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

Evolution of the 2-Tg Concept to Produce High Tg Polymers at Ambient Temperatures

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with
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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. The research described herein 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.

Meeting our first objective required the synthesis of the necessary donor and acceptor monomers, and consequently we examined a variety of synthetic approaches to create these compounds. In the case of donor monomers, we selected a palladium-assisted vinyl exchange reaction as the best route. Using this chemistry we successfully prepared 15 monomers based on vinyl ether chemistry.

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We also synthesized an equal number of maleimides using conventional synthetic chemistry, that being reaction of maleic anhydride with the requisite amine, followed by condensation of the maleimic acid to the maleimide itself. This chemistry required a great deal of patience, yet when done properly, led to the necessary monomers in high purity.

Our first polymerization studies were done in solvents in order to prepare a series of "benchmark" polymers for thermal analysis work. We 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 indicated they possessed the thermal stability necessary for performance in their required application.

The research turned toward bulk polymerization using room temperature initiator systems based on benzoyl peroxide and N,N-disubstituted aniline. Bulk polymerizations were conducted with a combination of donor and acceptor monomers, giving both linear and bulk polymers. It became apparent that these bulk polymerizations, though proceeding at a reasonable rate at room temperature, did not proceed to complete conversion due to vitrification (vitrification is a phenomenon which interferes with complete conversion when operating under bulk polymerization conditions). However, research within a series of linear polymerizations demonstrated that parameters could be adjusted to increase conversions to desirable levels.

During the course of this research a new concept, termed the 2-Tg concept, evolved to synthesize high Tg polymers at room temperature. In the 2-Tg approach, a low Tg component is coreacted with monomers designed to form a high Tg network, wherein the low Tg component acts as the "solvent" during the polymerization itself. At some point the low Tg component phase separates and becomes "property inert" with respect to the high Tg performance. "Solvents" chosen were comonomers possessing polyoxyethylene or polydimethylsiloxane.

The 2-Tg approach has merit, and high Tg materials were prepared at or near room temperature using this chemistry. We strongly urge that the 2-Tg concept be further advanced to yield materials of practical value.

FOREWORD

This report covers research performed by the University of Florida, Gainesville, 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 July 1988. The report was submitted in November 1988.

The research was performed in the Department of Chemistry by Dr. Choon H. Do, Mr. Mike Johnson, and Dr. Mark A. Smith under the direction of Dr. Kenneth B. Wagener, the principal investigator. Dr. George Butler, an expert in the field of donor acceptor polymerization chemistry, served as a consultant during the course of this research.

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.

The synthesis of high Tg polymers at room temperature historically has been regarded as a difficult problem to solve, in that the glass transition temperature is largely a function of the cure temperature when the synthesis is approached in a conventional manner (Figure 1). The work of Gillham[2] shows that while the glass transition temperature of a variety of polymers can be higher than the cure temperature, it is not sufficiently high to be useful under conventional curing approaches. A second problem is manifested in terms of vitrification,[3] as illustrated in Figure 2. Vitrification describes a phenomenon in which the immobility of functional groups in the solid state prevents further reaction in a polymerization system. Thus, when polymerizations are attempted in the bulk state, which is a goal of this research, vitrification leads to a cessation of polymerization. Consequently, in the course of this research we have developed a concept, which is called the 2-Tg concept, to overcome both of these problems, i.e., to achieve glass transition temperatures above those of ambient cure temperature, and to avoid the negative effects of vitrification.

It has been the goal of this research to use this concept to synthesize such polymers by employing donor acceptor polymerization chemistry to create - at or near ambient temperatures - matrix resins that exhibit many, if not all, of the desirable mechanical properties mentioned above.

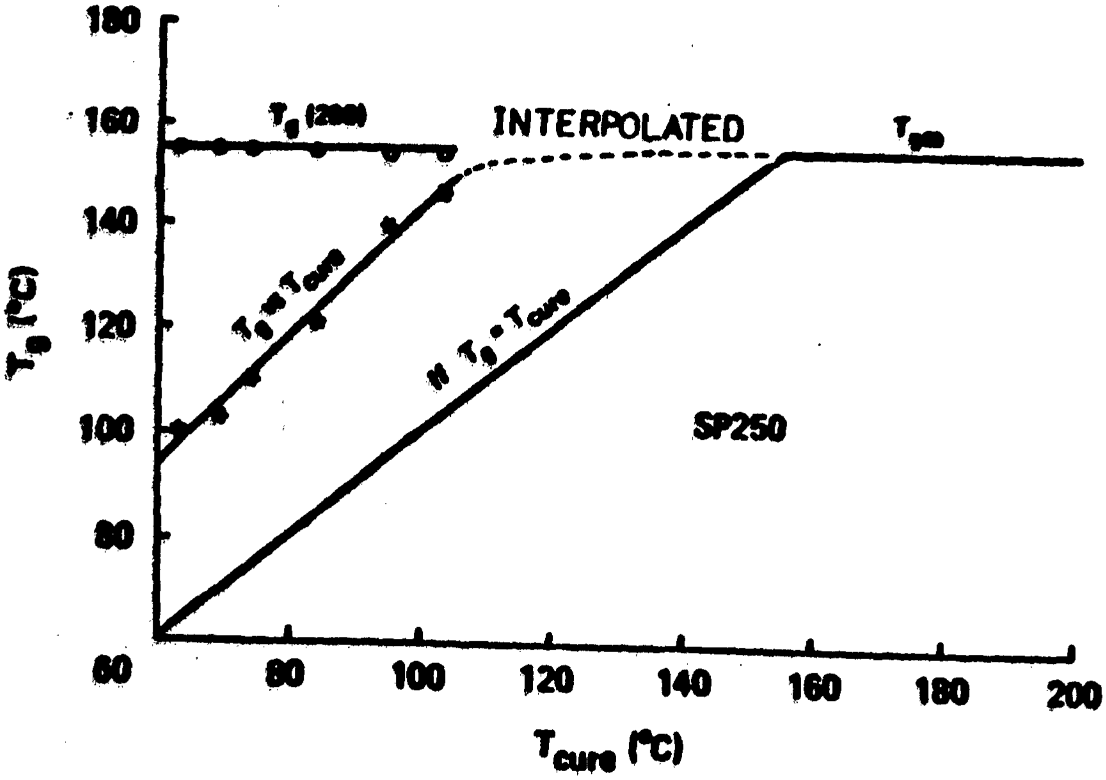


Figure 1. T_g Versus T_{cure}

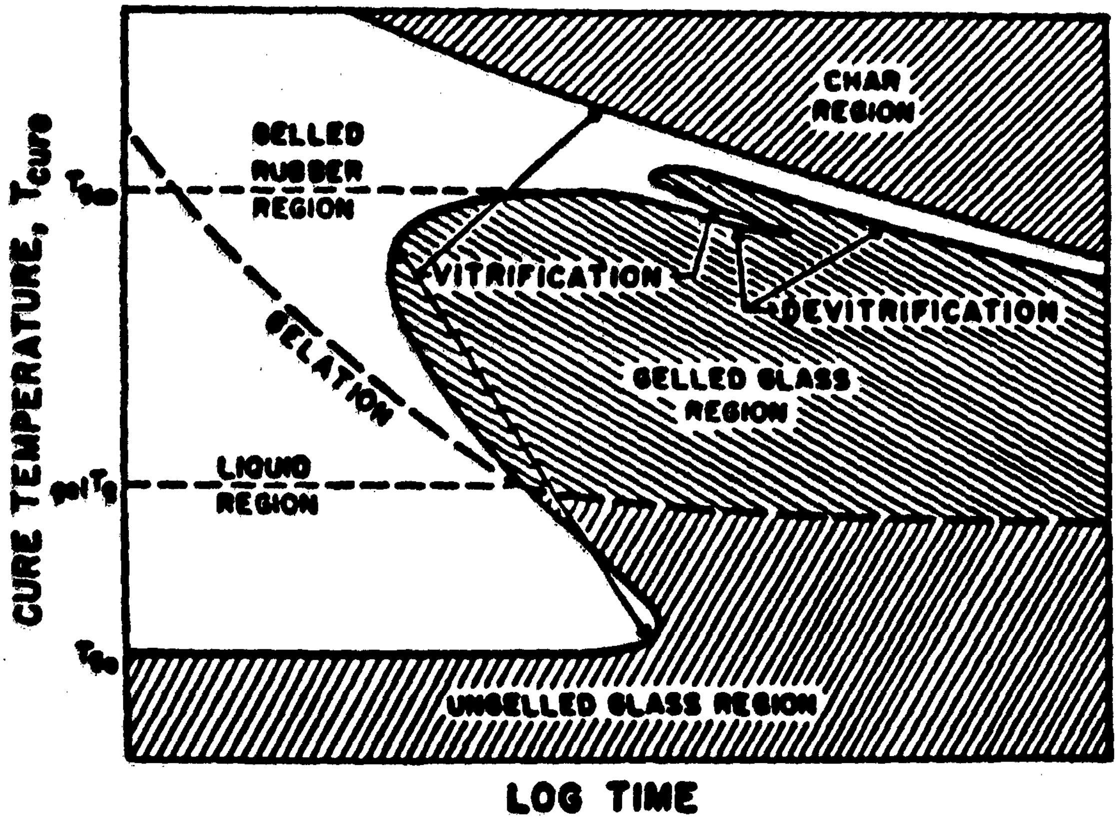


Figure 2. Isothermal Time-Temperature-Transformation Diagram of a Thermosetting Polymer

Donor acceptor polymerization is one type of chain propagation, addition type polymerization of vinyl groups initiated by radicals. Figure 3 exemplifies donor acceptor polymerization. Two monomers are required, one possessing an electron donor group ("D" in Figure 3) and the other possessing an electron acceptor group, "A". As is shown in Figure 3, each monomer often is slow to polymerize by itself at room temperature, yet copolymerization is rapid yielding essentially alternating copolymers.[4-16]

This chemistry can be used to synthesize matrix copolymers by using di- and tetrafunctional donors and di- or tetrafunctional acceptors such that copolymerization will lead to matrix copolymer systems. Several vinyl ether based donor di- and tetrafunctional comonomers have been investigated, in combination with a variety of maleimide based, acceptor di- and tetrafunctional comonomers. In each case a two part radical initiator system was used, one part dissolved in the donor and the other part in the acceptor, such that copolymerization (curing) did not occur prior to combination of the comonomers.

Conventional cure chemistry is done at above-ambient temperatures to complete the chemical reaction needed to create thermoset resins. High temperature 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. However, high temperature curing is not a goal of this research.

The problem at hand, then, was to identify reaction chemistry that proceeds to completion at or near 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. A successful result would mean that high temperature curing would no longer be required.

It has been 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 crosslink reduces the mobility of the network as a

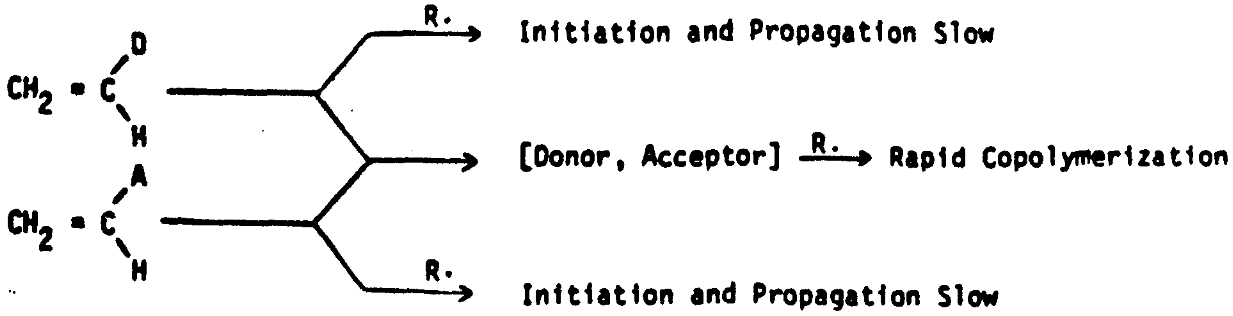


Figure 3. The Donor Acceptor Polymerization Concept

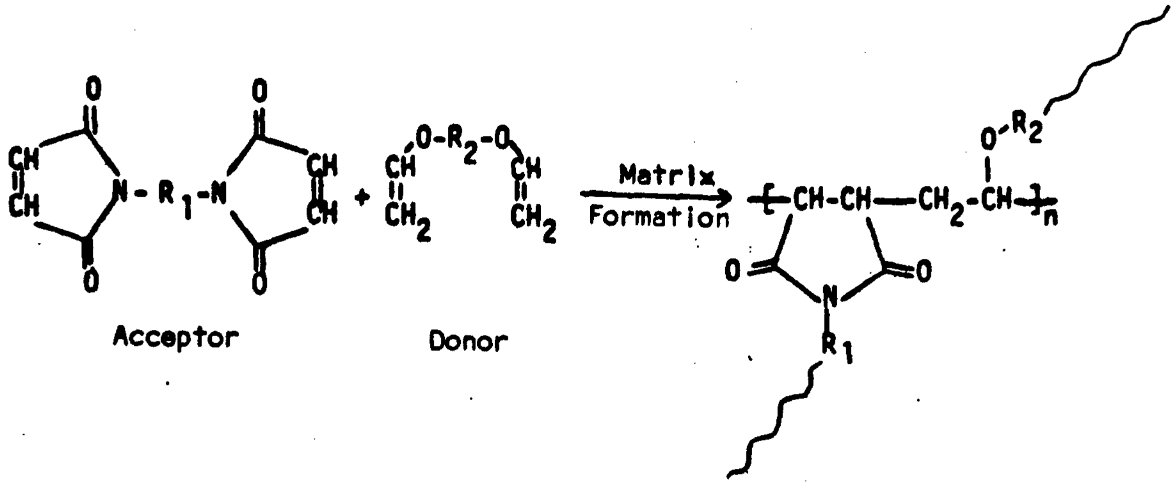


Figure 4. An Example of Donor Acceptor Polymerization to Yield High Crosslink Density Matrix Polymers

whole, thus leading to high glass transition temperatures.[1,17] It has also been necessary to create multiphase matrix polymers wherein one phase permits the other to achieve a maximum degree of relaxation during polymerization. This is the essence of the 2-Tg concept, described in the body of this report, and represents a form of self annealing chain polymerization. The multiphase matrix resins that result also should reduce the brittleness often associated with high crosslink density.

In fact, donor acceptor polymerization at ambient temperatures described in this report has yielded matrix polymers possessing a high density of crosslinks. By choosing di- or tetrafunctional donor and acceptor monomers exemplified in Figure 4, it has been possible to achieve the high crosslink density required in relatively short reaction times, wherein the actual mechanical performance of these polymers depends upon the nature of R_1 and R_2 in the comonomers. 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 chemistry. 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 after self annealing (the 2-Tg concept).

2. MONOMER SYNTHESIS

__Di- and Tetrafunctional Vinyl Ethers__. Due to the lack of availability of monomers of this nature, it was necessary to devise synthetic routes to both low molecular weight versions of di- and tetrafunctional ethers and high molecular weight versions of the same. Additionally, we synthesized tetrafunctional versions of polydimethylsiloxane to be used in the 2-Tg approach to high Tg materials.

The synthesis of di- and tetrafunctional vinyl ethers proved to be difficult, and it was necessary to explore a number of synthetic routes to create monomers of interest to us. Specifically, we examined Williamson ether synthesis chemistry,[18] phase transfer synthesis chemistry,[19] mercuric acetate catalyzed vinyl transetherification,[20] and palladium II catalyzed vinyl transetherification reactions.[21] Of these many approaches, the palladium catalyzed route appeared to be the most effective and indeed gives high purity di- and tetrafunctional polyethers and polysiloxanes. This latter result is significant since it provided a low energy route for the synthesis of divinyl ethers in high purity.

Figure 5 shows the synthetic route chosen for investigation in a typical Williamson ether synthesis. This is a reported procedure[18] 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 Sn2 chemistry occurs at the primary alkyl halide carbon, thereby creating the tetrafunctional vinyl ether. We found this to be an unacceptable procedure to prepare di- and tetrafunctional vinyl ethers, mainly for experimental reasons. The reactions are slow, incomplete, and solubility is difficult to predict, and since the reactions themselves are not complete, the result is a mixture of di- and tetrafunctional monomers in the instances where tetrafunctional monomers are sought.

