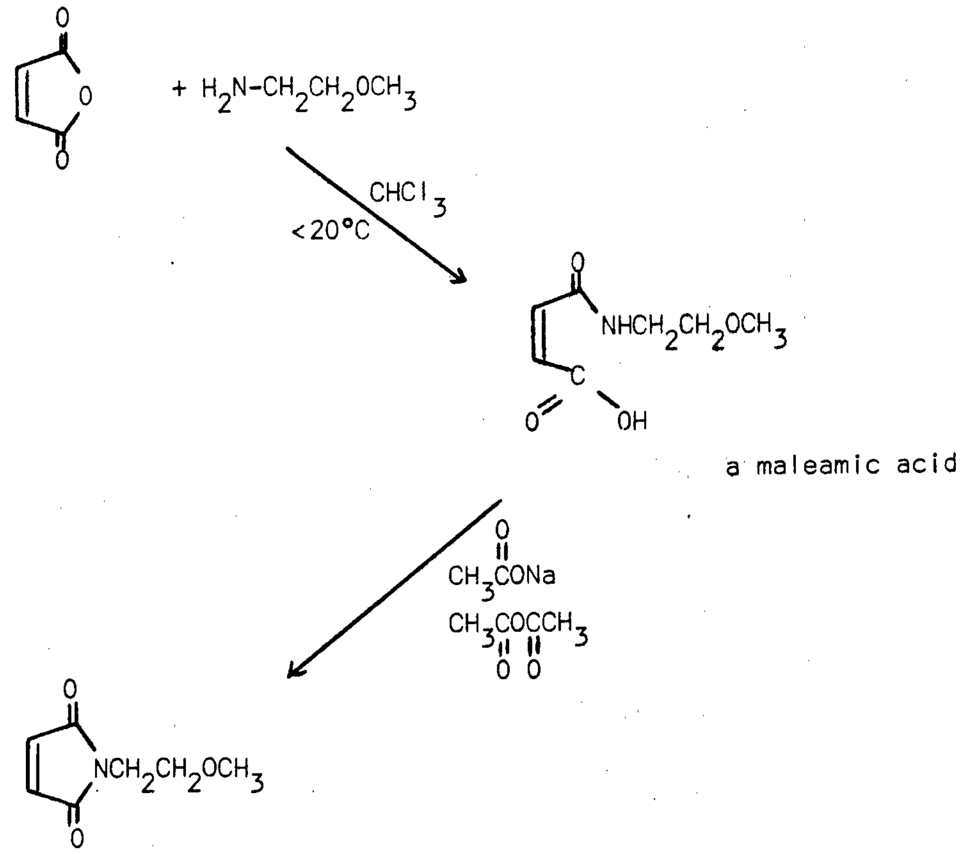


Fig. 10. Maleimide Synthesis

Bismaleimide

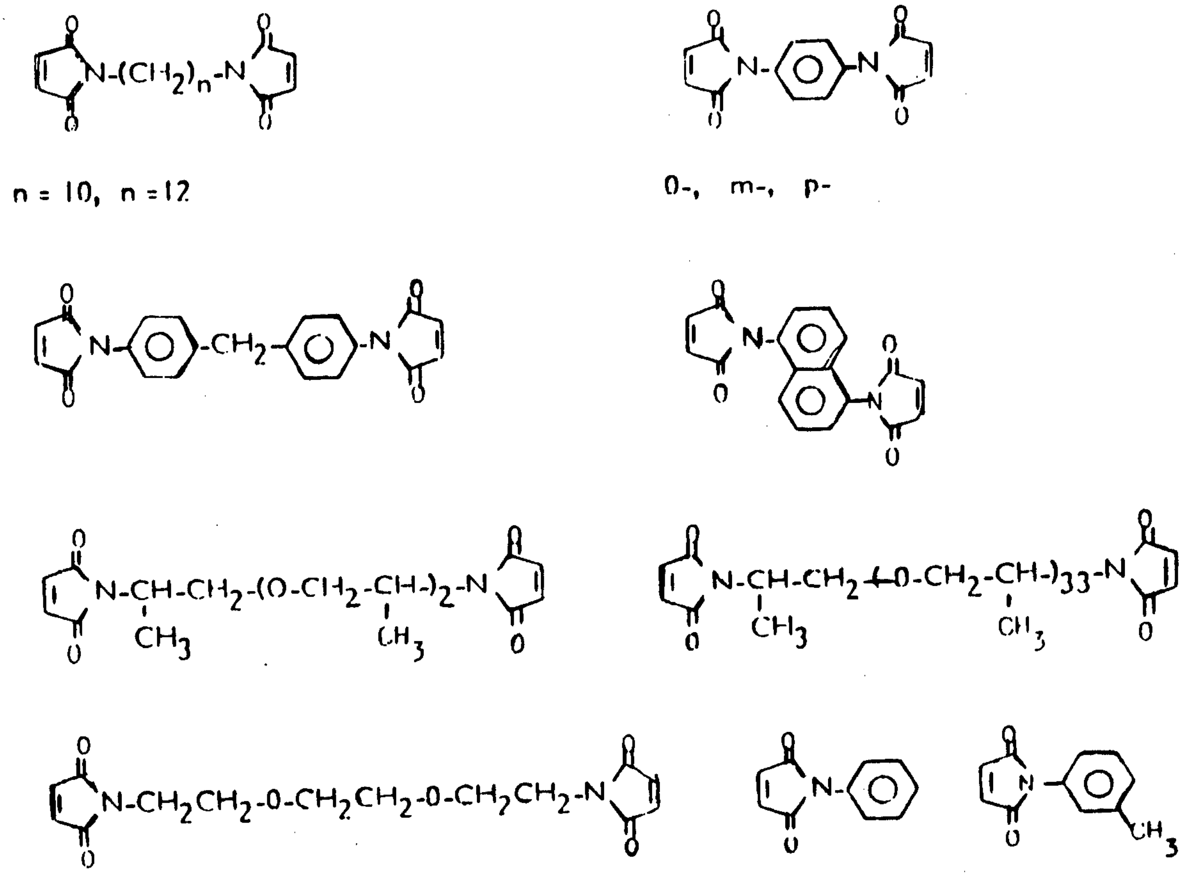


Fig. 11. Structures of Bismaleimides Available

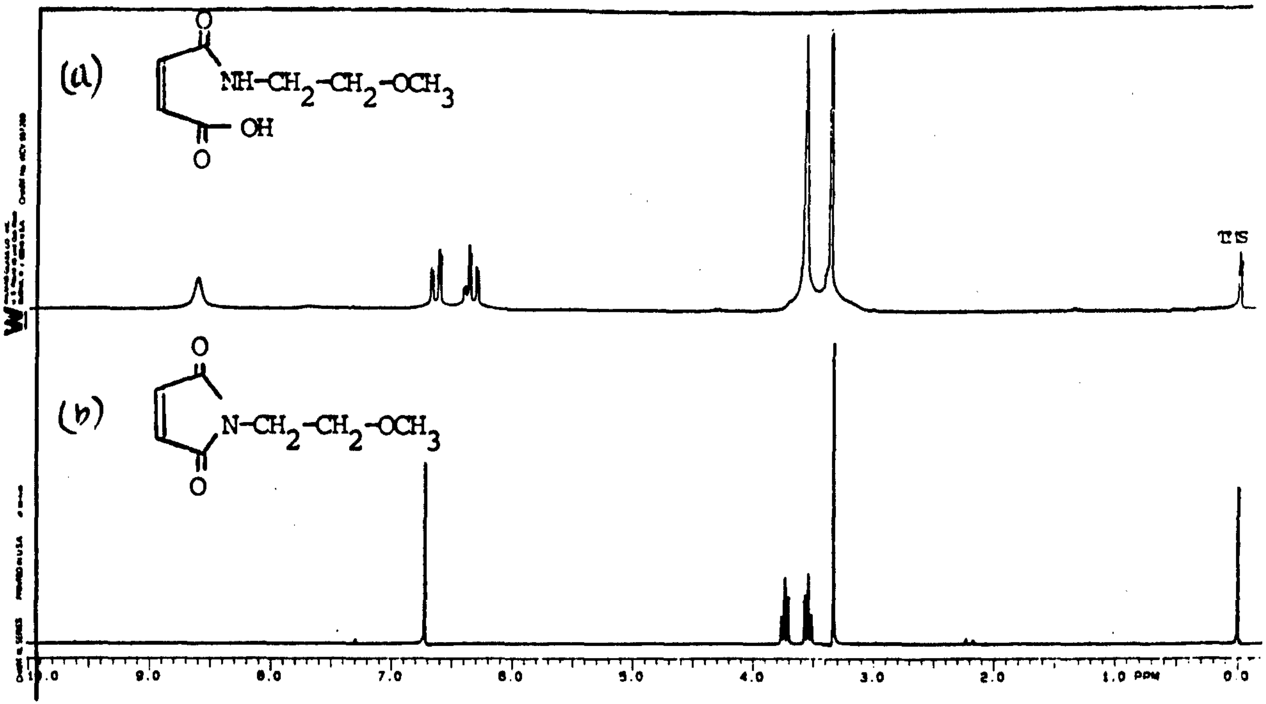
have been prepared using this procedure. Figs. 12 through 15 give the high field proton and carbon NMR spectra of two amic acid and maleimide compounds providing sound evidence for the high purity of the monomers being formed.