Our attention was turned 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 Figure 6. 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

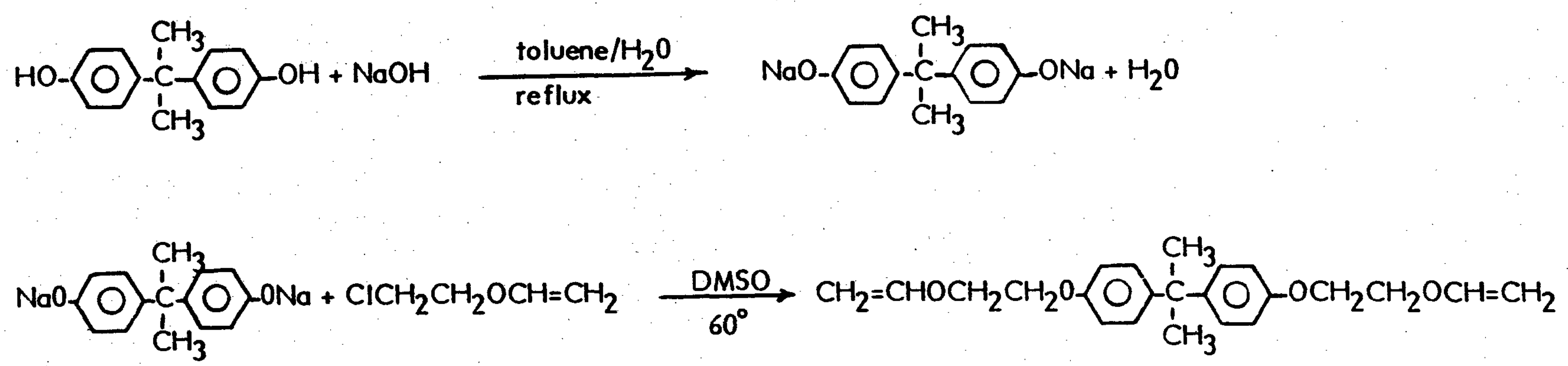
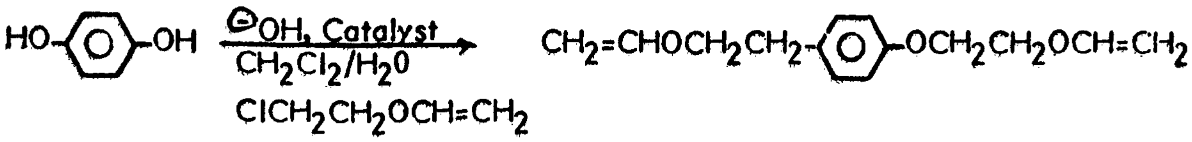


Figure 5. Williamson Ether Synthesis



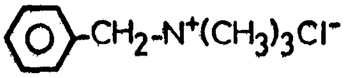
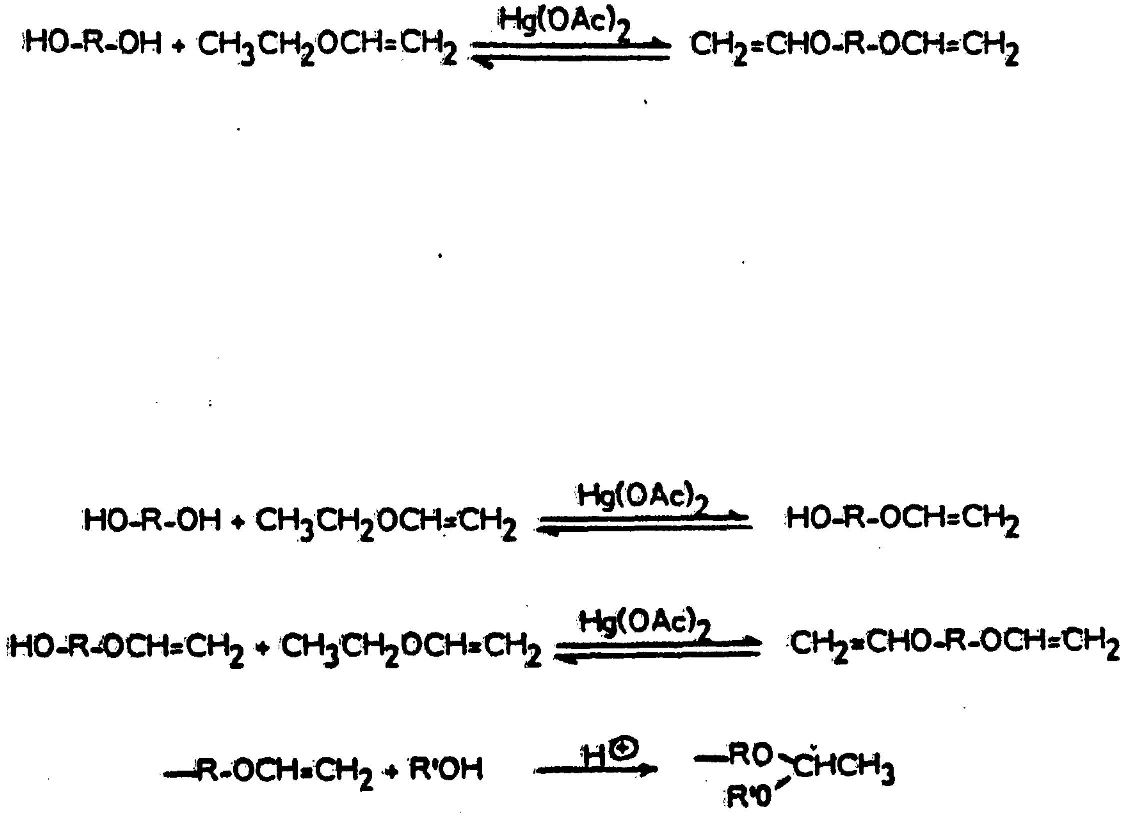
	Catalyst	Base
A.		NaOH
B.	15-Crown-5	NaOH
C.	18-Crown-6	KOH

Figure 6. Phase Transfer Catalysis

catalyst itself. This phenomenon is quite interesting, since phase transfer catalysis cationic polymerization has not been reported previously. We did not investigate phase transfer catalyst further, but a publication[19] that recently came to our attention reports that tetrafunctional vinyl ethers of bis phenols can be produced under certain conditions using phase transfer catalysts.

Mercuric acetate catalyzed transetherification chemistry[20] was investigated as shown in Figure 7. This reaction is done with excess ethyl vinyl ether being present at a reflux temperature less than 40°C. Only a catalytic amount of mercuric acetate is required. An equilibrium is established such that both di- and tetrafunctional vinyl ethers are formed again in instances where tetrafunctional monomers are desired. The mechanism for such a reaction is shown in Figure 8. Note that a byproduct, ethanol, is created in this reaction, and in order for the reaction to be driven to completion, it becomes necessary to remove ethanol as it is being formed. This proves to be difficult since the boiling point of ethanol is higher than ethyl vinyl ether. Consequently, in an attempt to distill ethanol, ethyl vinyl ether is removed instead, and equilibrium is 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, and this problem leads to only about 90 percent completion of the exchange. Thus, one is left with 10 percent 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) or polydimethylsiloxane is used, however, separation of the product from the difunctional vinyl ether may not be possible. To avoid this problem, an adsorption or trapping of ethanol as it was being formed was attempted with a drying agent or molecular sieves. This approach proved to be completely unsuccessful in investigating the usual drying agents such as Dryrite^{TM}, etc. The use of molecular sieves also proved unsuccessful though it did



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

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

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

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

Figure 7. Mercuric Acetate Catalyzed Vinyl Transetherification

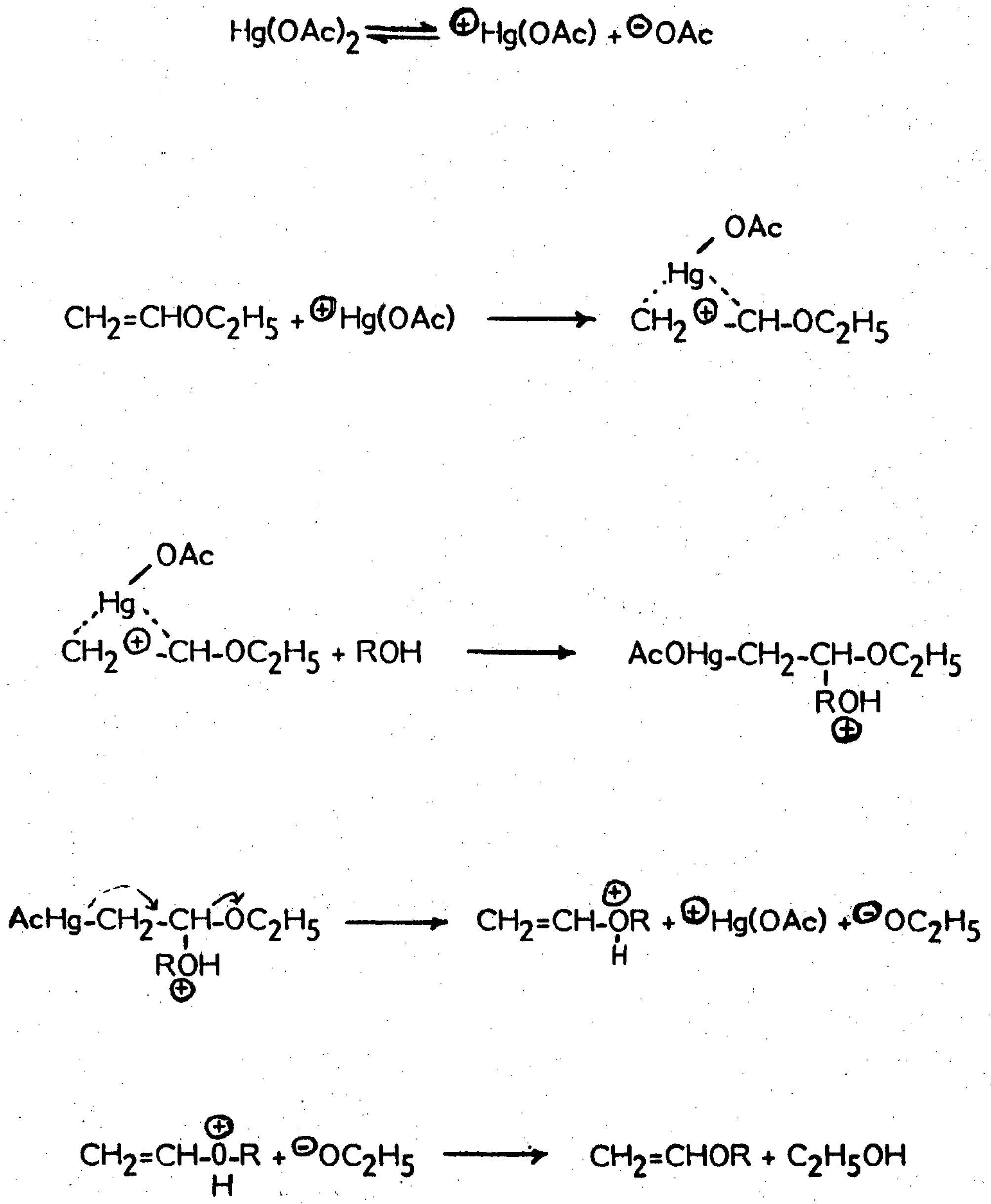


Figure 8. Mechanism of Mercuric Acetate Catalyzed Vinyl Transetherification

appear as if the equilibrium was shifted slightly to the right, perhaps yielding 95 percent conversion.

Palladium II catalyzed vinyl transetherification[21] is by far the best route to the preparation of the desired monomers. Figure 9 shows the reaction and mechanism responsible for conversion to di- and tetrafunctional 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 Figure 10, which displays NMR spectra of the tetrafunctional vinyl 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.

The palladium catalyzed transetherification reaction is also used to synthesize tetrafunctional vinyl ethers of polydimethylsiloxanes, as shown in Figure 11. The exchange reaction proceeds smoothly and provides a new tetrafunctional monomer for copolymerization in general, and for application in the 2-Tg concept in particular. As is observed in the case of the PEG polyethers, conversions are essentially quantitative.

Figure 12 shows the vinyl ethers that have been synthesized by various techniques. It is clear that the procedure is general, high yielding, and has been an important step in the achievement of the goals set forth in this project.

Di- and Tetrafunctional Maleimides. The preparation of di- and tetrafunctional maleimides proved to be rather facile, once reaction conditions were established to maintain the small percentage of side reactions that often accompany maleamic anhydride chemistry. Figure 13 shows the reaction sequence that was chosen in the preparation of a typical maleimide compound.[22,23] In the first step, nucleophilic ring opening of the anhydride link is accomplished at temperatures less than 20 °C in either

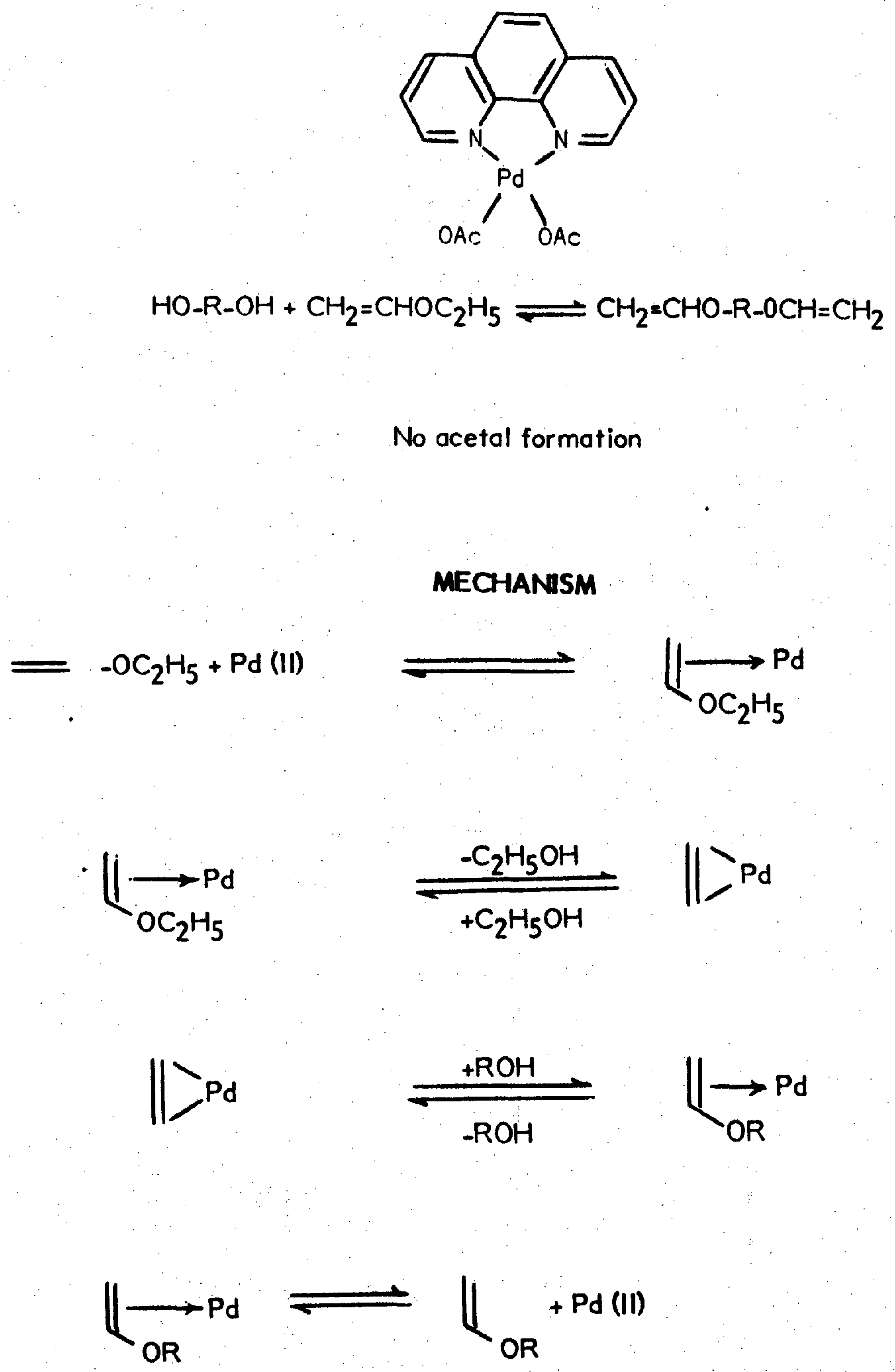
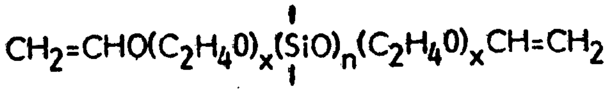


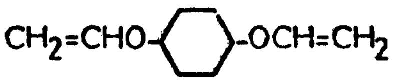
Figure 9. Palladium (II) Catalyzed Vinyl Transetherification



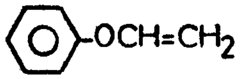
$CH_2{=}CHO(C_2H_4O)_x(SiO)_n(C_2H_4O)_xCH{=}CH_2$

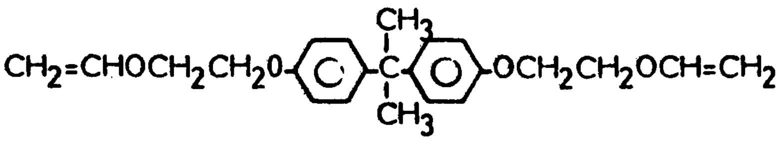
$CH_2{=}CHO\text{-}(CH_2)_n\text{-}OCH{=}CH_2$

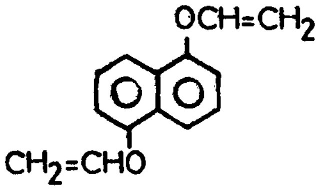
$n = 5, 7, 12$



$CH_3CH_2OCH_2CH_2OCH_2CH_2OCH{=}CH_2$







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

$n = 13, 22, 44$

Figure 12. Vinyl Ether Synthesis

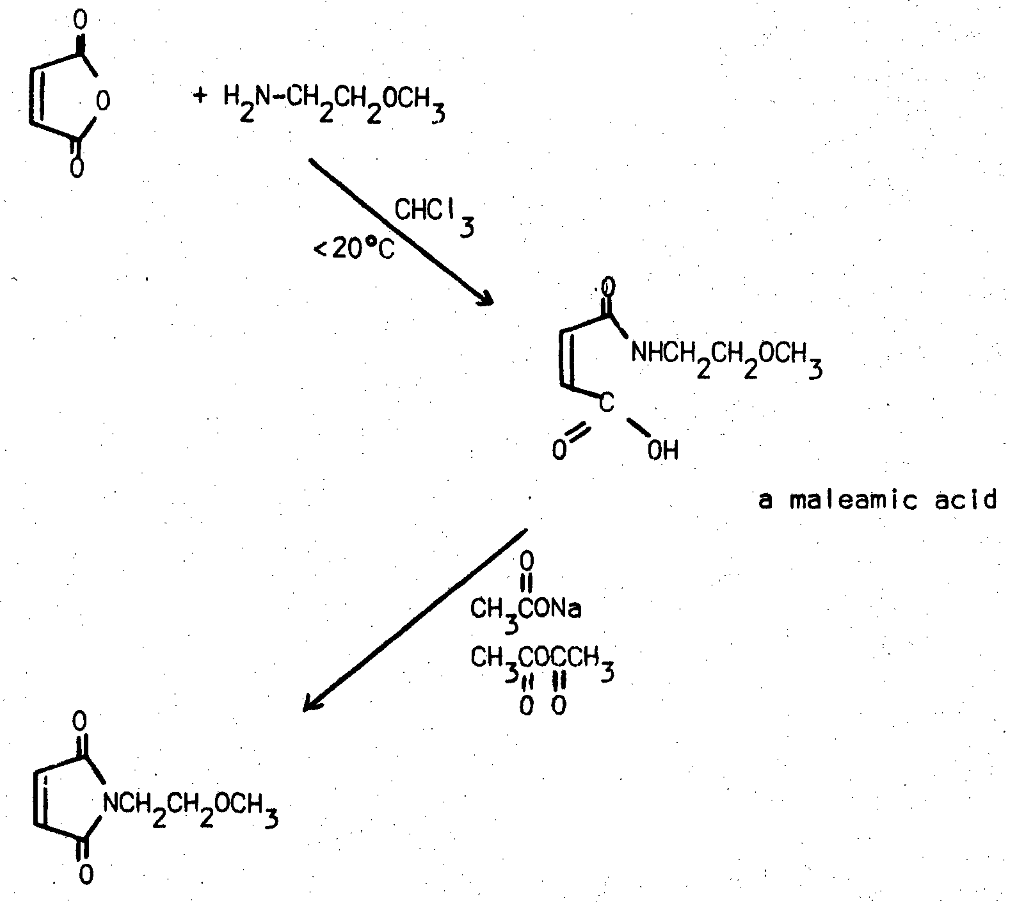


Figure 13. Maleimide Synthesis

methylene chloride or chloroform to generate a maleamide acid. The maleamic acid is purified at this point, followed by ring closure to the maleimide using the dehydrating system, sodium acetate and acetic anhydride. The 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 requires a great deal of patience in preparing the necessary maleimides since side polymerizations can be induced at high temperatures. Figure 14 shows the di- and tetrafunctional maleimides that have been prepared using this procedure. Figures 15 through 18 give the high field proton and carbon NMR spectra of two amic acids and maleimide compounds, providing sound evidence for the high purity of the monomers being formed.

3. THE HOMOPOLYMERIZATION OF DI- AND TETRAFUNCTIONAL MALEIMIDES

Homopolymers of maleimides are not new, and in fact, represent a class of polymers that offer utility in the electronics industry, which are known as bismaleimides (tetrafunctional monomers in the context of this report).[24] These polymers often are used as insulating materials in circuit board construction. Preparation, however, requires high temperature chemistry wherein radicals are used to initiate the polymerization to form the structurally useful network polymers. Similar homopolymers were synthesized in the course of this research in order to provide benchmark data for thermal properties, specifically in the case of achievable glass transition temperatures. Polymerizations were done either at 60°C using AIBN as the initiator, or at 250°C with no initiator present. In the latter case, no solvent was present as well. The polymers exhibit a light pink color after the polymerization, with the color possibly being due to slight oxidation. Polymers were soluble in typical solvents in the case of difunctional maleimide

Bismaleimide

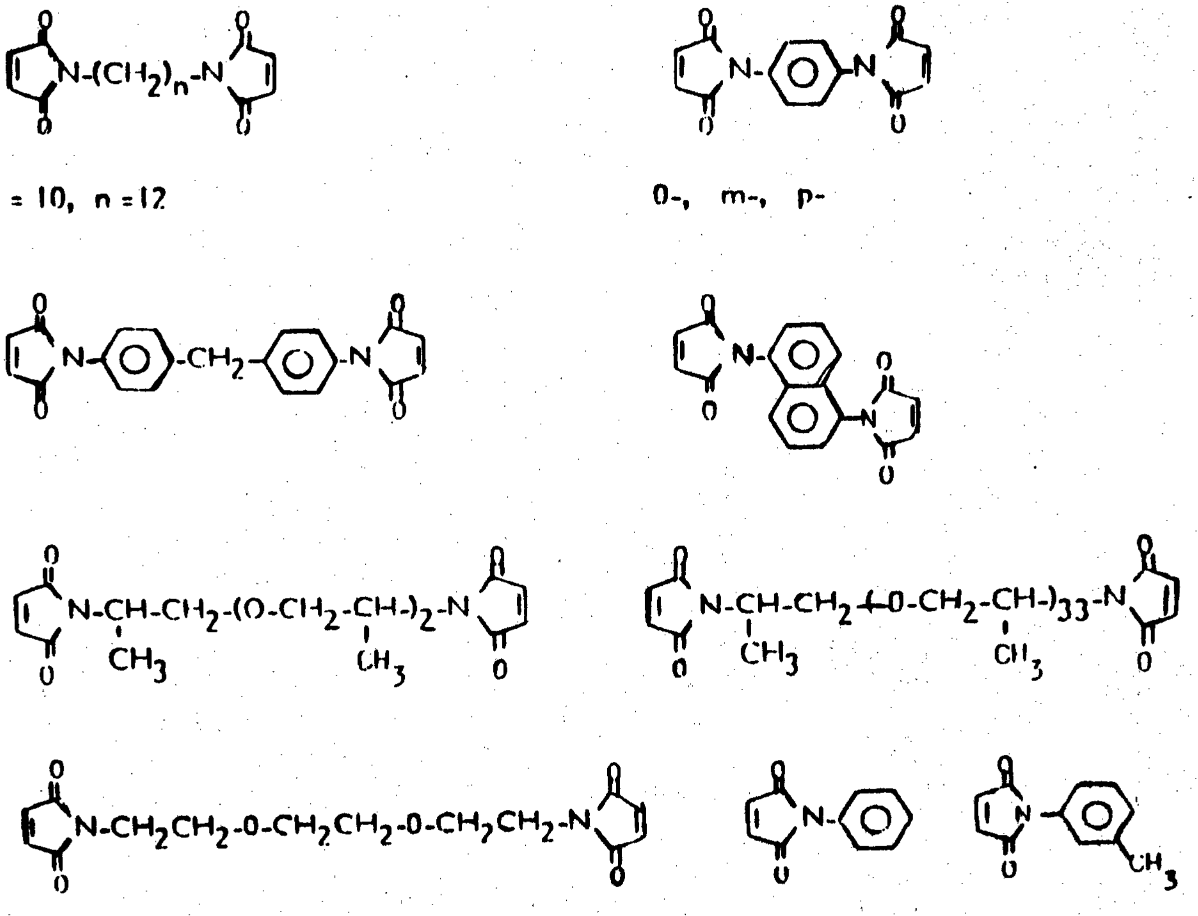
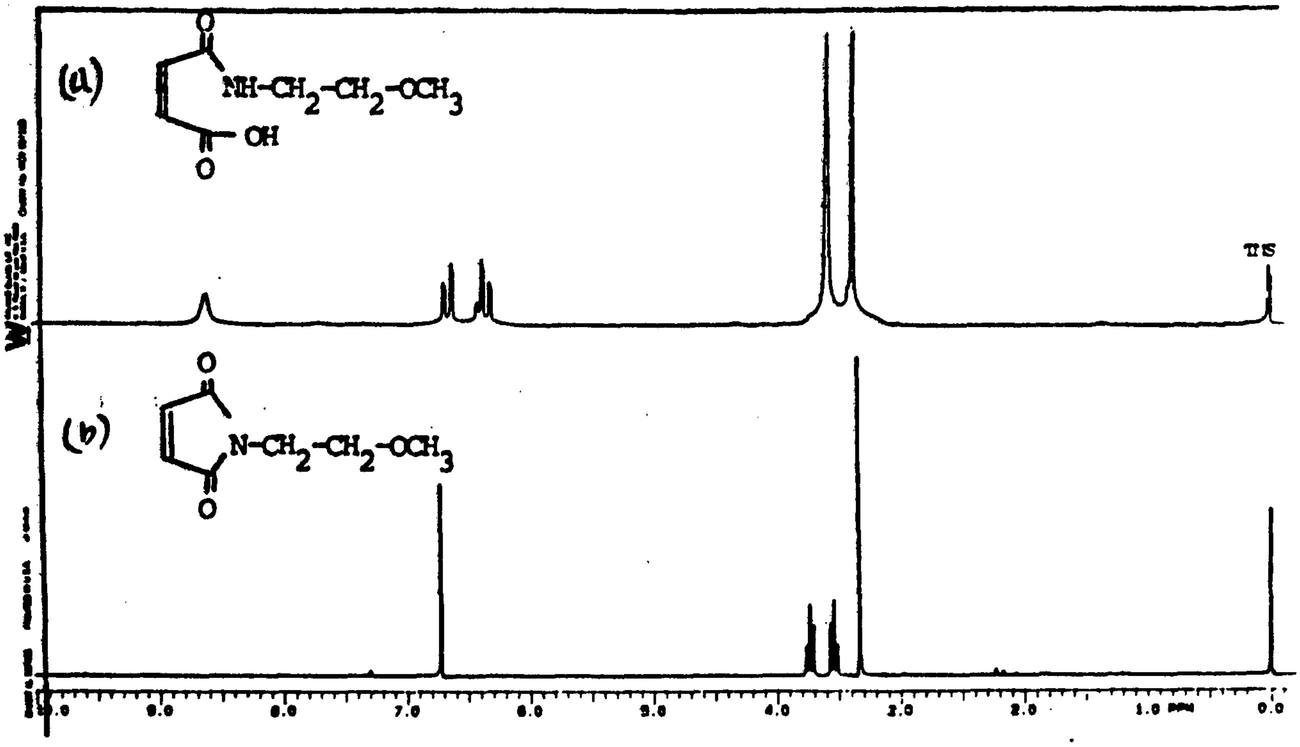
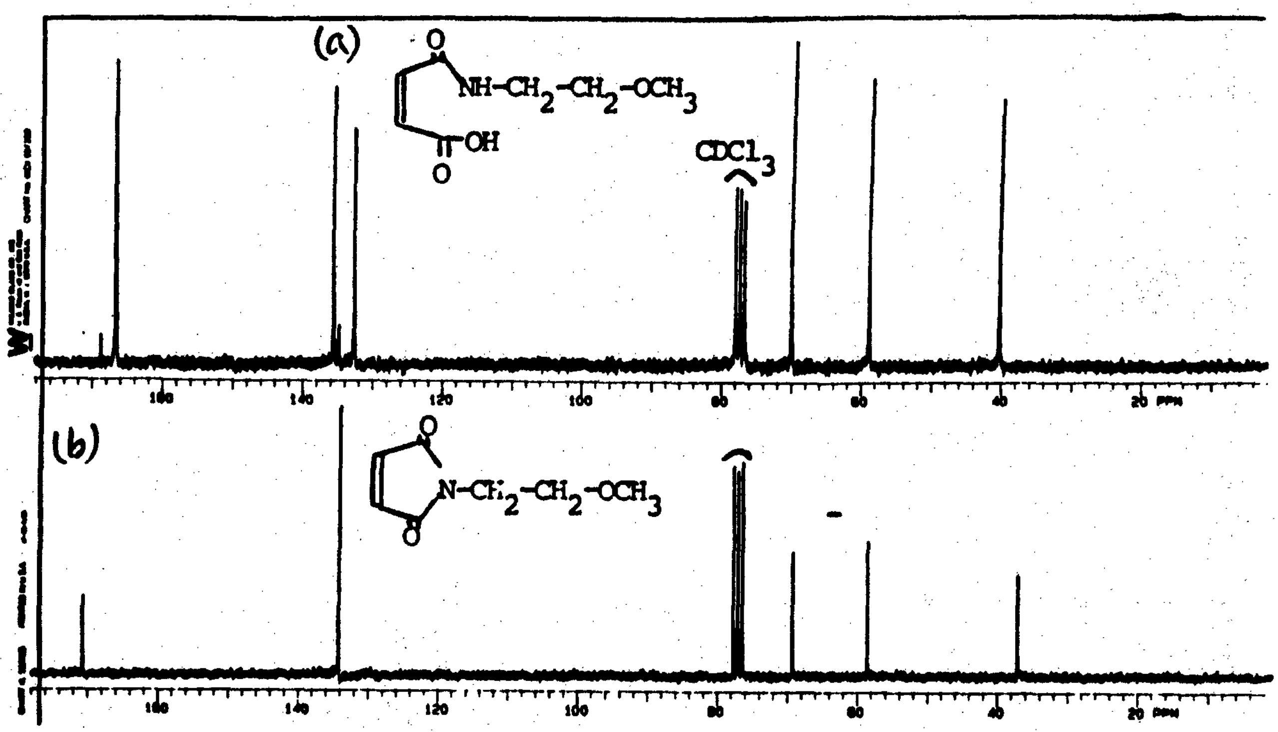


Figure 14. Structures of Bismaleimides Available



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

Figure 15. Proton NMR Spectra of N-(2-Methoxyethyl) Maleamic Acid and N-(2-Methoxyethyl) Maleimide



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

Figure 16. Carbon NMR Spectra of N-(2-Methoxyethyl) Maleamic Acid and N-(2-Methoxyethyl) Maleimide