Polymerizations. Five types of polymerizations have been investigated to date these being:

- The homo polymerization of di and tetra functional maleimides using radical polymerization or thermal initiation techniques.
- The polymerization of difunctional maleimides with difunctional vinyl ethers to give linear polymers.
- The polymerization of difunctional vinyl ethers with tetra functional maleimides to give network polymers.
- The polymerization of tetra functional vinyl ethers with difunctional maleimides to give network polymers, and
- The polymerization of tetra functional vinyl ethers and tetra functional maleimides to give network polymers having the highest density of crosslinks.

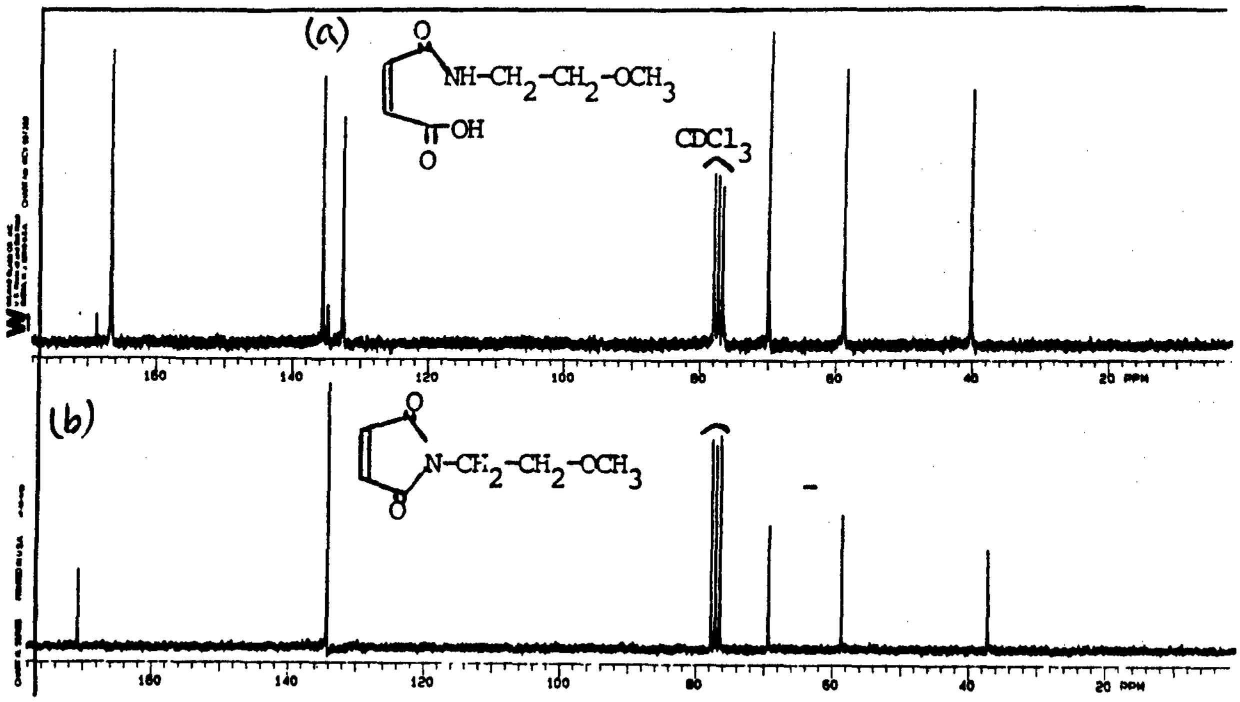
These polymerizations were done in order to give us our first thermal data with respect of stability of these polymers and to obtain a feeling as to how easily these polymerizations could be achieved at room temperature. In some cases polymerizations were done in bulk but for the most part, our work was done using methylene chloride to facilitate the reaction. Once we have an understanding of the thermal stability of these polymers we will turn our attention exclusively to bulk polymerization techniques. We chose dimethyl aniline in combination with benzoyl peroxide as the initiator pair and did the polymerizations either at 60° or room temperature. Most of the work has been done at room temperature. Comments follow on each of the polymerization types.

The thermo homopolymerization was done either at 60° using AIBN as an initiator or at 250° with no initiatior present. In the latter case, no solvent was present as well. These polymer samples exhibited light pink color after the polymerization was done and



200 MHz ^{1}H NMR spectra, solvent = $CDCl_3$.

Fig. 12. Proton NMR Spectra of N-(2-Methoxyethyl) Maleamic Acid and N-(2-Methoxyethyl) Maleimide



50 MHz ^{13}C NMR spectra, solvent = $CDCl_3$.

Fig. 13. Carbon NMR Spectra of N-(2-Methoxyethyl) Maleamic Acid and N-(2-Methoxyethyl) Maleimide

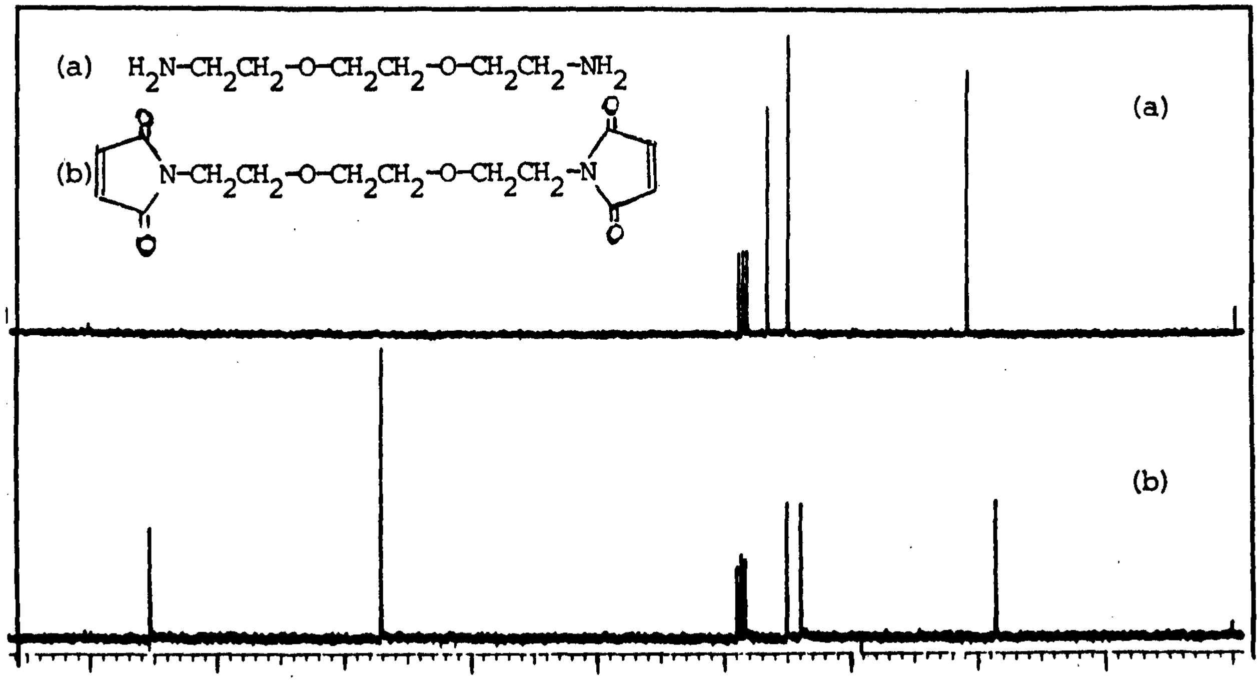


Fig. 14. Carbon NMR Spectra of 1,2 Bis(2-Aminoethoxy)ethane and N,N'-(1,2-Diethoxyethane) Bismaleimide

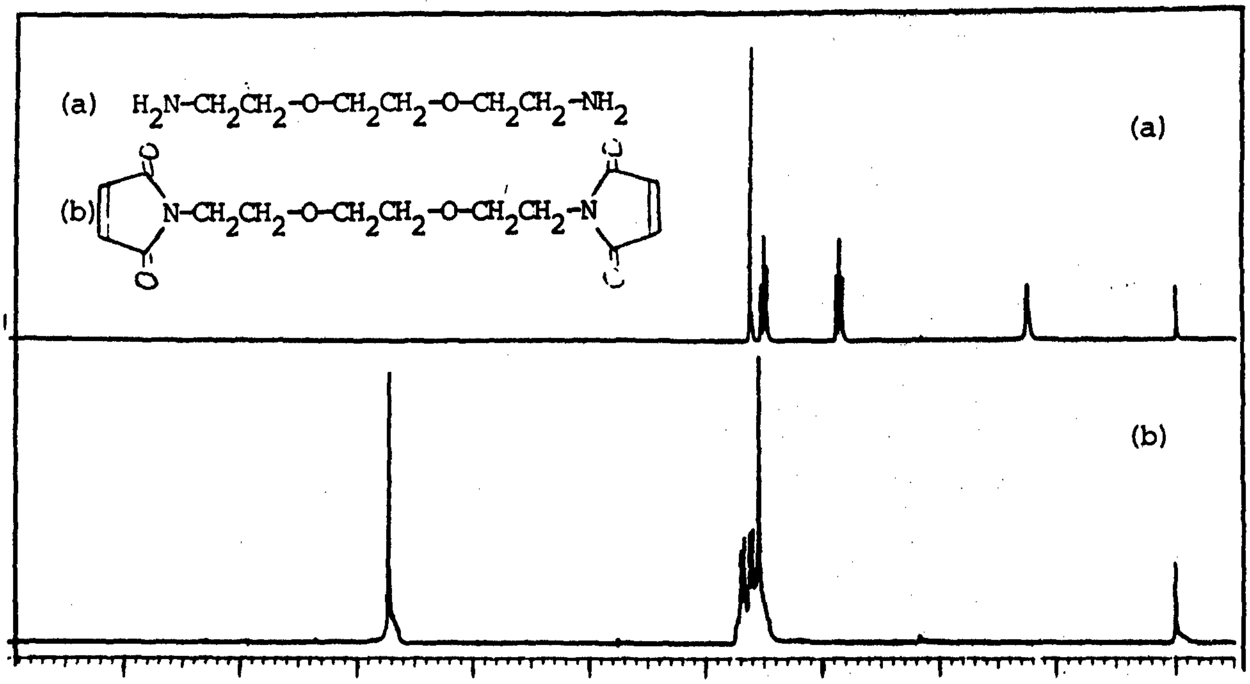


Fig. 15. Proton NMR Spectra of 1,2 Bis(2-Aminoethoxy)ethane and N,N'-(1,2-Diethoxyethane) Bismaleimide