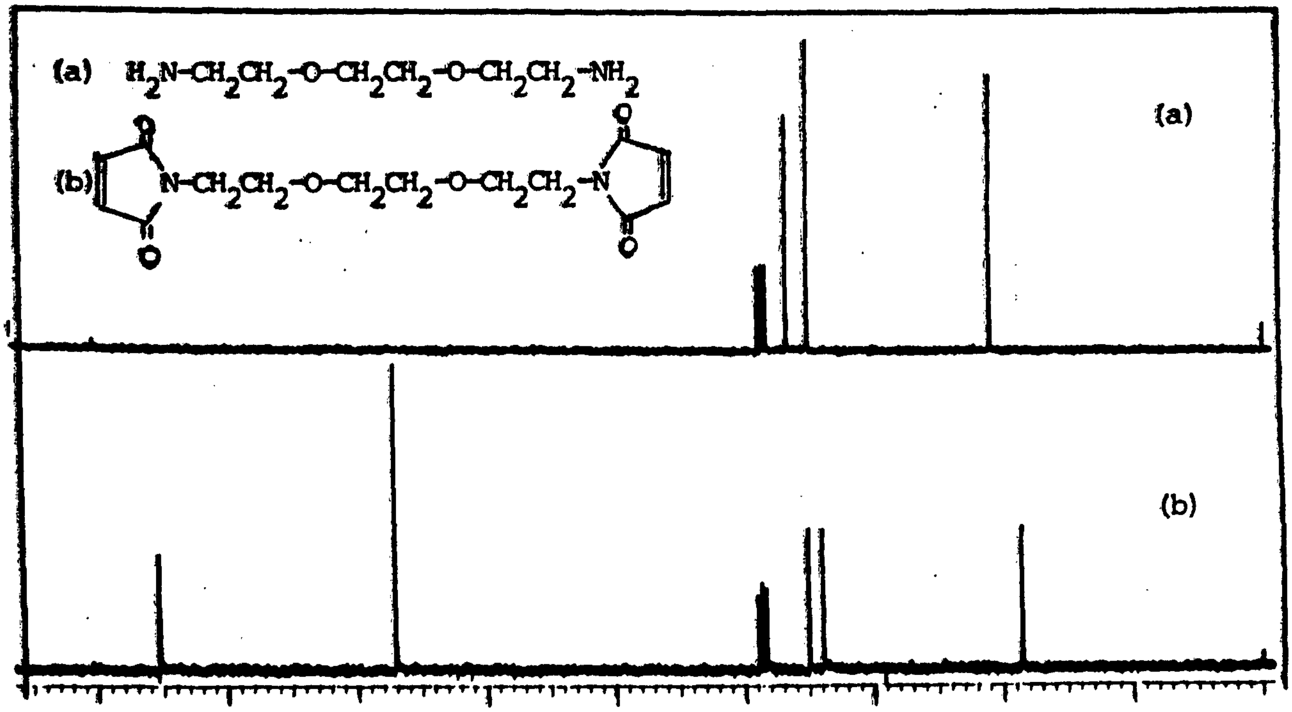


Figure 17. Carbon NMR Spectra of 1,2 Bis(2-Aminoethoxy)ethane and N,N'-(1,2-Diethoxyethane) Bismaleimide

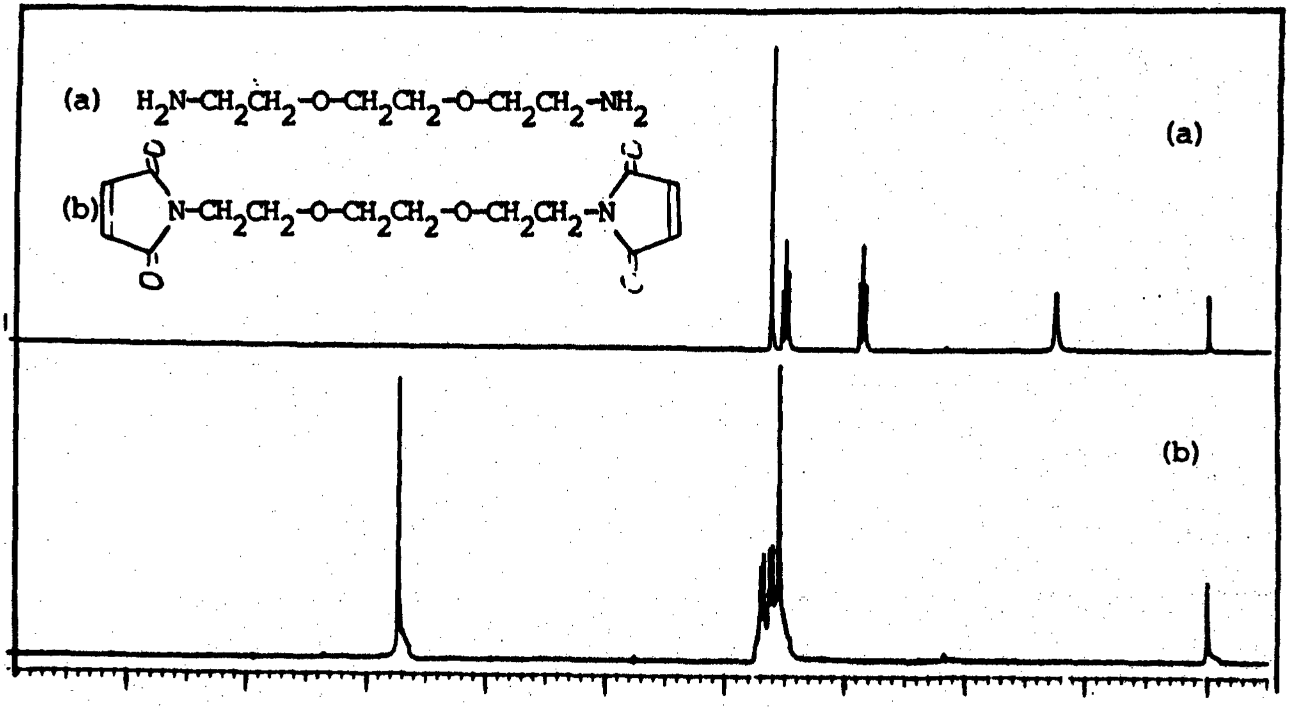


Figure 18. Proton NMR Spectra of 1,2 Bis(2-Aminoethoxy)ethane and N,N'-(1,2-Diethoxyethane) Bismaleimide

polymerizations and, of course, were not soluble in the case of tetrafunctional maleimide polymerizations.

Figures 19 through 22 give thermal and NMR data for the linear homopolymerization of the difunctional monomer, 2-methoxyethyl maleimide, a model compound for the polyether maleimide network copolymers that have been prepared. Both thermal and radical homopolymerization techniques were undertaken, and in each case, 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. Figure 21 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 thermal polymerization occurs 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. This is not regarded as significant. Figure 22 shows a melting point of the monomer 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 database points for comparison with network polymers, such that the degree of network formation necessary in producing useful resins can be estimated. Of course, the utility of these linear polymers is low due to their solubility, i.e., a lack of solvent resistance.

Figure 23 shows DSC curves for a tetrafunctional maleimide spaced with propylene oxide before heating and after heating at 150°C for a half hour. This experiment provides 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

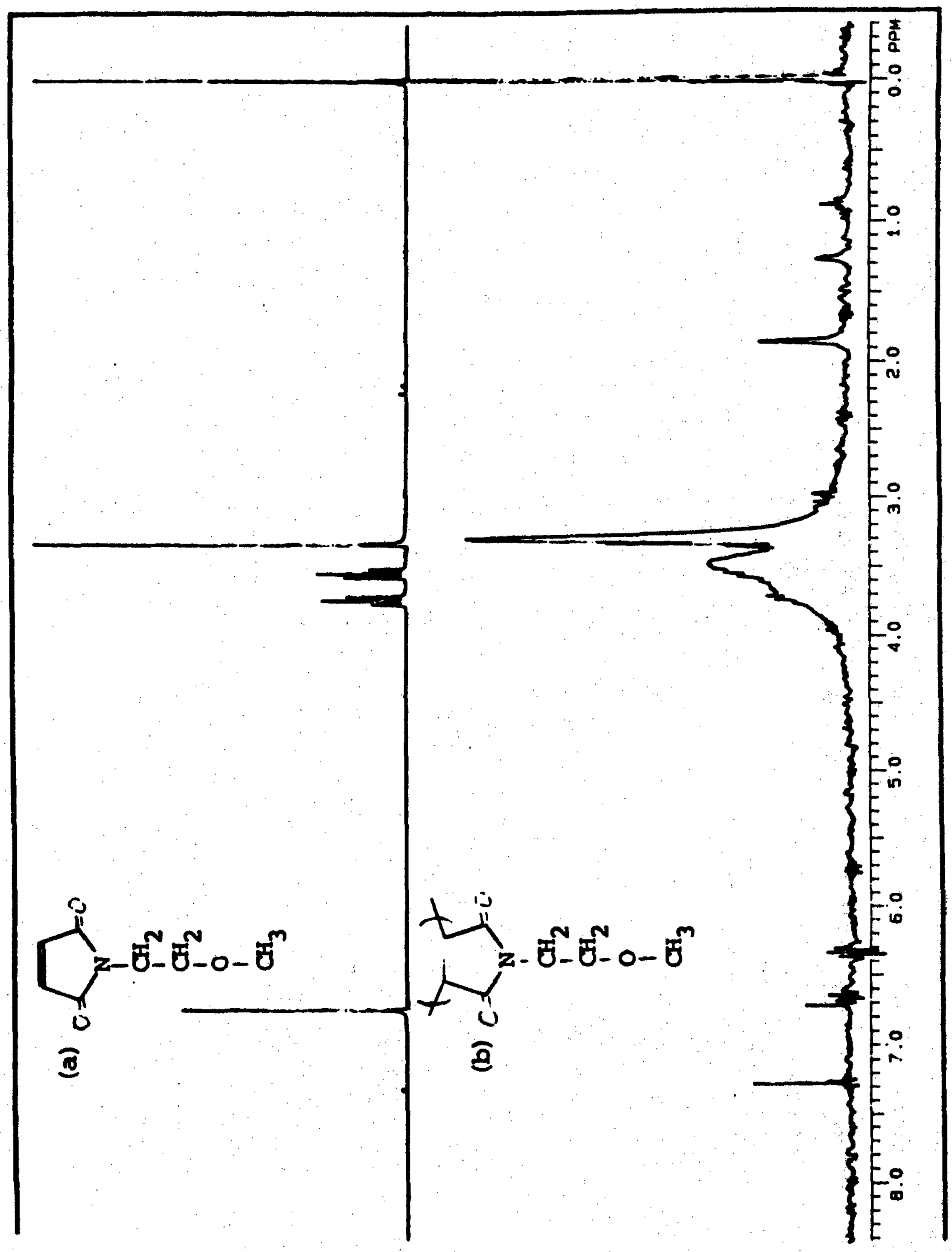


Figure 19. Proton NMR Spectra of N-(2-Methoxyethyl) Maleimide and Poly N-(2-Methoxyethyl) Maleimide

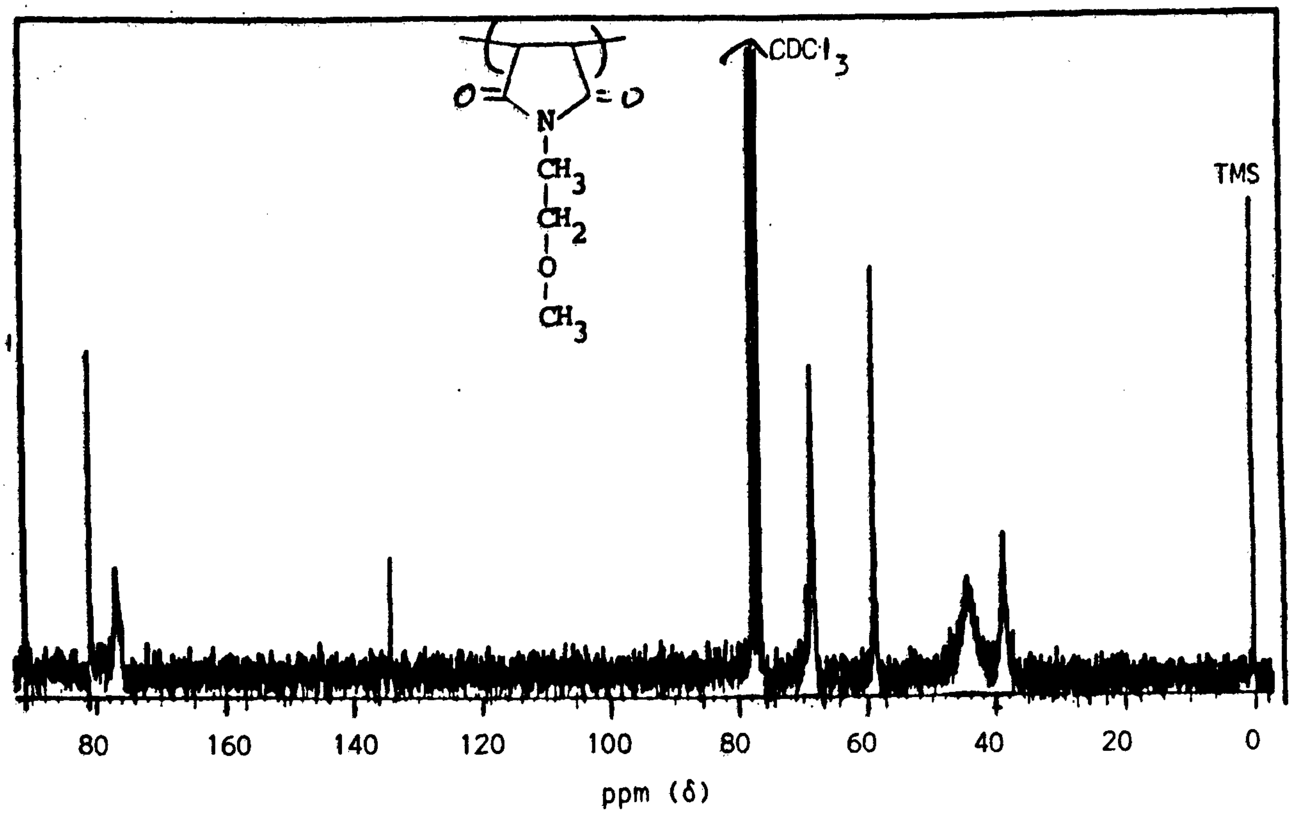


Figure 20. Carbon NMR Spectrum of Poly N-(2-Methoxyethyl) Maleimide

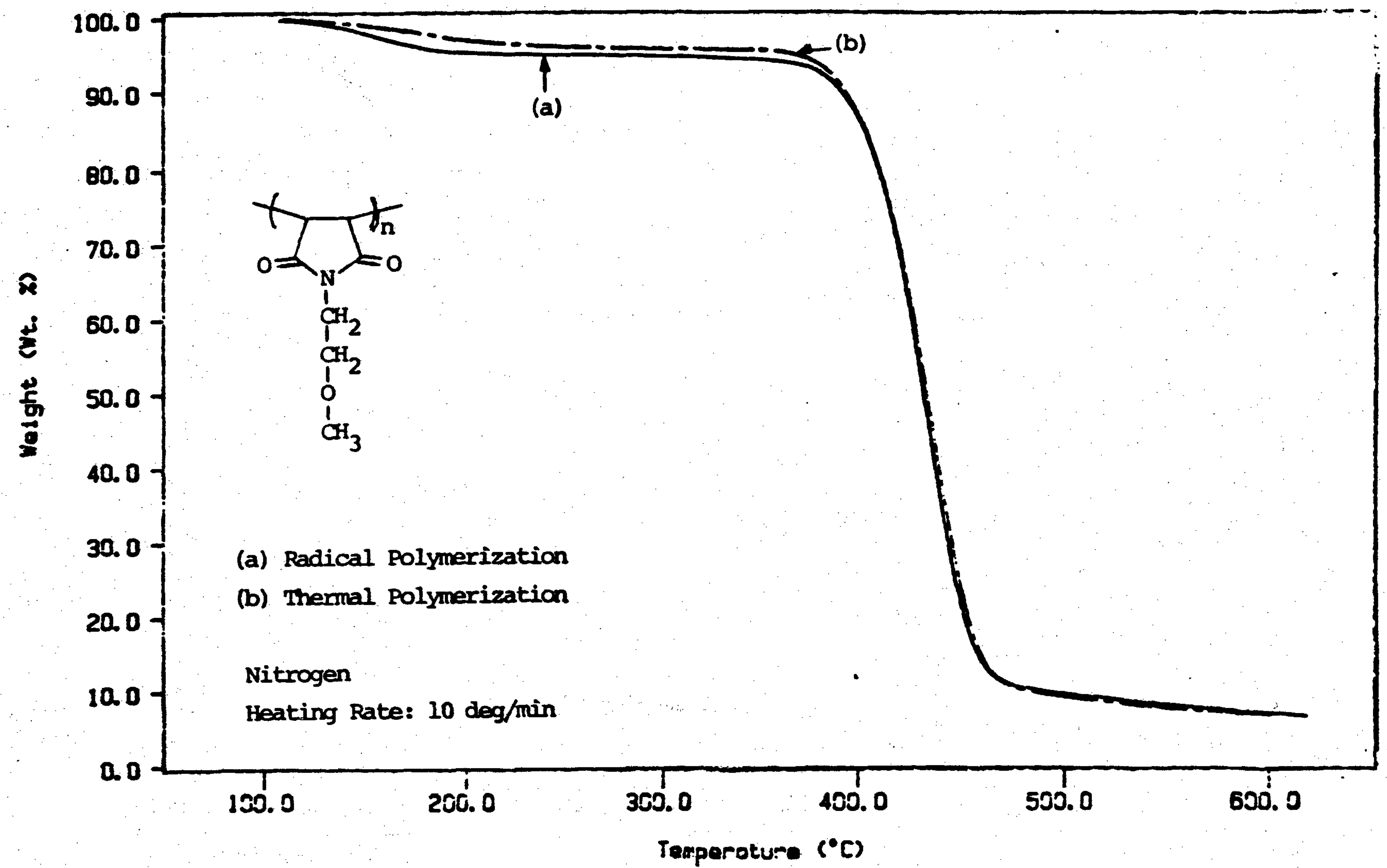


Figure 21. TGA Curve of Poly N-(2-Methoxyethyl) Maleimide

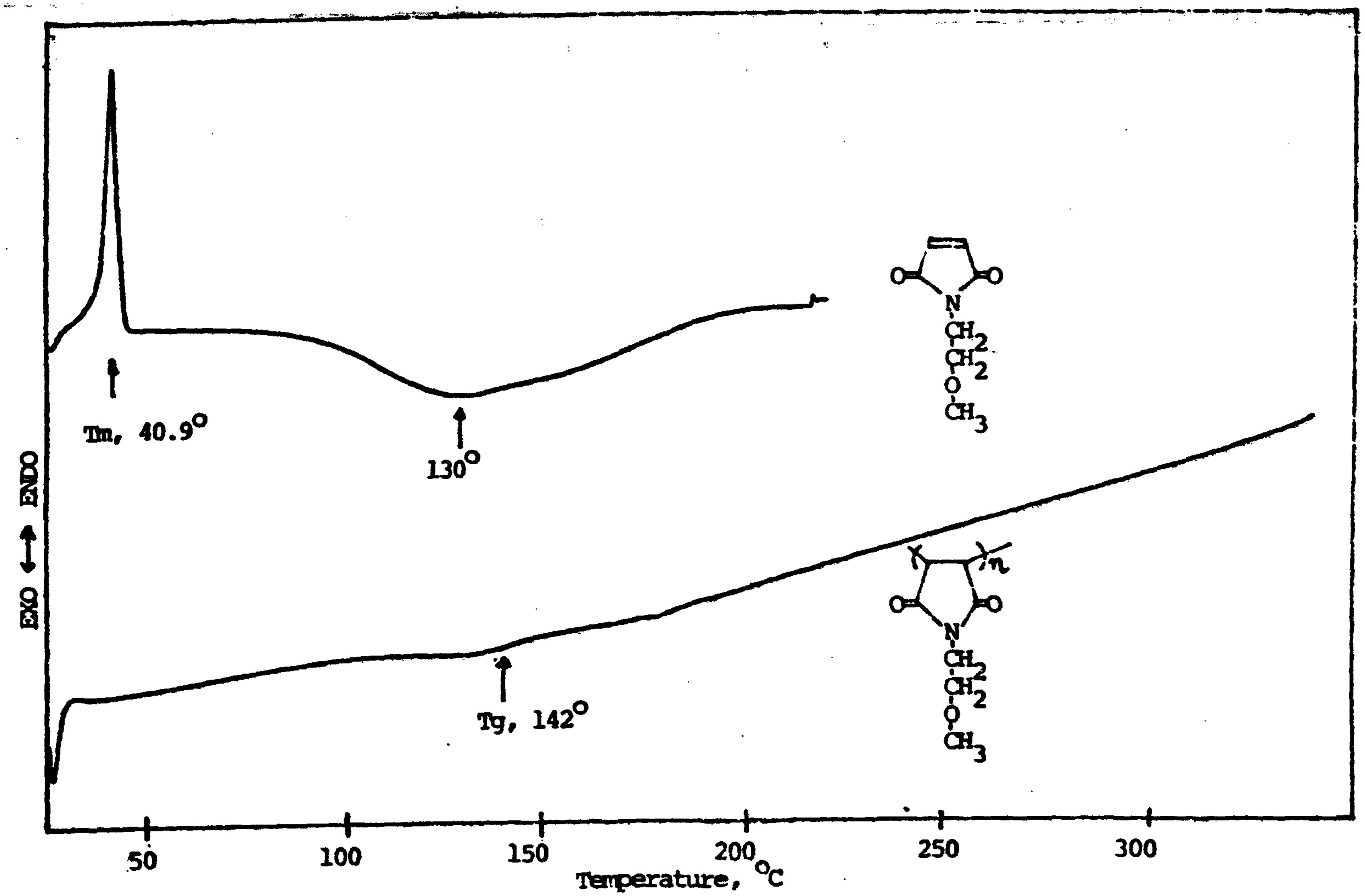


Figure 22. DSC Curves of N-(2-Methoxyethyl) Maleimide and Poly N-(2-Methoxyethyl) Maleimide

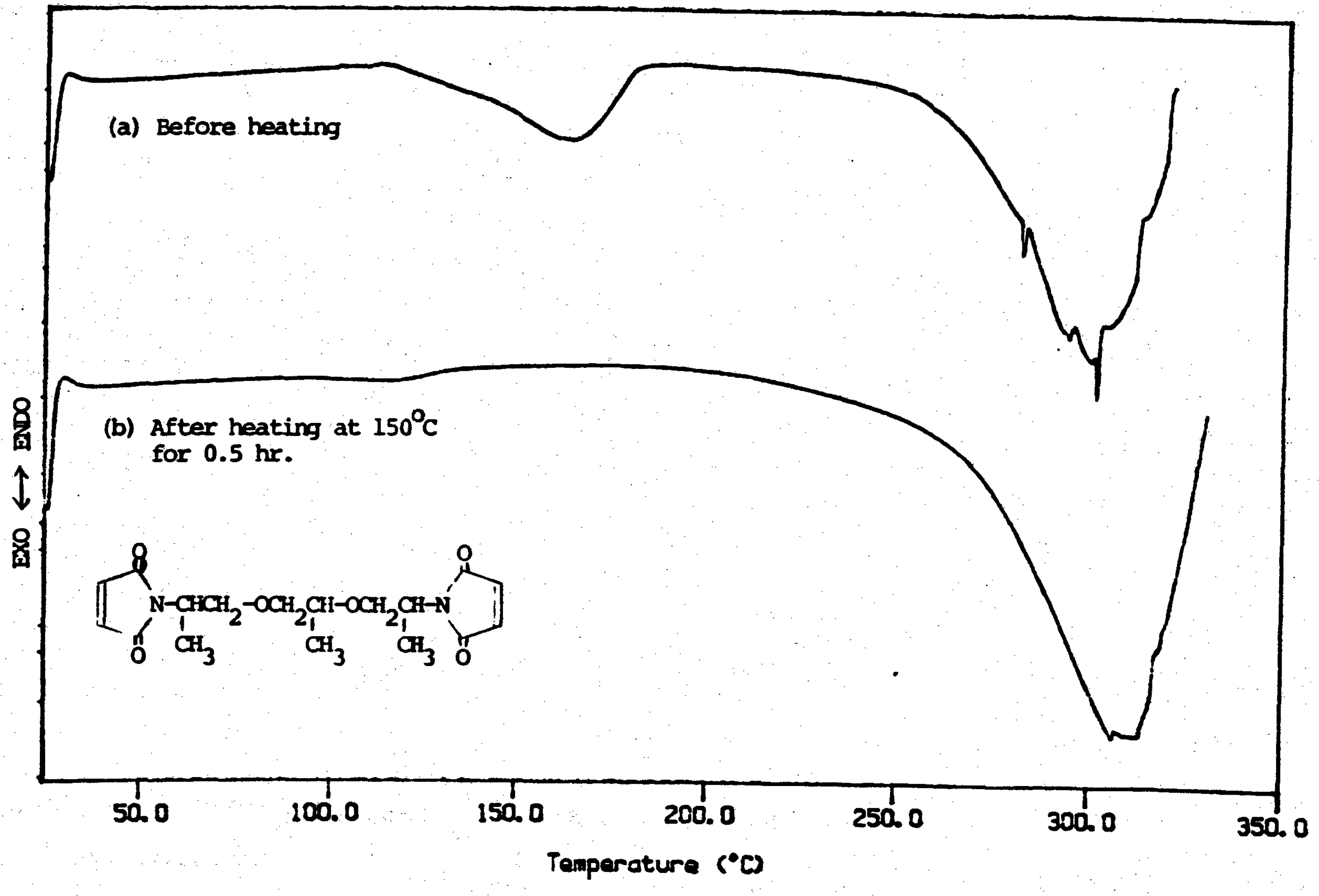
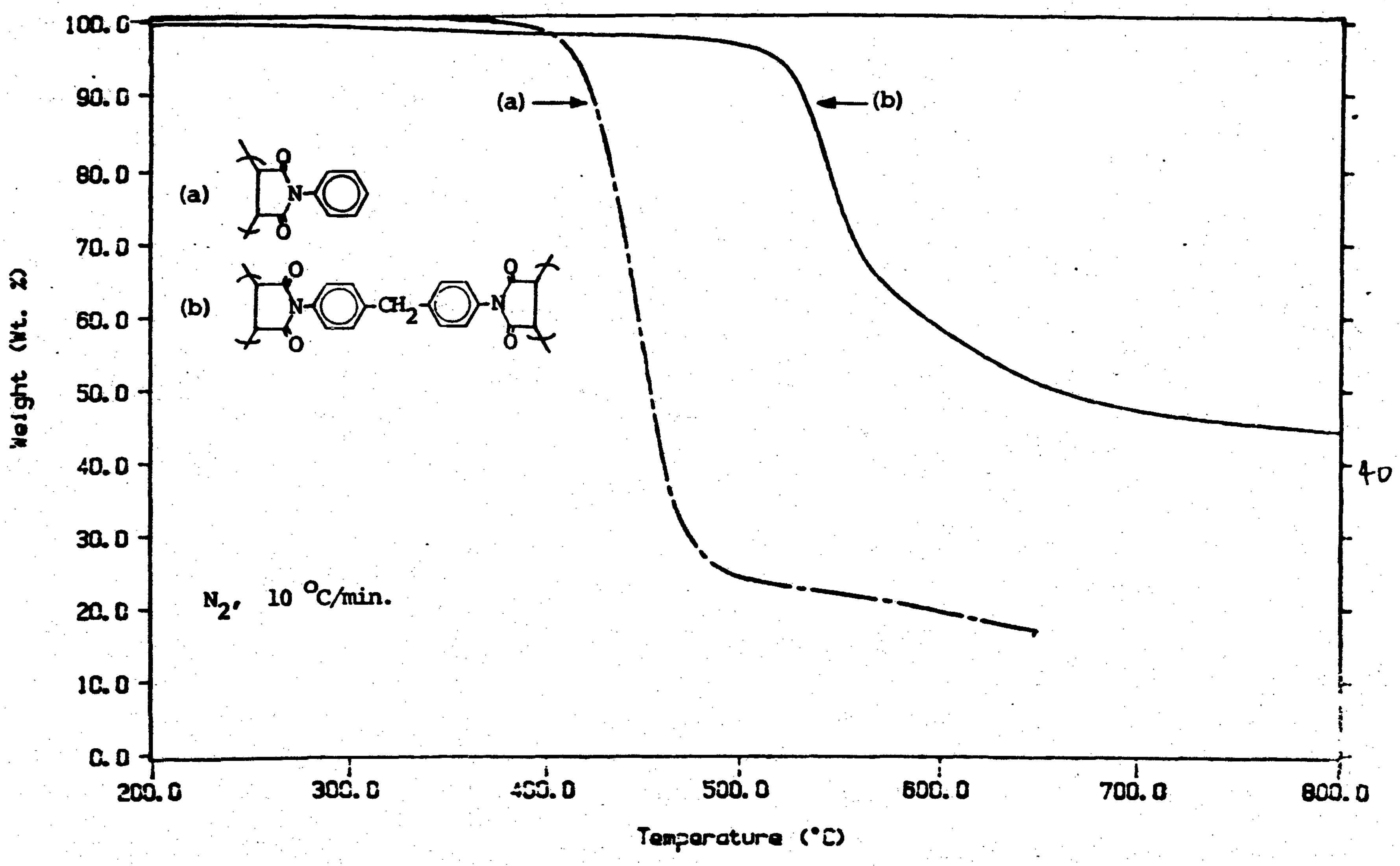


Figure 23. DSC Curves of N,N'-(1,2-Diisopropoxyisopropane) Bismaleimide

glass transition temperature of around 140°C. These polymers in this case were insoluble, yet nonetheless, the evidence is interesting - that low temperature thermal homopolymerization, 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 is low in molecular weight, however, yielding vapor pressure osmometry values less than 5000.

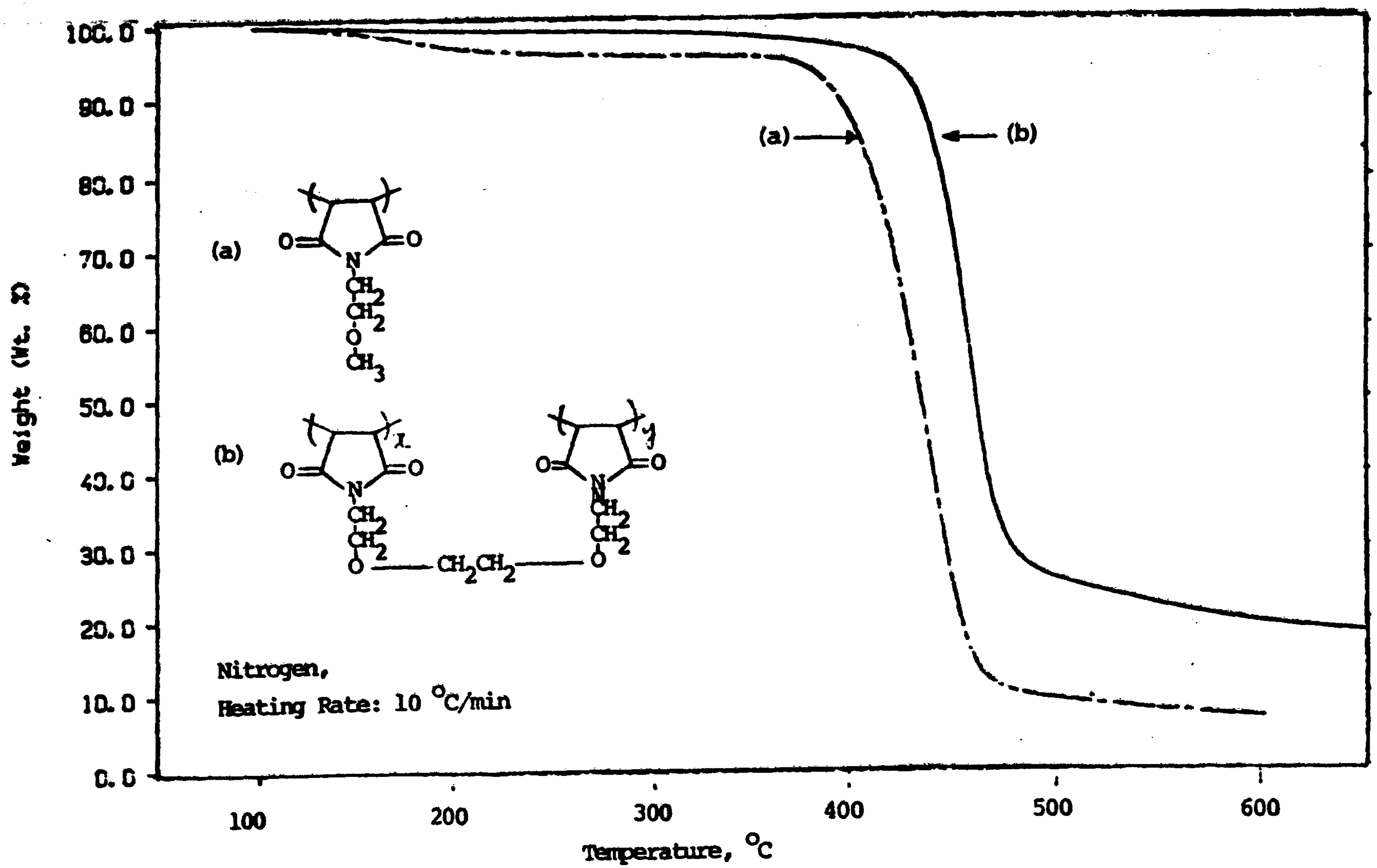
Figures 24 through 27 show TGA data for a series of tetrafunctional maleimide homopolymers in comparison with their linear analogues. For example, in Figure 24 a dramatic increase in thermal stability is observed from slightly less than 400°C to slightly more than 500°C in the case of the thermal maleimide compared with its analogous tetra functional monomer. A similar increase is also observed for 2-methoxyethyl maleimide in comparison with its tetrafunctional monomer, though the increase in stability is somewhat less than is observed for phenyl maleimide. This is not really a surprise since it is a case of dealing with flexible versus rigid crosslinks between chains; however, it is important that flexible links between chains be present to provide the impact resistance sought 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, evidence shows that good thermal stability also exists for polymers under ambient exposure conditions. Figure 26 shows that thermal stability is not a function of the nature of polymerization, i.e., radical or thermal polymerization, as was the case for linear polymerizations (Figure 21).

Figure 27 compares the thermal stability of the requisite diamine with its tetrafunctional maleimide polymer. Polymer 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.