it could possibly be due to slight oxidation. The polymers were soluble in the case of difunctional monomer polymerization and not soluble in the case of tetra functional monomer polymerization as would be expected.

Figs. 16 through 19 give thermal and NMR data for the polymerization of 2-methoxyethyl maleimide, a model compound for the polyether maleimides that have been prepared. Both thermal and radical homopolymerization techniques were undertaken and in each case the carbon and NMR proton spectra show signals as would be anticipated for the repeat unit that is presented, i.e., no enolate radical repeat unit is observed in these polymerizations. Fig. 18 shows that the thermal stability of the polymer itself, at least in nitrogen, is not a function of the type of polymerization that was induced. This would be expected since thermo polymerization spectra occur through a radical procedure. Thermal stability in nitrogen is quite high, i.e., 350°C before an onset of weight loss is observed. A slight difference between these two spectra is observed in the range 100-350°C, a difference which is attributed most likely to the loss of volatiles such as water. We don't regard it as significant. Fig. 19 shows a melting point and a slight exotherm at 130°C which appears to be related to the thermal polymerization of such a monomer. The DSC curve also shows a glass transition temperature around 140°C. Other characterizations of the polymer such as CHN analysis are consistent with the expected structure. These linear polymers provide us with database points that are going to be used for comparison with the network polymers such that we might be able to judge the degree of network formation necessary in producing useful resins. Of course, their utility is low due to their solubility, i.e., a lack of solvent resistance.

Fig. 20 shows DSC curves for a tetra functional maleimide spaced with propylene oxide before heating and after heating at 150° for a half hour. This experiment provides us with further evidence that thermal polymerization, i.e., without added initiator in bulk, indeed seems to occur in the regime 140-150°C, thereby yielding a polymer with a glass transition temperature of around 140°C. These polymers in this case of course are

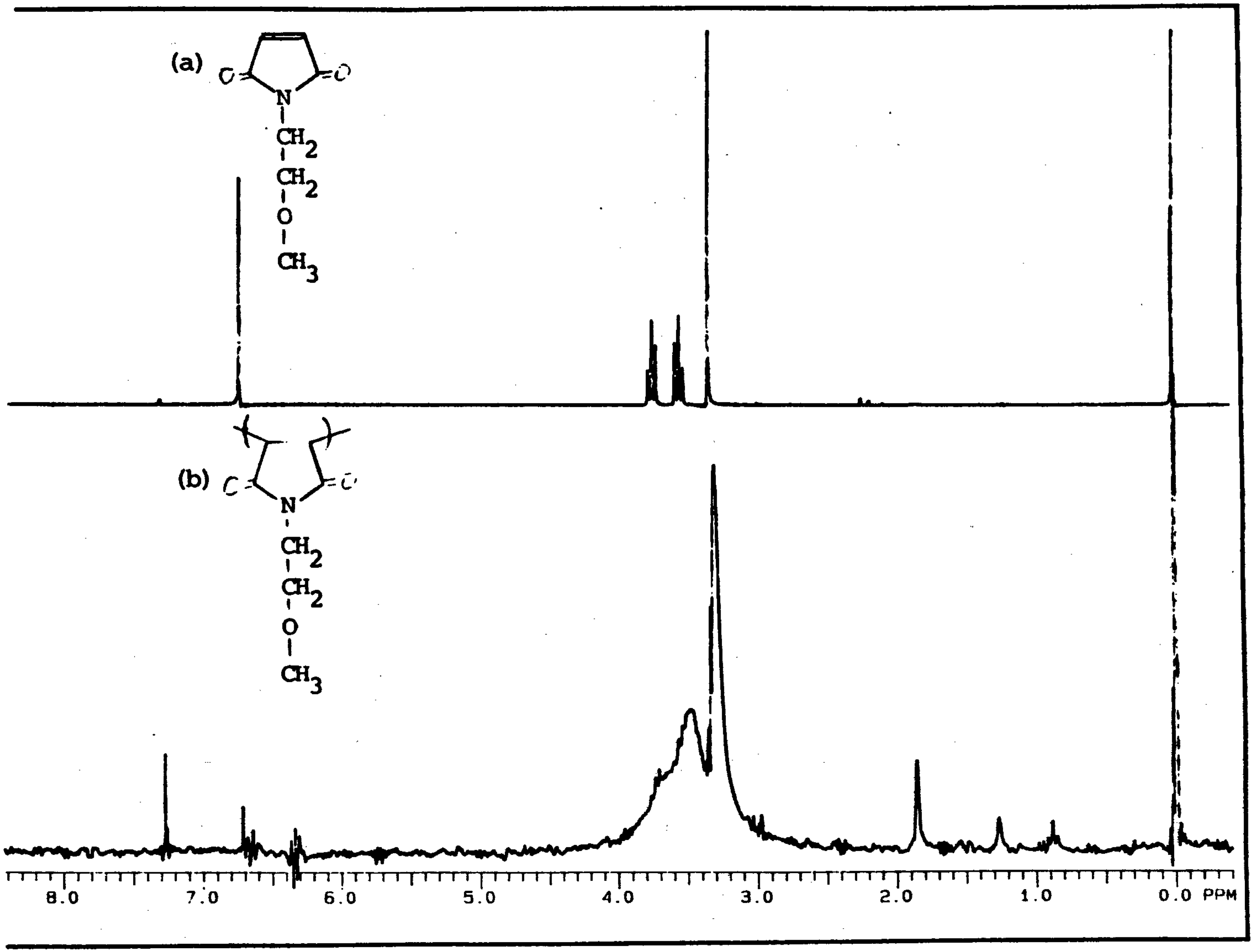


Fig. 16. Proton NMR Spectra of N-(2-Methoxyethyl) Maleimide and Poly N-(2-Methoxyethyl) Maleimide

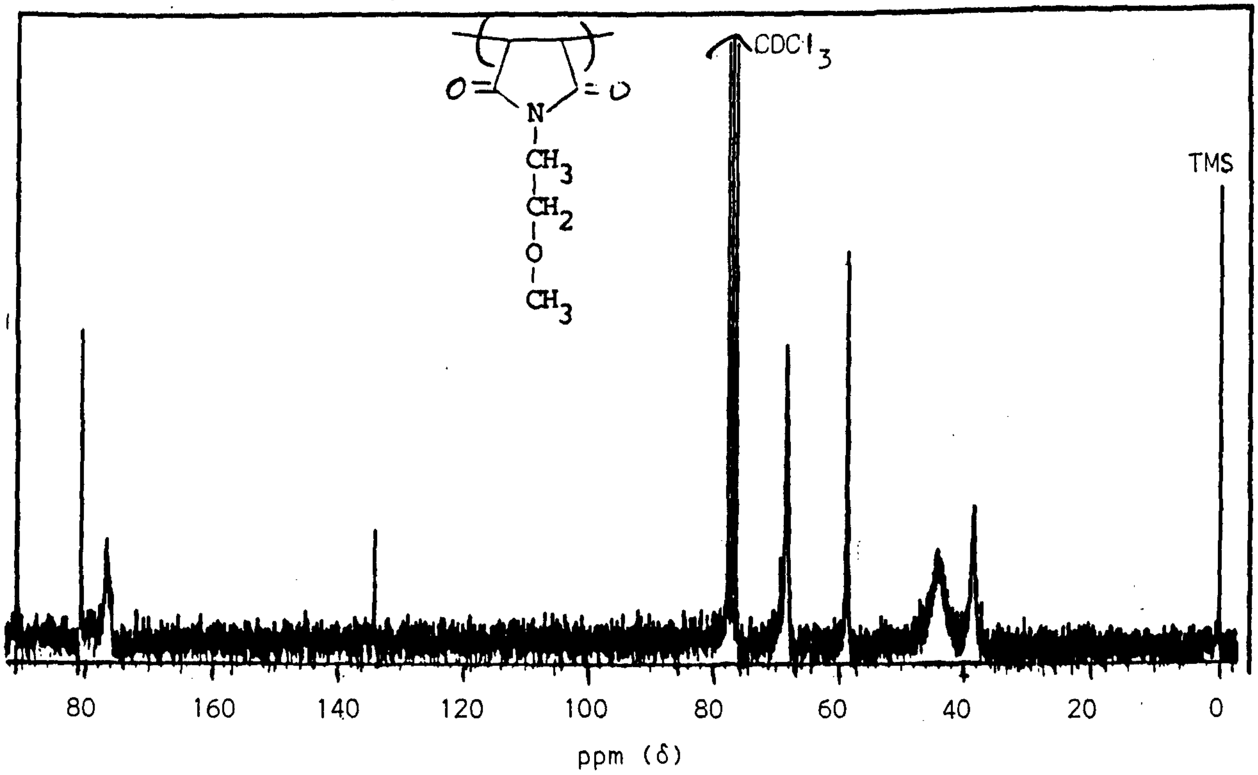


Fig. 17. Carbon NMR Spectrum of Poly N-(2-Methoxyethyl) Maleimide

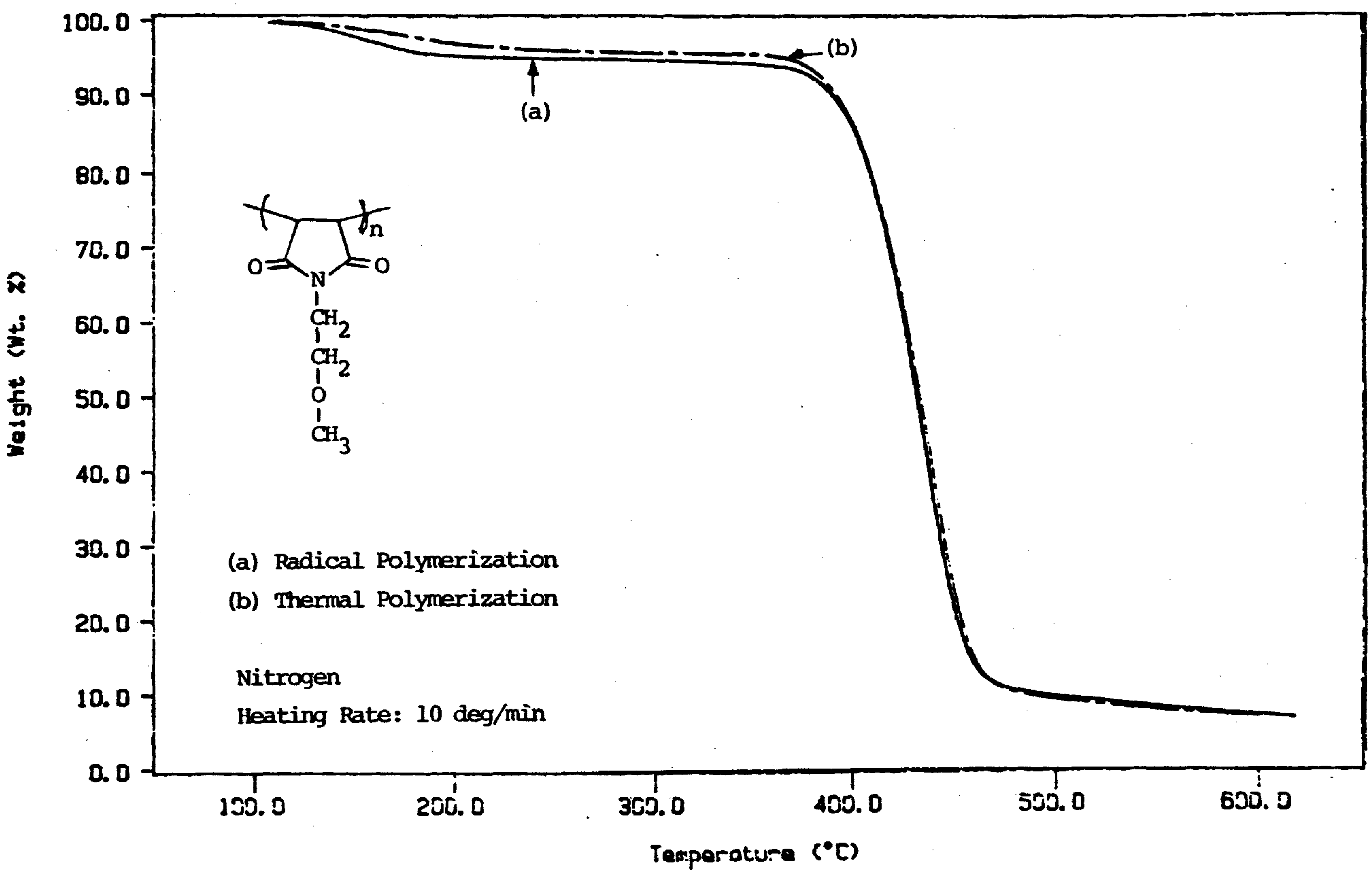


Fig. 18. TGA Curve of Poly N-(2-Methoxyethyl) Maleimide

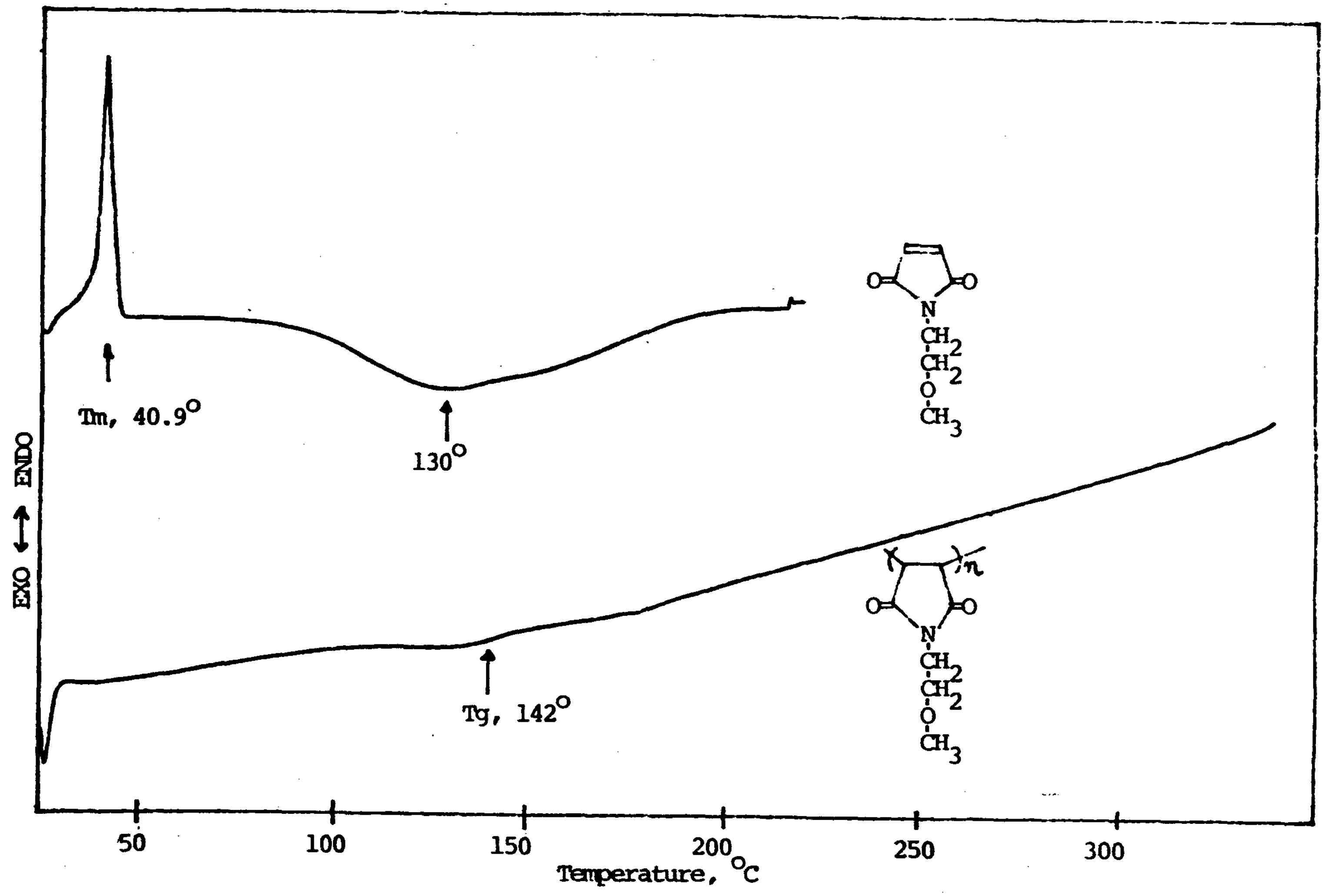


Fig. 19. DSC Curves of N-(2-Methoxyethyl) Maleimide and Poly N-(2-Methoxyethyl) Maleimide