(a) and (b) = radical polymerization

Figure 24. TGA Curves of Poly N-Phenyl Maleimide and Poly 1,1'-(Methylenedi-4,1-phenylene) Bismaleimide



(a) and (b) thermal polymerization

Figure 25. TGA Curves of Poly N-(2-Methoxyethyl) Maleimide and Poly N,N'-(1,2-Diethoxyethane) Bismaleimide

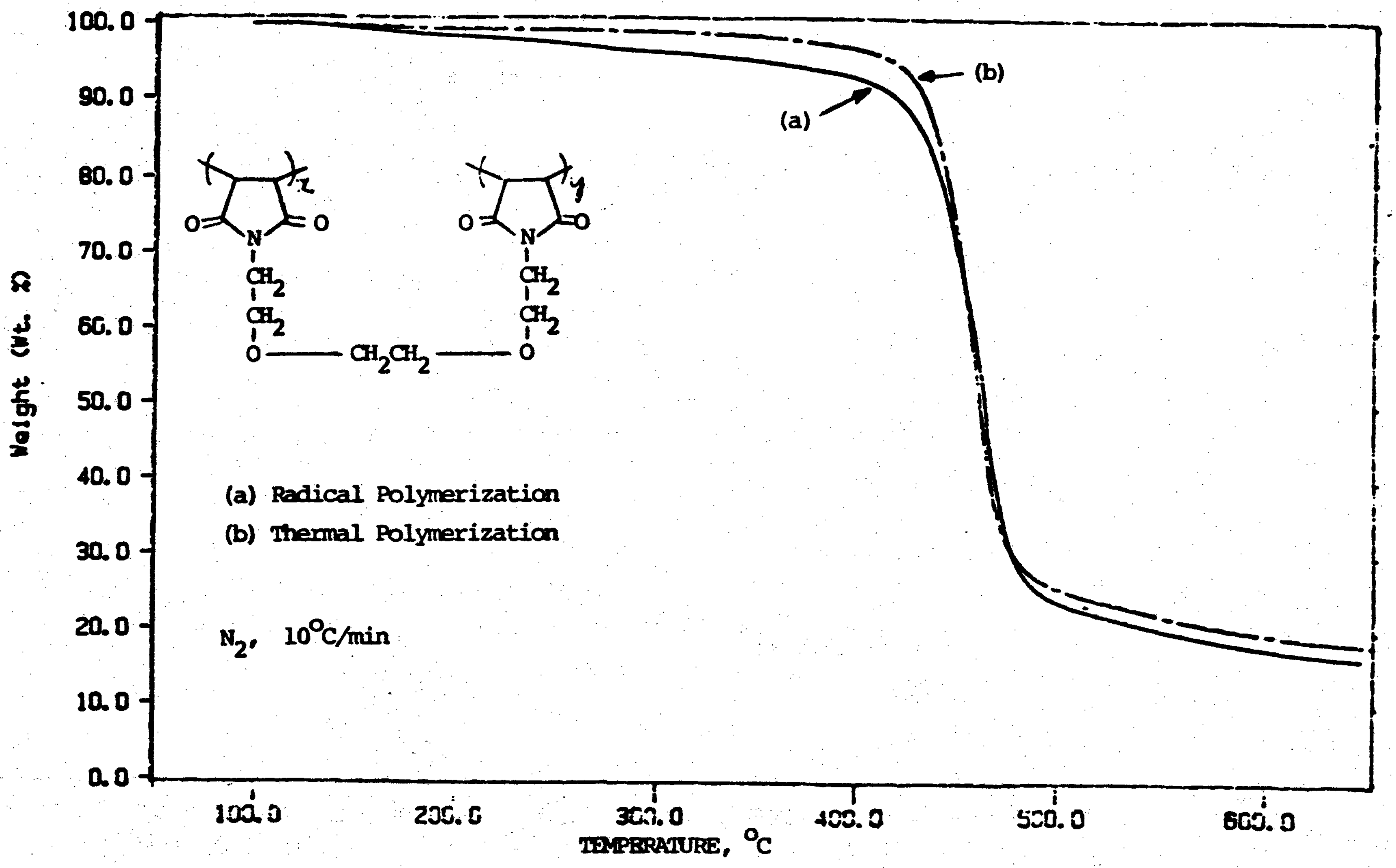
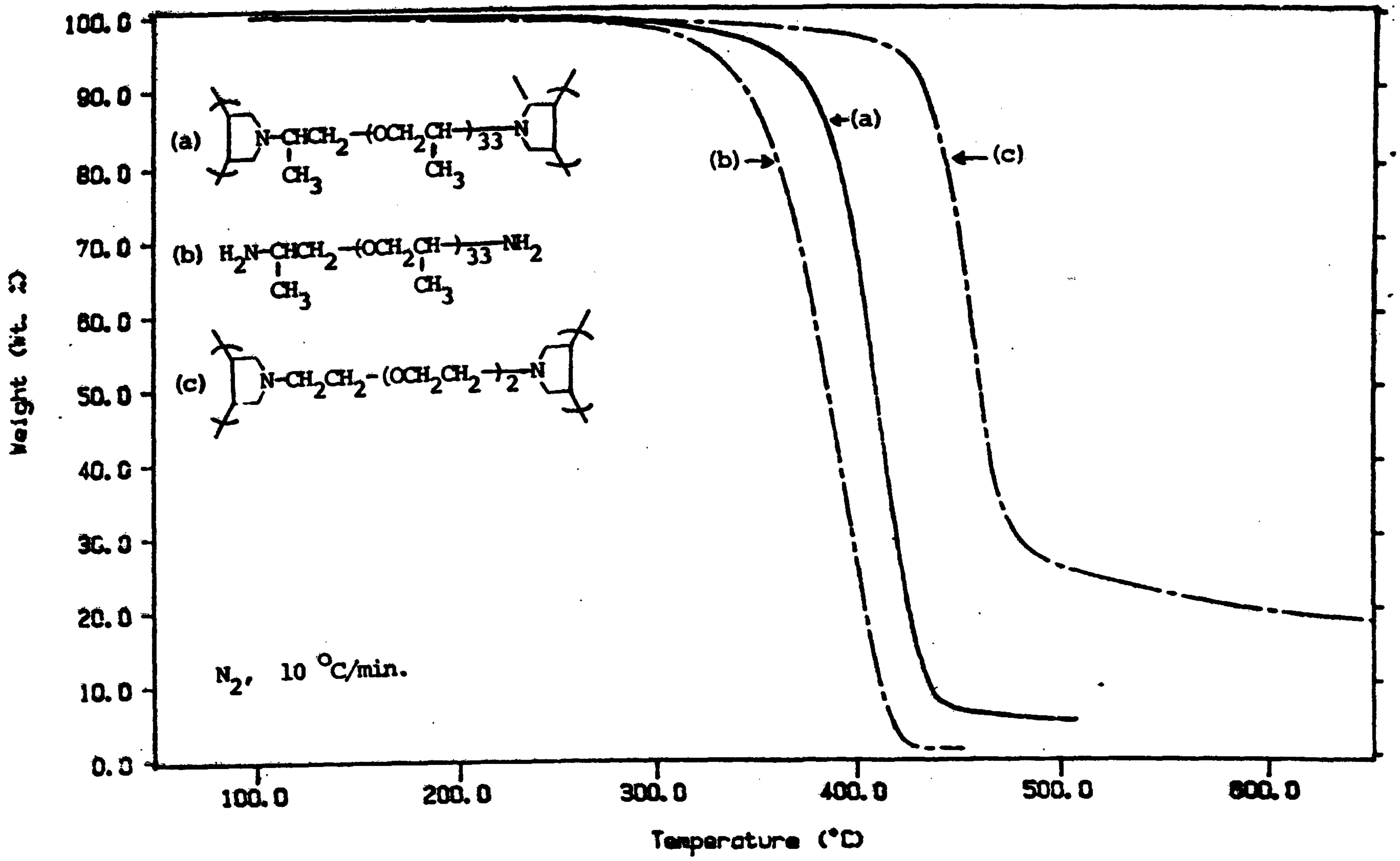


Figure 26. TGA Curves of Poly N,N'-(1,2-Diethoxyethane) Bismaleimide



(a) and (c) = thermal polymerization

Figure 27. TGA Curves of Poly N,N'-(1,2-Diethoxyethane) Bismaleimide, a Poly(Oxypropylene) diamine, and a Homopolymer of a Poly(Oxypropylene) Bismaleimide

4. LINEAR SOLUTION COPOLYMERIZATION OF VINYL ETHERS AND MALEIMIDES

A series of linear donor acceptor polymers were synthesized using difunctional vinyl ethers and difunctional maleimides, wherein the synthesis was conducted in solution in order to create polymers whose glass transition temperature would reach at a maximum value. Here, the solvent permits the growing polymer chain to achieve its highest molecular weight (vitrification is not a factor), followed by precipitation under conditions which permit the polymer to exhibit its highest possible glass transition temperature. A typical synthesis is shown in Figure 28, where polymerizations were conducted with a standard Horner-Schwenk initiator system in methylene chloride at room temperature. Figures 29 and 30 show the DSC behavior and TGA behavior respectively for linear polymers prepared in this fashion. Decomposition temperatures are in the range of 320-380°C, and glass transition temperatures, which are a function of the nature of the substituent (R in Figure 28), were within the range of 130-160°C. Though these values are of interest, it is apparent that the glass transition temperatures are lower than needed for the materials sought in this research. However, since the polymers are linear, rather than networks, the results were encouraging, since network polymers typically have Tg values 30-60°C higher than their linear analogues.

5. NETWORK SOLUTION COPOLYMERIZATIONS OF VINYL ETHERS AND MALEIMIDES

Once having established benchmark thermal values for linear polymers, a series of network polymers were prepared in solution in order to observe the magnitude of increase in the glass transition temperature. As described previously, the polymerizations were conducted in solution to alleviate problems associated with vitrification, thus permitting the growing network to relax to its most stable thermodynamic state. Consequently, the highest possible glass transition temperatures could be observed. The synthesis of such polymers using tetrafunctional maleimides and tetrafunctional vinyl ethers is shown in Figure 31. Typical DSC data and TGA data are given in Figures 32 and 33,