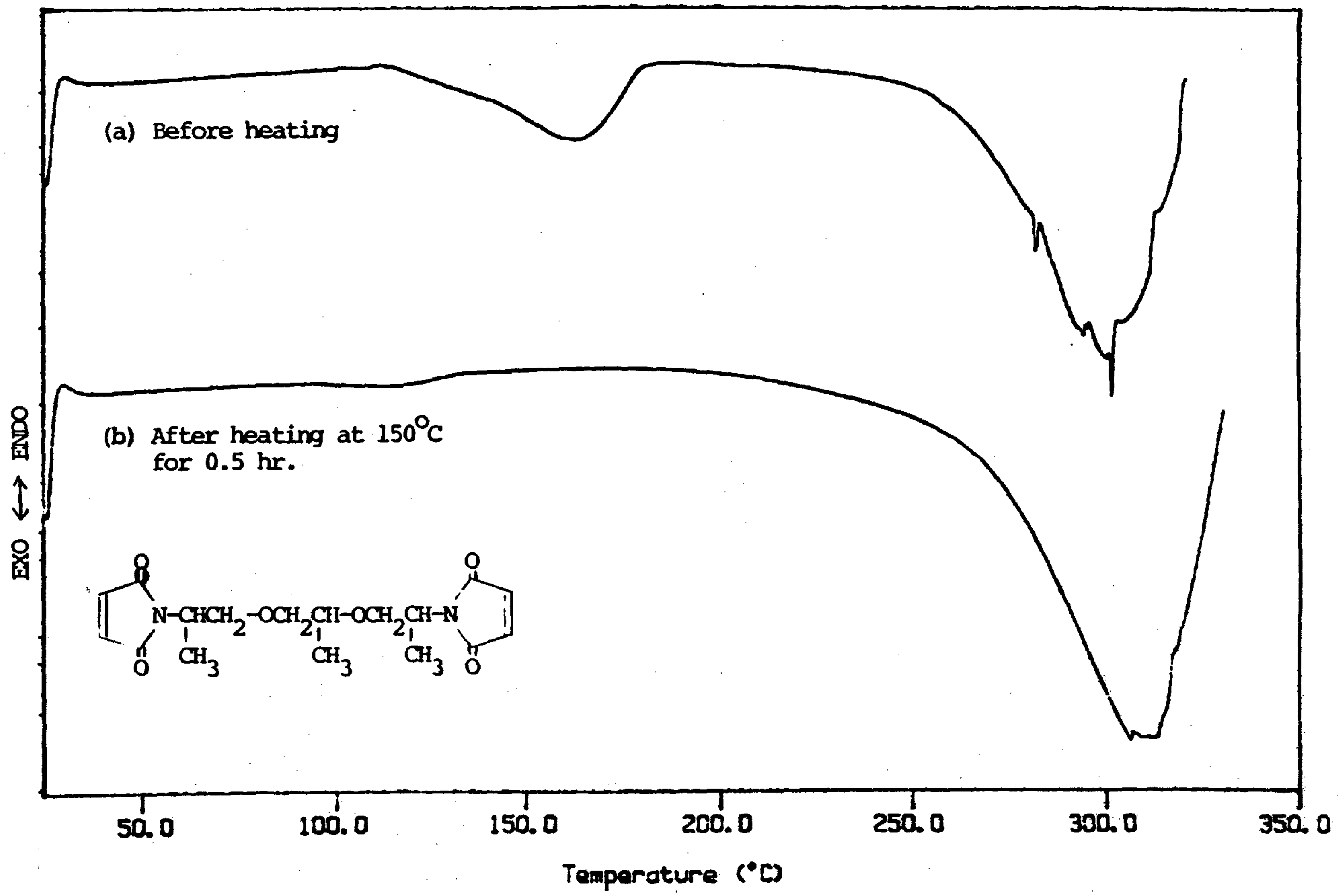
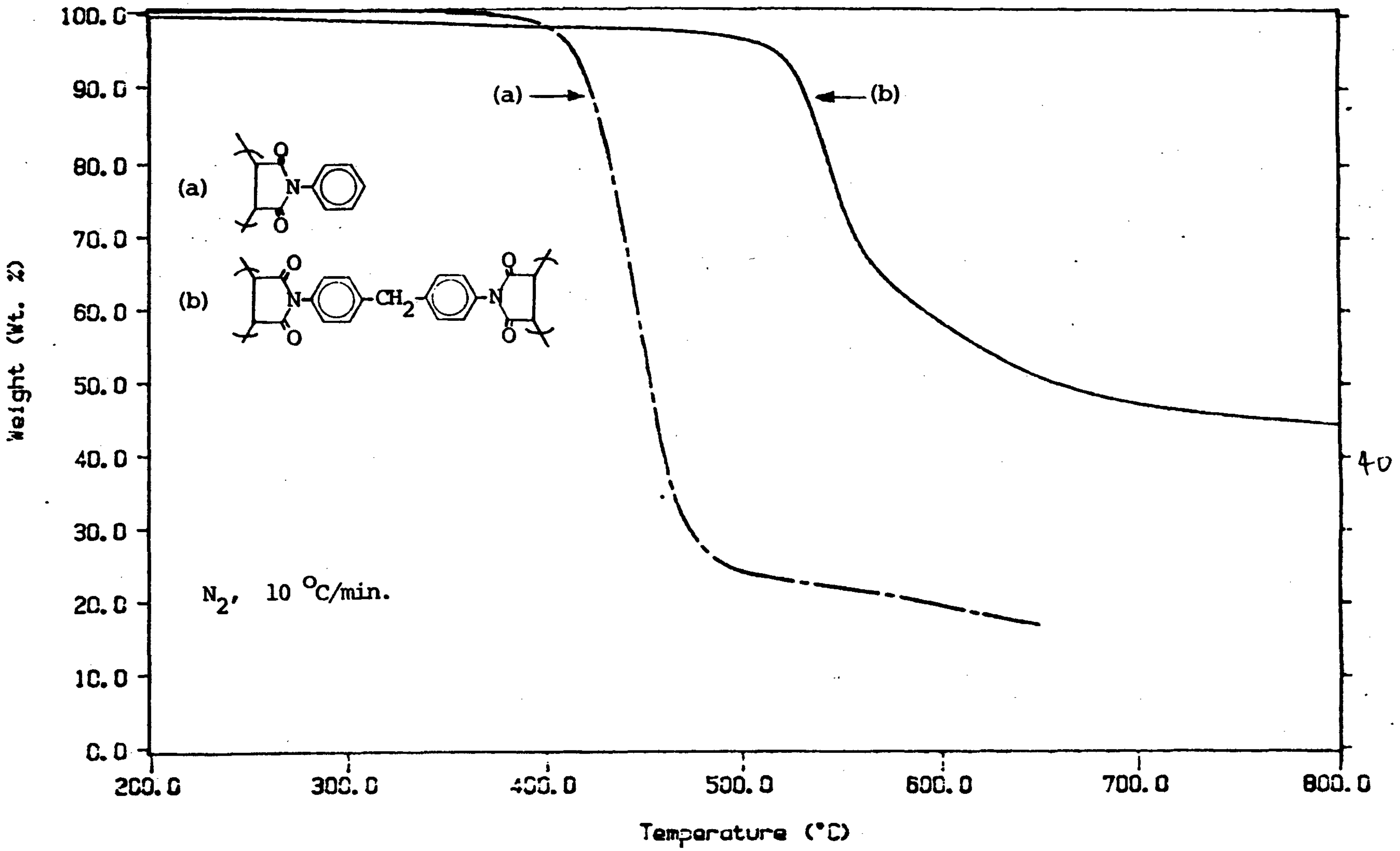