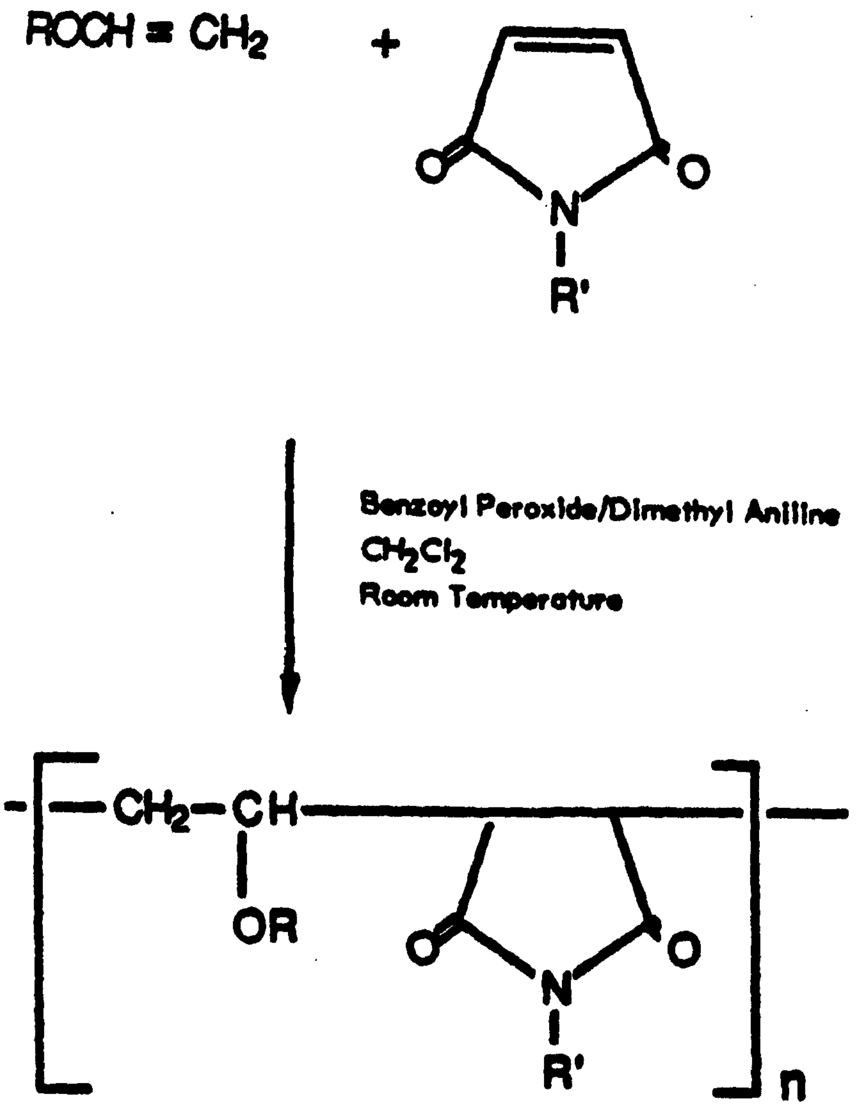


Figure 28. Synthesis of Linear Polymers via Donor Acceptor Polymerization

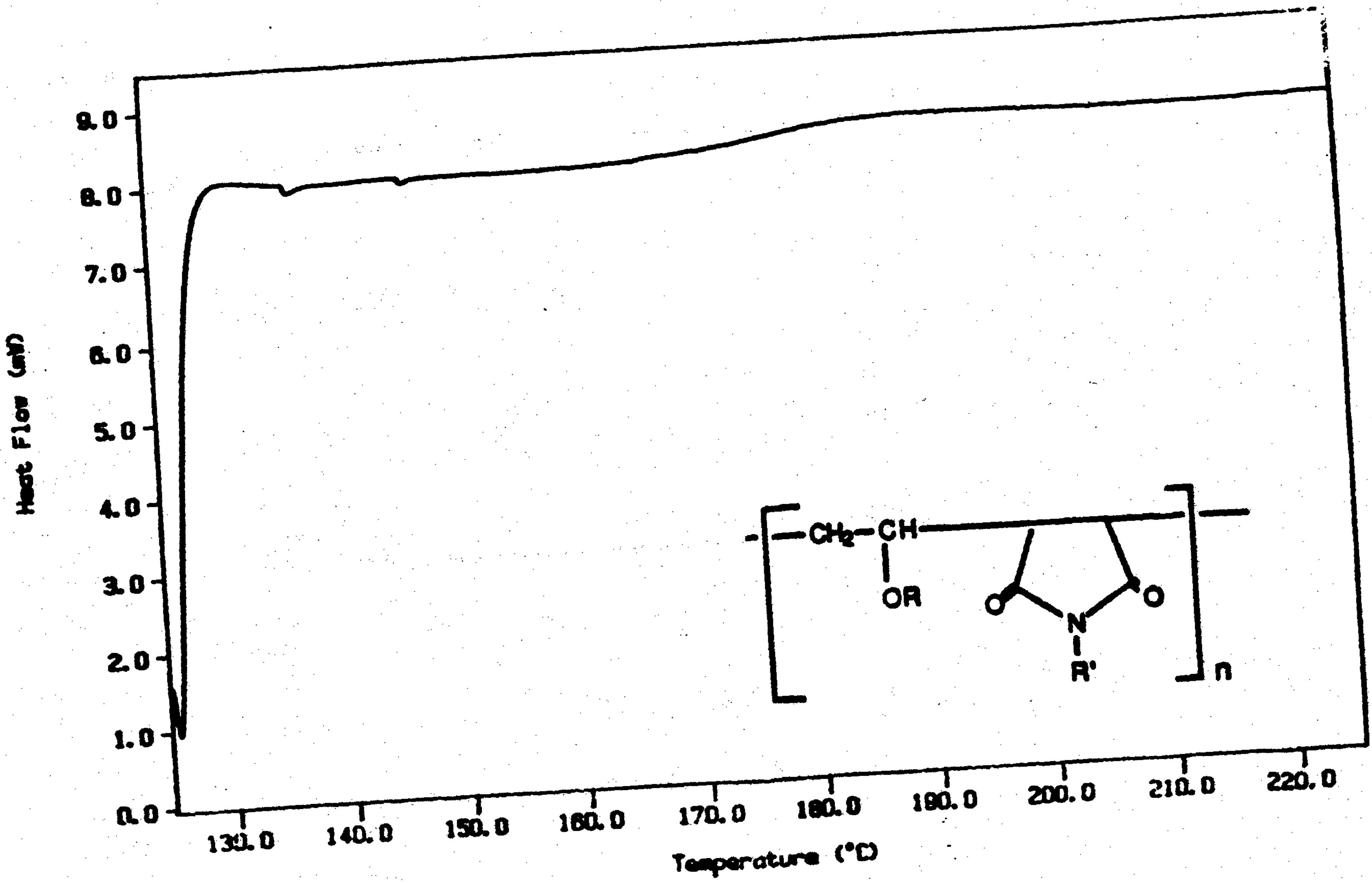


Figure 29. DSC Behavior for Linear Donor Acceptor Polymers Prepared in Solution

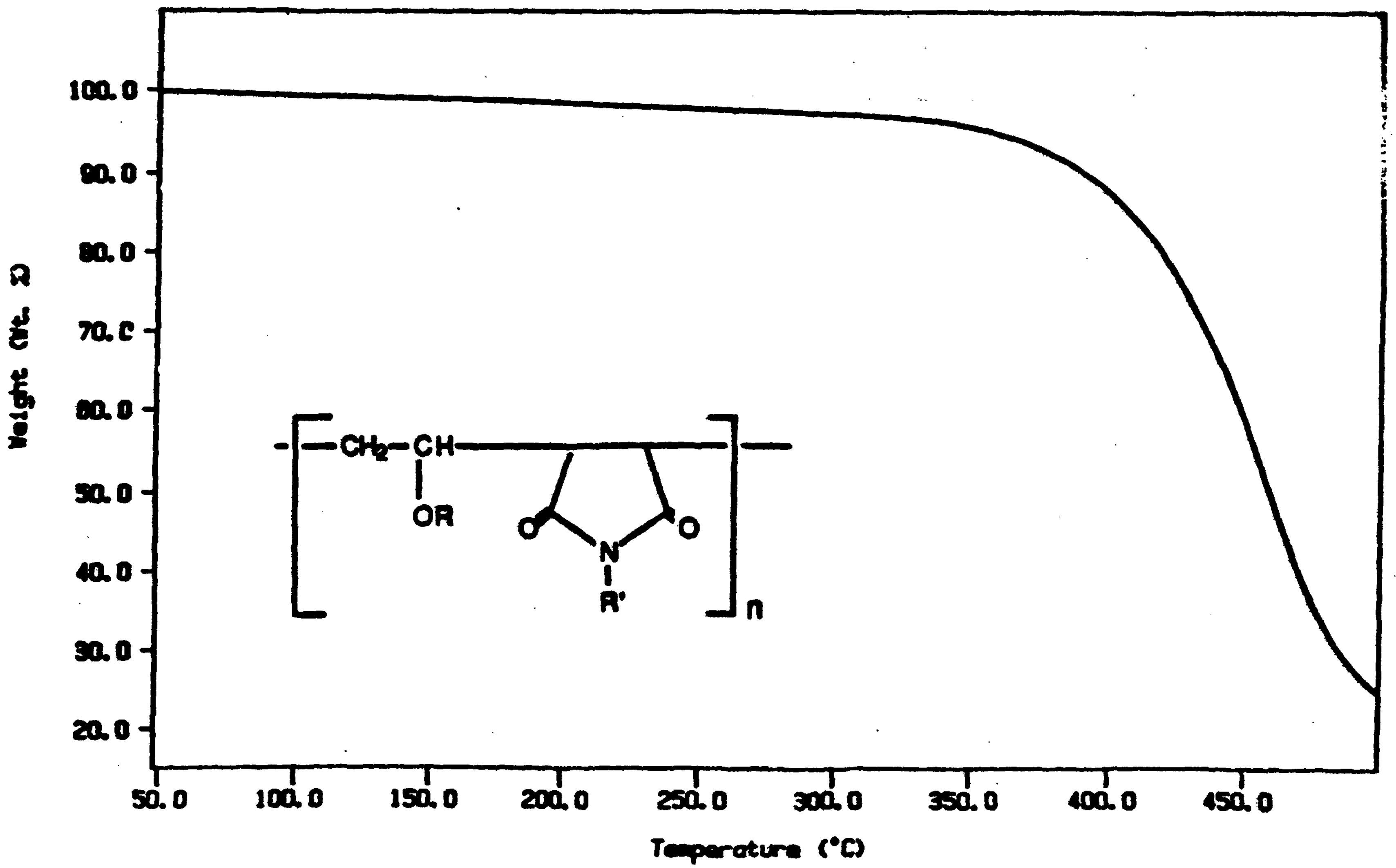


Figure 30. TGA Behavior for Linear Donor Acceptor Polymers Prepared in Solution

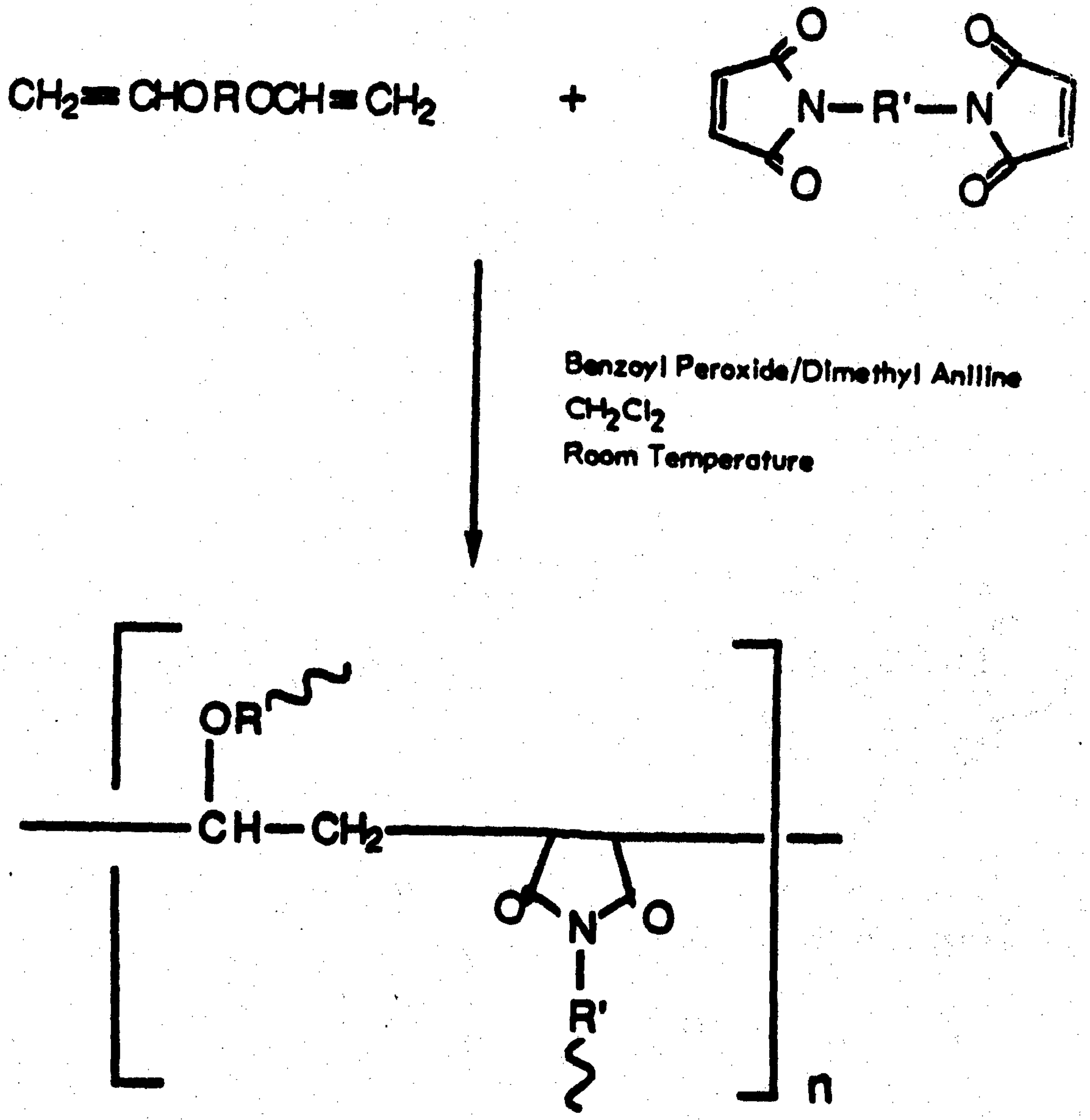


Figure 31. Synthesis of Network Polymers in Solution

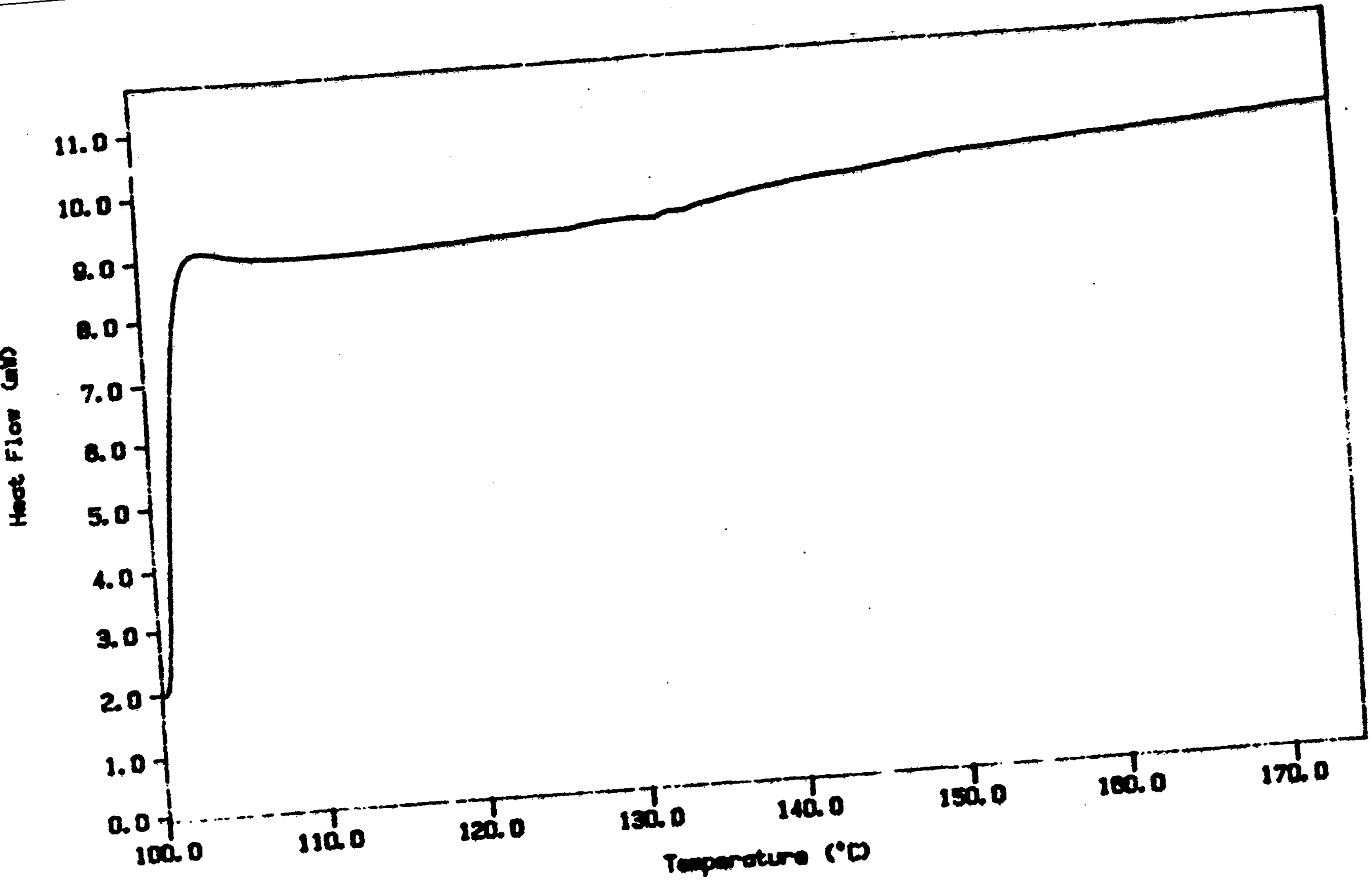


Figure 32. A Typical DSC Curve for Network Polymers Prepared in Solution

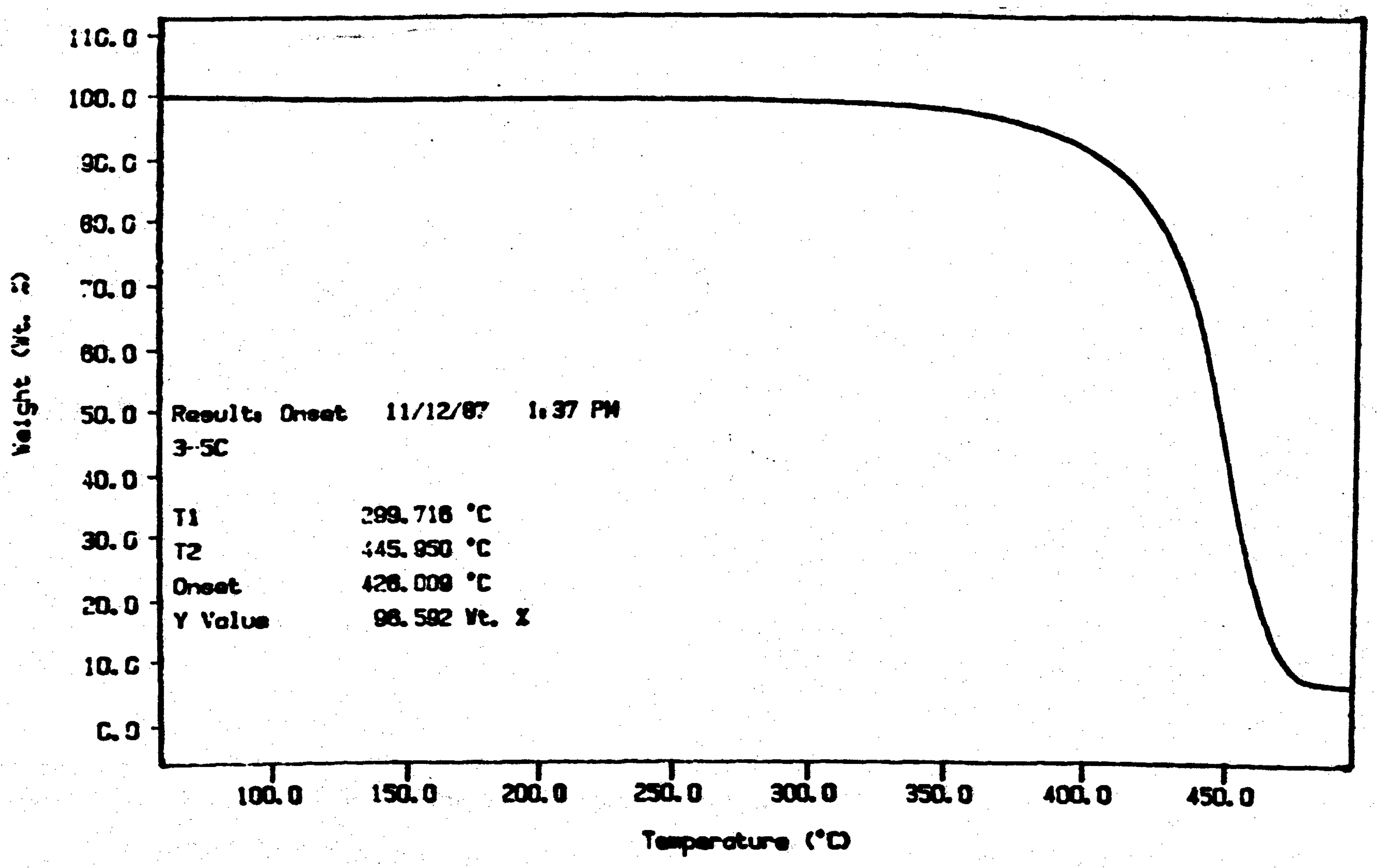


Figure 33. A Typical TGA Curve for Network Polymers Prepared in Solution

respectively. These polymerizations were conducted in a manner identical to that for generation of linear polymers in solution, yet as the polymerization proceeded, gel formation was observed as is expected in the formation of any network polymer. The polymerization was permitted to continue until apparent reaction had ceased, then the samples were precipitated and purified as done in a manner identical to that for the linear polymer systems.

The thermal performance of these network polymers was significantly better than that for the linear polymers, again as might be expected. For example, TGA decomposition temperatures were in the range of 350-470°C, or up to 100 degrees higher than the case of linear polymers. More importantly, the DSC glass transition temperatures showed an increase to a range of 170-210°C, again significantly higher than the case for linear polymers. It should be noted that both of these ranges are acceptable with respect to the thermal performance sought in the desired materials.