Fig. 20. DSC Curves of N,N'-(1,2-Diisopropoxyisopropane) Bismaleimide

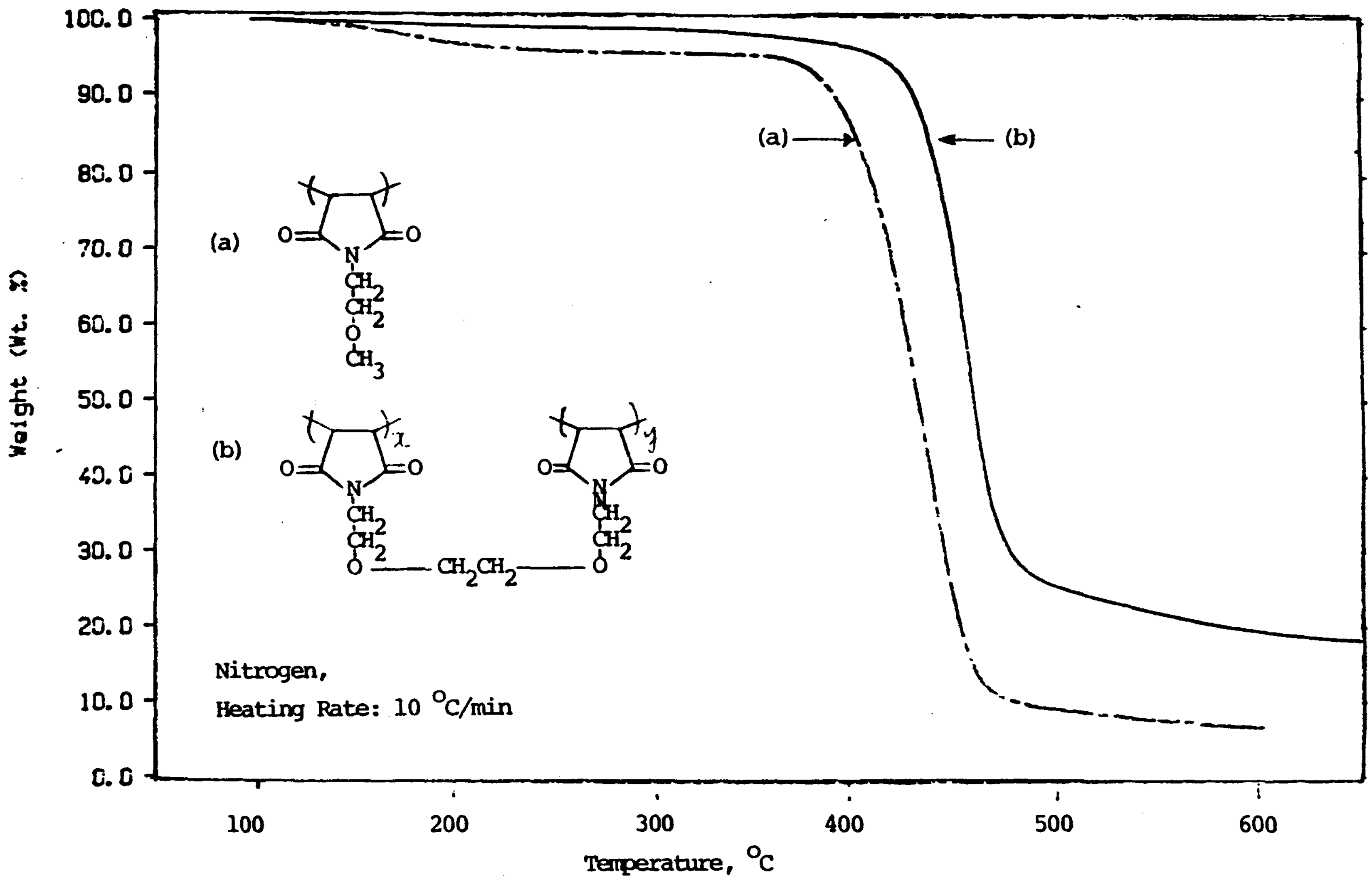
insoluble, yet nonetheless, the evidence is interesting - that thermo polymerization which at once had been thought not to be possible for maleimides, indeed appears to occur over a period of a half hour at a relatively low temperature. The linear polymer that was reported previously is low in molecular weight, however, with vapor pressure osmometry numbers less than 5000. Figs. 21 through 24 show TGA data for a series of tetra functional maleimide homopolymers in comparison with their linear analogues. For example, in Fig. 21 one observes a dramatic increase in thermal stability from slightly less than 400°C to slightly more than 500°C in the case of the thermal maleimide compared with its analogous tetra functional monomer. A similar increase is also observed for 2-methoxyethyl maleimide in comparison with its tetra functional monomer though the increase in stability is somewhat less than is observed for phenyl maleimide. This is not really a surprise since one is dealing with flexible versus rigid crosslinks between chains; however, we feel it is important that flexible links between chains be present to provide the impact resistance that one seeks in such a resin and it is clear to note that flexible spacers indeed can be useful since thermal stability here is observed up to 450°C. These runs were done in nitrogen; however, recent evidence shows that good thermal stabilty will exist for polymers under ambient exposure condition and we are collecting data on thermal analysis of polymers of this nature in air. Fig. 23 shows that thermal stability is not a function of the nature of polymerization, i.e., radical or thermal polymerization.

Fig. 24 compares the thermal stability of the requisite diamine with its tetra functional maleimide polymer. Sample B shows that the diamine has thermal stability to somewhat less than 270°C whereas its polymer shows thermal stability exceeding that value with an onset roughly of 340°C. However, the most stable polymer is apparently based on oxyethylene with thermal stability as high as 400°C, and consequently it appears as if the appropriate spacer will be polyoxyethylene, particularly for the polymers which will be phase separating due to high molecular weights of polyoxyethylene. At the moment our chemistry is best suited to place the polyoxyethylene spacer within the tetra



(a) and (b) = radical polymerization

Fig. 21. TGA Curves of Poly N-Phenyl Maleimide and Poly 1,1'-(Methylenedi-4,1-phenylene) Bismaleimide



(a) and (b) thermal polymerization

Fig. 22. TGA Curves of Poly N-(2-Methoxyethyl) Maleimide and Poly N,N'-(1,2-Diethoxyethane) Bismaleimide

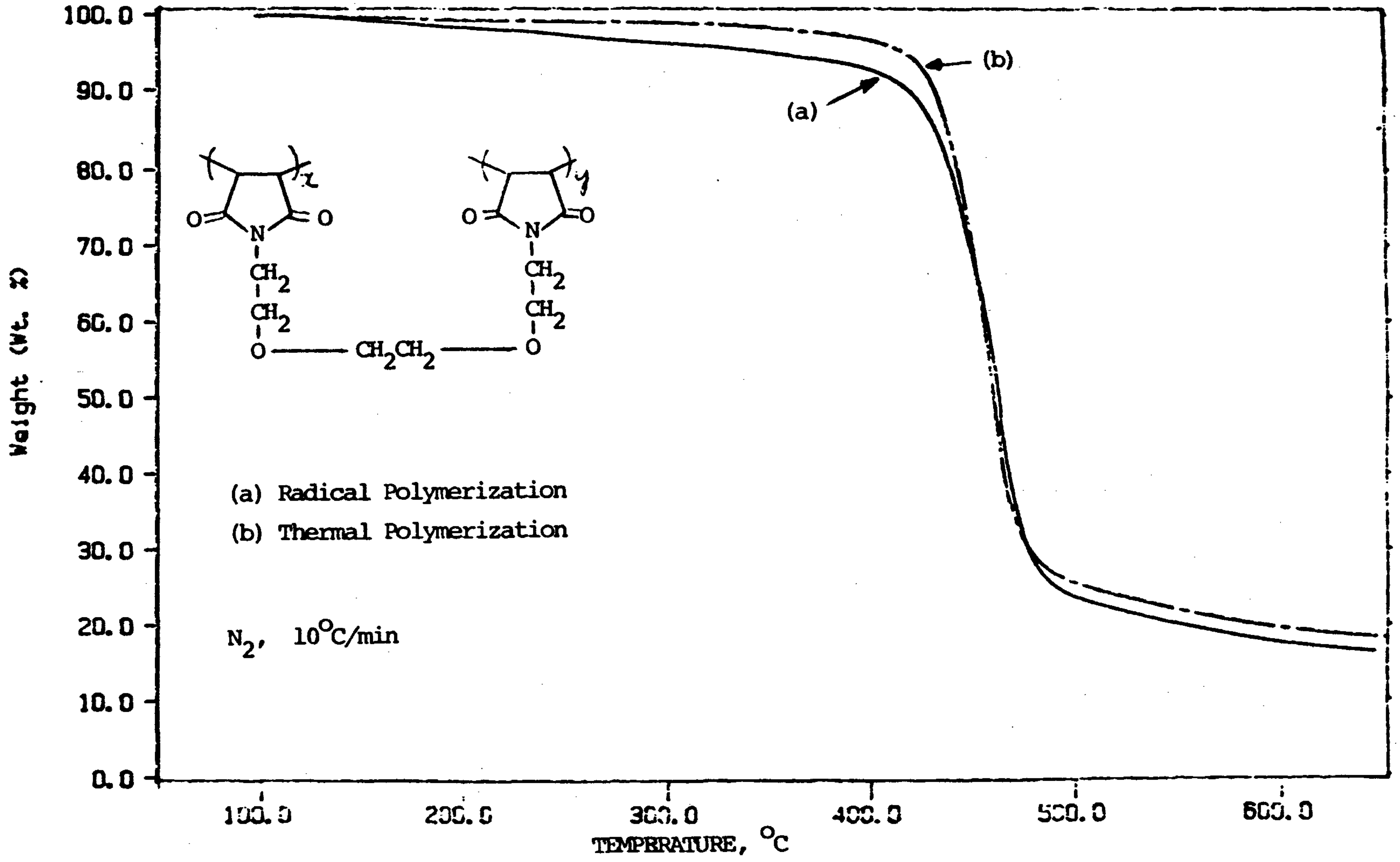
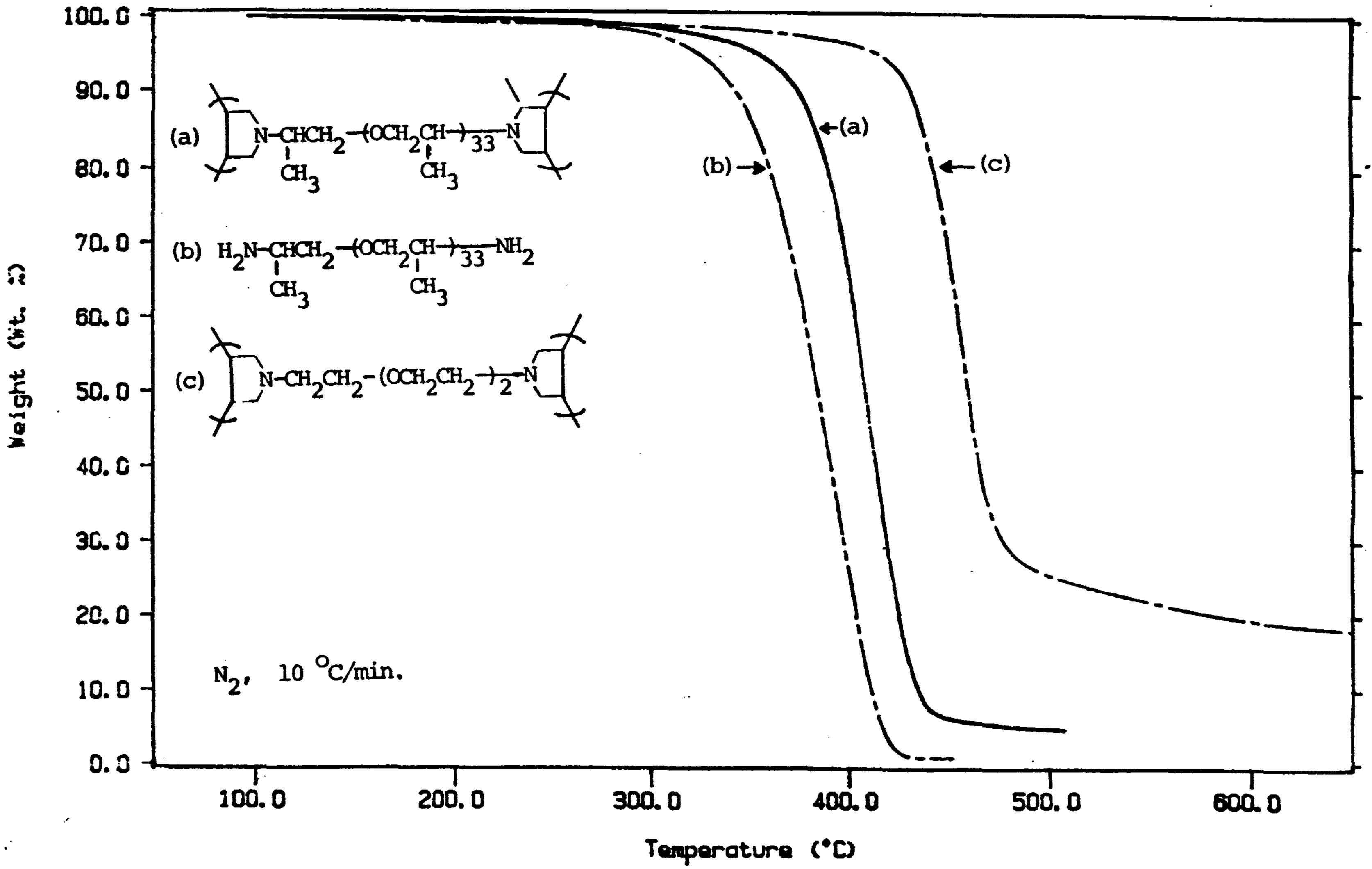


Fig. 23. TGA Curves of Poly N,N'-(1,2-Diethoxyethane) Bismaleimide



(a) and (c) = thermal polymerization

Fig. 24. TGA Curves of Poly N,N'-(1,2-Diethoxyethane) Bismaleimide, a Poly(Oxypropylene) Diamine, and a Homopolymer of a Poly(Oxypropylene) Bismaleimide

functional vinyl ether, since our synthetic approach to this compound provides an easier purification of the monomer than would be the case for tetra functional maleimide.

The remaining four types of polymerizations have been done in methylene chloride at room temperature as has been stated before. At the moment we are collecting thermal data on the polymers as they are being formed. A typical synthesis is shown in Fig. 25. Structural characterization has been done by infrared spectroscopy and in the case of linear polymers, NMR spectroscopy. These data support the structures that are shown in Figs. 26 through 32. Upon examining these figures one can arrive at the following conclusions:

1. The glass transition temperature for the copolymers is similar to that for the homopolymer of maleimides in the range of 140-150°C.
2. The glass transition temperature for the network polymers is higher than that for the homopolymers appearing in the range of 175-200°C.
3. We are having a difficult time actually measuring glass transition temperature particularly in the case where polymerizations of tetra functional maleimides with tetra functional vinyl ethers. It may be due to the high network density that exists in these polymers. In any event, we have submitted samples to Wright-Patterson AFB for further testing and DSC analysis to determine glass transition temperature.
4. The onset of weight loss data that is presented (this work was done in air) shows a high degree of stability for these polymers with values exceeding 300°C in every case, and in some cases with values approaching 500°C. We feel thermal stability will not be a problem for these polymer types and are pleased not to have to worry about this sort of property.

3. DIRECTION OF THE RESEARCH

We have virtually completed our first phase of the research, that being to find synthetic routes to necessary monomers of vinyl ethers and maleimides, and while we continue to do synthetic work of this nature, we feel confident that the procedures that

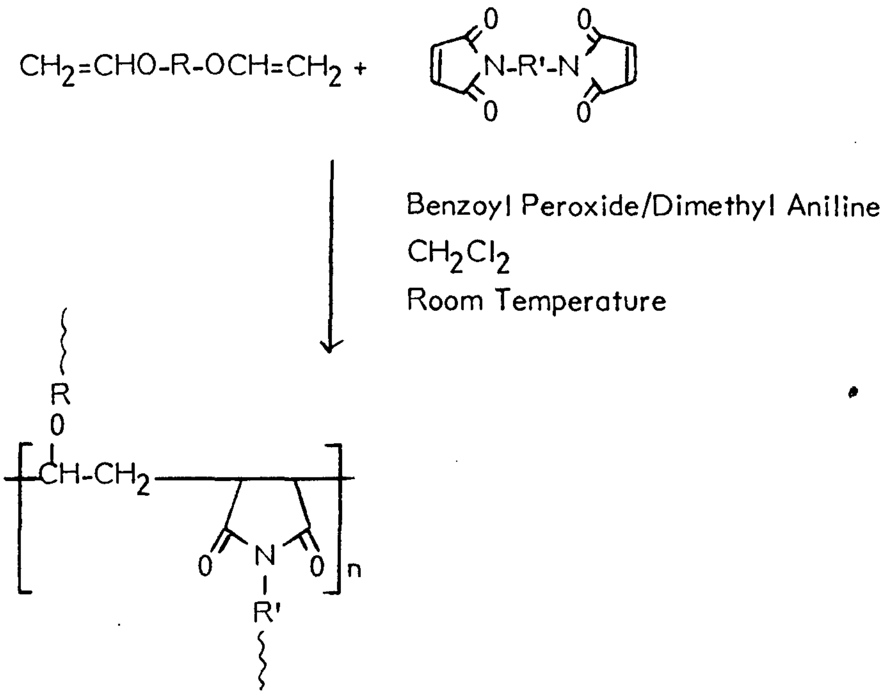
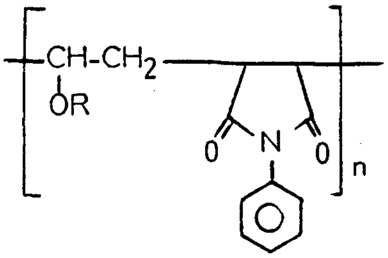


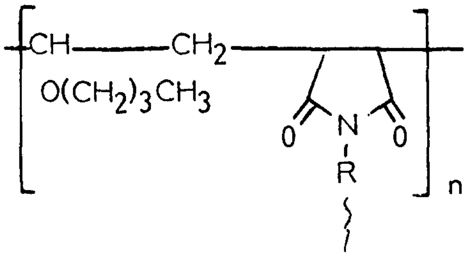
Fig. 25. Synthesis of Network Polymers



R	Tg	Onset of Weight Loss*
$CH_3(CH_2)_3-$	134°C	371°C
$CH_3(CH_2)_7-$	158°C	335°C

*In Air

Fig. 26. Thermal Data for Copolymers of Various Vinyl Ethers with N-Phenyl Maleimide



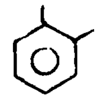
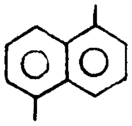
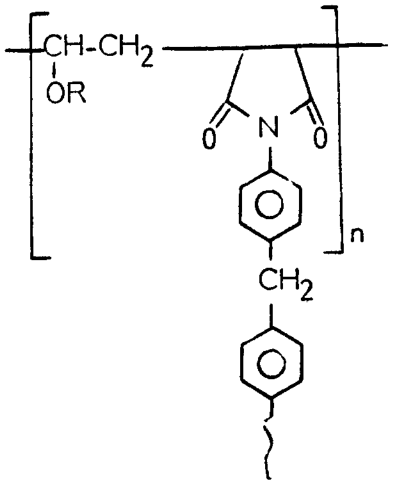
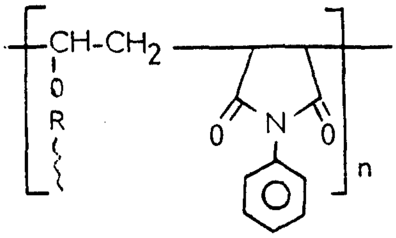
R	Tg	Onset of Weight Loss
		
		
		
$-C_2H_4OC_2H_4OC_2H_4-$		
$-(CH_2)_{12}-$	176°C	

Fig. 27. Thermal Data for Copolymers of Various Maleimides with n-Butyl Vinyl Ether



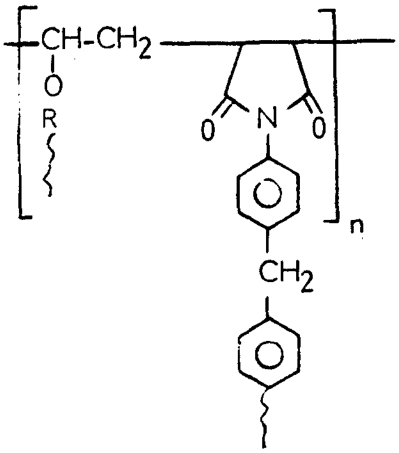
R	Tg	Onset of Weight Loss
$CH_3(CH_2)_3$—		
$CH_3(CH_2)_7$—	197°C	
$CH_3CH_2(OC_2H_4)_2$—		

Fig. 28. Thermal Data for Copolymers of Various Vinyl Ethers with 1,1'-(Methylenedi-4,1-phenylene) Bismaleimide



R	Tg	Onset of Weight Loss
$-(CH_2)_4-$		362°C
$-(CH_2)_{12}-$	213°C	342°C
$-(CH_2)_5-$		

Fig. 29. Thermal Data for Copolymers of Various Bis Vinyl Ethers with N-Phenyl Maleimide



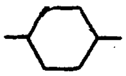
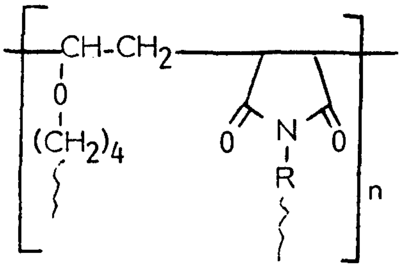
R	Tg	Onset of Weight Loss
$-C_2H_4OC_2H_4-$	168°C	384°C
$-(CH_2)_4-$	168°C	382°C
		468°C
$-(CH_2)_{12}-$		378°C
$-(CH_2)_5-$	187°C	

Fig. 30. Thermal Data for Copolymers of Various Bis Vinyl Ethers with 1,1'-(Methylenedi-4,1-phenylene) Bismaleimide



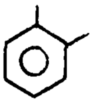
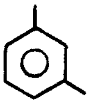
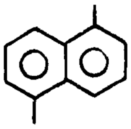
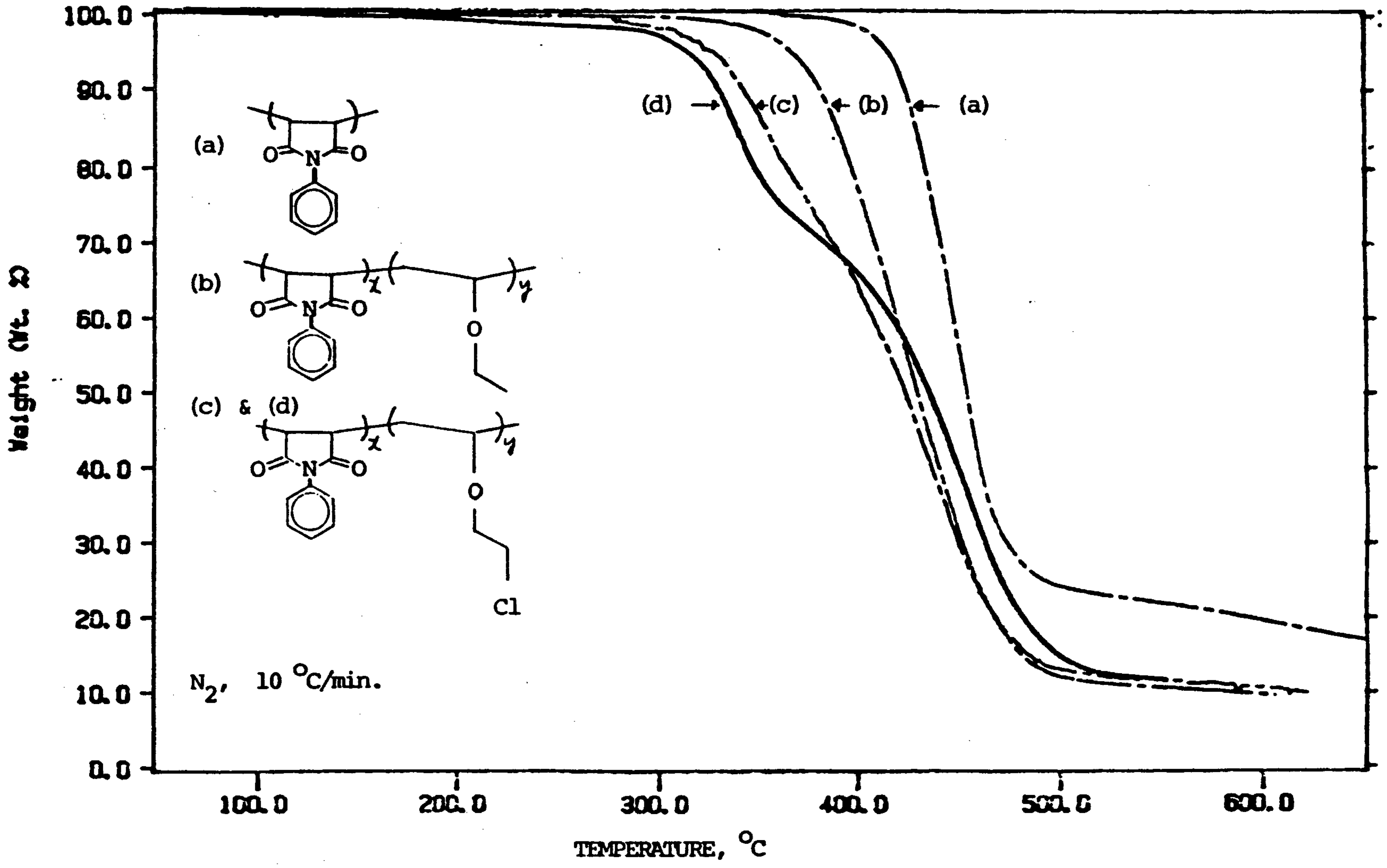
R	Tg	Onset of Weight Loss
		401°C
		374°C
		354°C
		394°C
$-C_2H_4OC_2H_4OC_2H_4-$		284°C
$-(CH_2)_{12}-$		364°C

Fig. 31. Thermal Data for Copolymers of Various Bismaleimides with 1,4-Divinyloxybutane



(c) = radical polym., 60°C, 24 hr., CH_2Cl_2

(d) = radical polym., 60°C, 24 hr., no solvent, excess CEVE.

Fig. 32. TGA Curves of Poly N-Phenyl Maleimide, N-Phenyl Maleimide Ethyl Vinyl Ether Copolymer, and N-Phenyl Maleimide 2-Chloroethyl Vinyl Ether Copolymer

are in hand will provide us with necessary starting materials. We are completing our thermal work on the polymers described previously, filling in the gaps that are present in the tables shown in the last few figures. Though we don't have all the data in hand, we feel comfortable in saying that thermal stability is present for these polymers and that perhaps the glass transition temperature for the polymers themselves is sufficiently high to make them structurally useful. If indeed a value of 120°C can be representative of the network polymer, then the requirement that these polymers have structural stability at temperature of 350°F is being met. We will continue thermal investigation of these polymers by DSC and TGA techniques, principally with the intent of improving methodology to detect the glass transition temperature for these polymers. We will also be collecting isothermal data on stability of these polymers via collaboration with Bruce Reinhardt at the AF Laboratory.

Within a month we will have a solids probe installed in our 200 MHz NMR instrument and then hopefully will be able to collect NMR data regarding the structure of these network polymers. Data of this type have never been generated before, and we feel it would be very useful in assigning structure to these polymers and perhaps then we will be able to more carefully determine structure property relationships.

New investigations will begin on the effect of the nature of the catalyst. For now, we have stayed with the amine peroxide catalyst pair since it is a well-known system and since it did produce polymerization results at room temperature that were sufficiently interesting. However, we want to study the effect of changing the nature of the amine, perhaps changing the nature of the peroxide and indeed looking at other catalyst systems in greater detail to see if we can optimize the initiator system.

Ultimately we want to work only in bulk polymer systems with an optimized catalyst such that we can provide samples of resins to our Materials Science Department for mechanical performance testing. We feel this goal can be achieved before the end of 1987.

REFERENCES

1. "High Performance, Low-Energy-Curing Resins". Report of the Committee on Room-Temperature-Curing Resins Systems. Publication NMAB-412. National Academy Press. Washington, DC (1984).
2. Ham, G. High Polymers, Vol. XVIII, Copolymerization, pp. 788-9, Intersicence Publishers, New York (1984).
3. Crivello, J. V.; Rice, S. T. U.K. Patent Application, GB21433540A (1985).
4. Galluci, R. R.; Going, R. C. J. Org. Chem. 48, 342 (1983).
5. Watanabe, W. H.; Conlon, L. E. J. Am. Chem. Soc. 79, 2828 (1957).
6. McKeon, J. E.; Fitton, P.; Griswold, A. A. Tetrahedron 28, 227 (1972); McKeon, J. E.; Fitton, P. Tetrahedron 28, 233 (1972).
7. Barrales-Rienda, J. M.; Ramos, J. G.; Chaves, M. S. J. Fluorine Chem. 9, 293 (1977); Kraiman, E. A. Macromolecular Synthesis, Collective Vol. 1, p. 203.

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