Note also that this polymerization procedure, i.e., polymerization in solution, permits full relaxation of the polymer chain, thereby creating a polymer whose glass transition temperature is at a maximum value. Consequently, it is clear that maximizing chain mobility by conducting the polymerization in solution is a positive feature which might be imitated during bulk polymerizations, if in fact the "solvent" could covalently bound into the network polymer itself. These data, both for the linear and network systems, suggest that donor acceptor polymerization yielding useful network polymers is viable if the network can be fully relaxed during its formation. This is the essence of the 2-Tg concept.

6. BULK POLYMERIZATIONS OF MALEIMIDES AND VINYL ETHERS

A specific goal of this research is to create network polymers in the absence of solvents such that problems associated with solvent could be avoided. Consequently, bulk polymerizations were next in the series of studies done during the course of this research, where the first experiments were conducted using the AIBN as the initiator at 60°C. These relatively high temperature polymerizations were done in order to create network polymers having optimal thermal properties, and typical series of polymerizations are described in Figure 34. All polymerizations were taken to apparent completion, i.e., for time periods that would assure a maximum degree of monomer conversion. Figure 34 also shows a series of network polymers which were prepared containing polyoxyethylene 1000-tetrafunctional vinyl ether (Compound **5**), polypropylene oxide 2000-tetrafunctional maleimide (Compound **6**).

The data in Figure 34 show that the decomposition temperature for these copolymers fell in a narrow range between 370-400°C, which is acceptable for the applications in mind. Note also that even for compositions possessing as much as 20 percent by weight polyether, the decomposition temperatures are acceptable, and in fact, actually higher in value than is the case for some polymers containing 10 percent polyether.

This is a particularly encouraging result and suggests that the use of polyethers as "solvents" for the 2-Tg concept appears viable, at least from a perspective of thermal stability of these polymers. Stated differently, it means that the polymerization can occur wherein the polyether acts as the solvent early in the polymerization followed by gel formation as a result of the creation of networks. The difference between the true solution polymerization research is the "solvent" (the polyether) becomes covalently bound to the network, and thus does not become a volatile component.

After achieving this level of understanding for 60°C bulk polymerizations, attention was turned to polymerizations at ambient temperatures.[25-29] A Horner-Schwenk initiator system was used where formation of radicals at ambient temperature is illustrated in Figure 35. This initiator system is well known[30] and produces radicals of sufficient quantity at room temperature to induce radical polymerizations, particularly those that are easily initiated, such as is the case for donor acceptor polymerization. A series of polymerizations were conducted at ambient temperature with variables being

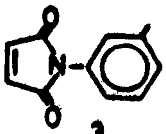
	Vinyl Ether	Maleimide	Polyether	Decomposition Temp.
A	1	3	-	398°
B	1	3,4	-	367°
B'	1	3,4	6 (10%)	
C	2	3	-	374°
C'	2	3	5 (10%)	368°
D	2	3,4	-	377°
D'	2	3,4	5 (10%)	373°
D"	2	3,4	5 (20%)	392°

$C_4H_9OCH{=}CH_2$

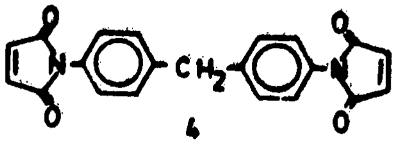
1

$CH_2{=}CHOC_4H_8OCH{=}CH_2$

2



3

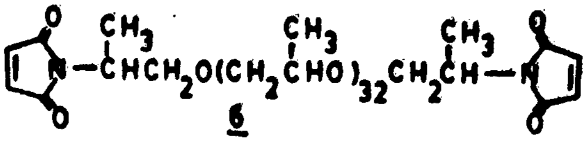


4

$CH_2{=}CHO(C_2H_4O)_nCH{=}CH_2$

5

n=22



6

Figure 34. Bulk Polymerizations with AIBN

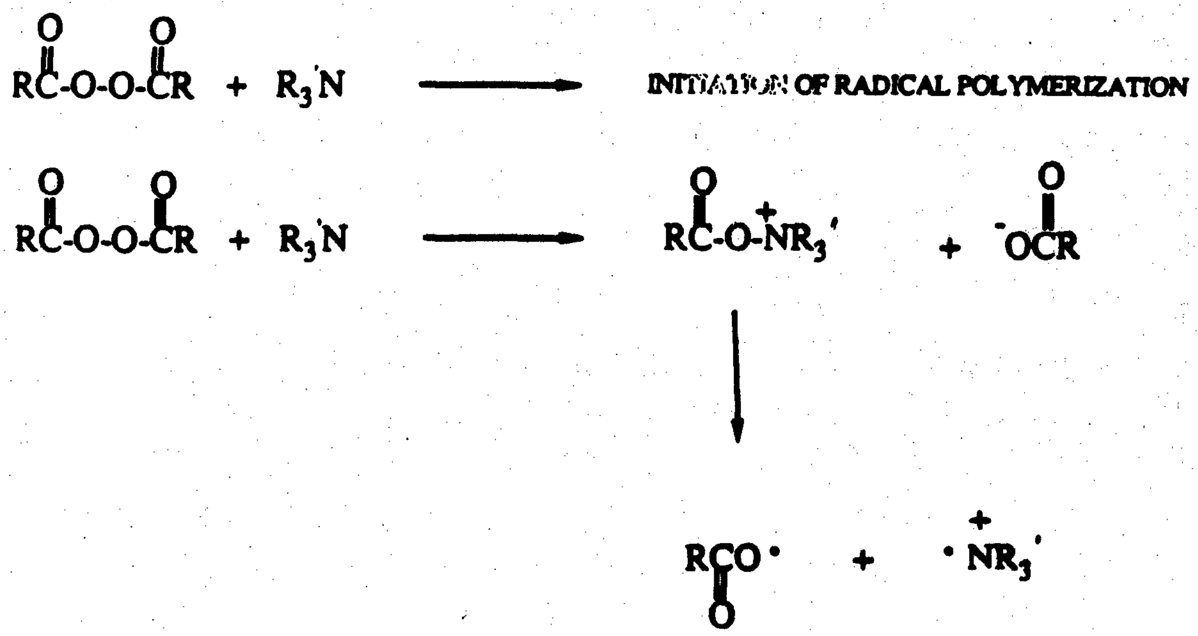


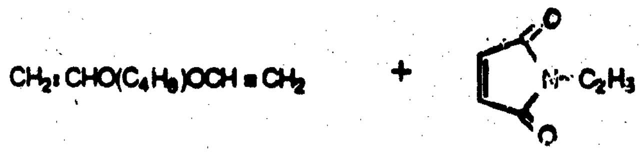
Figure 35. The Horner-Schwenk Initiator System

chosen as illustrated in Figure 36. While these reactions did not appear to proceed to complete conversion under ambient polymerization conditions, most likely due to vitrification, it is clear from solid state NMR spectra that the polymerizations proceeded well enough to generate network systems. Conversions of between 70 and 80 percent could be observed, as shown by the solid state NMR spectra in Figure 37. Network polymers prepared with varying weight percent polyether from 0 percent (no polyether was added) to 15 percent showed TGA thermal stabilities under nitrogen in the range of 400°C, and a glass transition temperature in the range of 170°C. Consequently, even though vitrification prevented complete conversion of functional groups, the polymers that were formed appeared to be possess thermal properties of interest for the applications at hand. It should be noted, however, that these polymers exhibit an exotherm, albeit a small one, at temperatures less than 200°C, suggesting that the reaction could be continued at temperatures higher than glass transition temperature.

Conclusions drawn from these bulk polymerizations suggest that network polymers, based on donor acceptor polymerization chemistry, may indeed possess the thermal properties required for the applications desired. However, an understanding of the reasons for a lack of complete conversion is important, and consequently, further research was undertaken to quantitatively determine the extent of cure in these reactions. This research is described in the following section.

7. A SPECTROSCOPIC STUDY OF THE EXTENT OF CURE

Determination of the extent of reaction in network polymerization (the extent of cure) is always difficult to accomplish, since the product of these reactions is an insoluble solid. Approaches to this problem have consisted of performing solid state analyses, such as measurement of the thermal behavior of these polymers by differential scanning calorimetry, where the presence of an exotherm is thought to represent further reaction (further conversion of functional groups or curing).[31] While this most likely is the case,

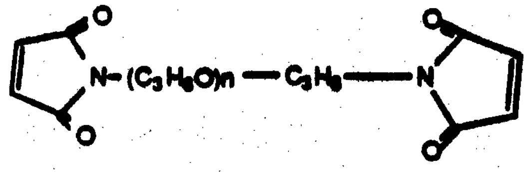


Polymerization variables

Choice of comonomer

$CH_2{=}CHO(C_2H_4O)nCH{=}CH_2$ MW 600, 1000, 2000

$CH_2{=}CHO(C_2H_4O)n\ (SiO)x(C_2H_4O)nC_2H_4OCH{=}CH_2$

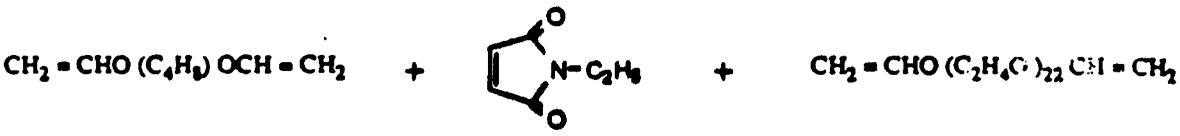


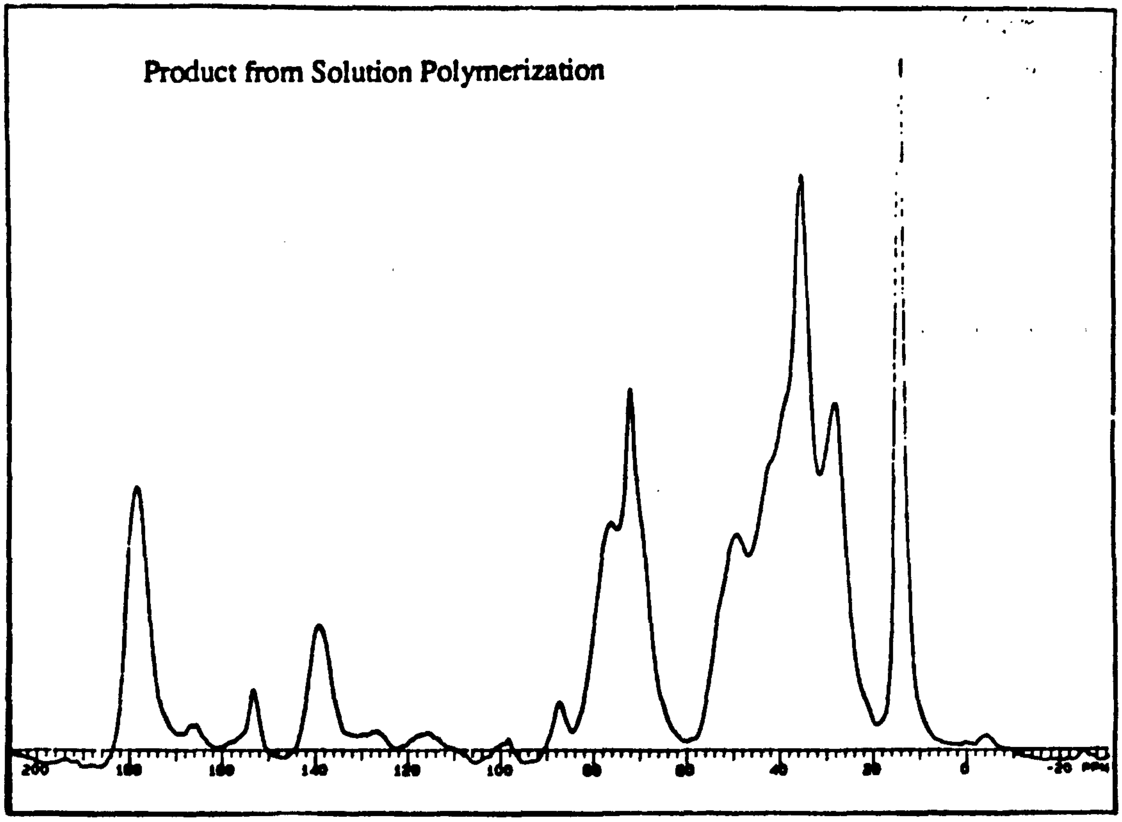
Weight percent of comonomer

Initiator system

Temperature

Figure 36. Bulk Polymerization at Ambient Temperature




Product from Solution Polymerization

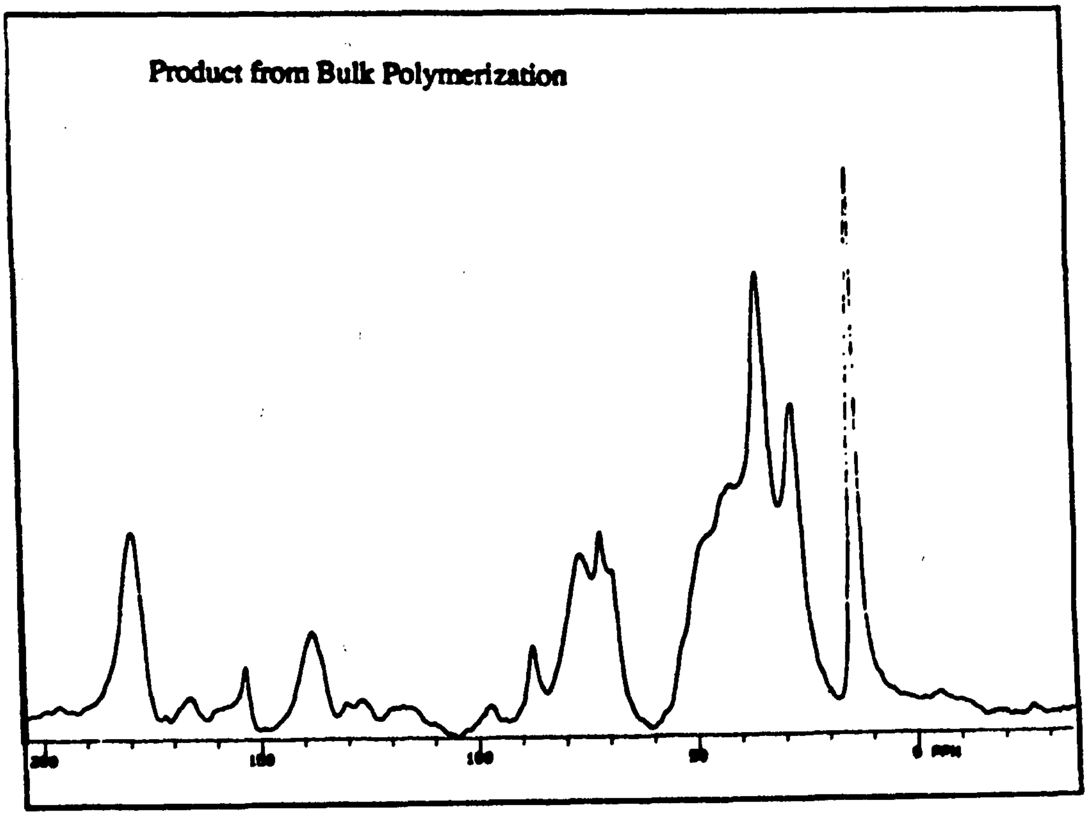

Product from Bulk Polymerization

Figure 37. Solid State NMR Spectra

it remains circumstantial evidence for a lack of full curing. Other methods approaching this problem include reflectance infrared spectroscopy where the change in functional group concentration is observed. This is difficult since it is a challenge to obtain meaningful quantitative data.

In the course of this research, we conducted a solid state NMR characterization of these polymers and witnessed a change in the concentration of the reacting functional groups, i.e., the maleimide functional group and the vinyl ether functional group (see Figure 37). While these spectra are useful, and in fact suggest that it may be possible to do solid state NMR determinations of percent of conversion, these data are qualitative in their nature, and simply suggest that extent of cure is not yet complete. Only estimates of the extent of use can be made.

In order to address this problem, a series of linear donor acceptor polymerizations of difunctional maleimides and difunctional polyethers were conducted in the bulk state, and consequently, polymerizations proceeded as might be the case for a bulk network polymerization. The polymerization continued until the solid state was formed at room temperature, i.e., until chain length had reached a point where solidification became an important change in state. An assumption was made that solidification represents "vitrification" as would be the case in network formation. The major difference, of course, is that the linear polymers remained soluble, and highly accurate solution NMR spectroscopy could be used to determine percent conversion. Using this technique, which we term "network imaging via bulk linear polymerization", we have studied the extent of reaction (cure) by proton NMR spectroscopy, varying parameters within the initiating system itself.

A specific donor acceptor copolymerization of N-methyl maleimide and N-butyl vinyl ether was chosen, using two different initiator systems, benzoyl peroxide/dimethylaniline, and benzoyl peroxide/dimethyltoluidine. Data from these polymerizations are presented in Figure 38. In these experiments, the weight percent peroxide was varied

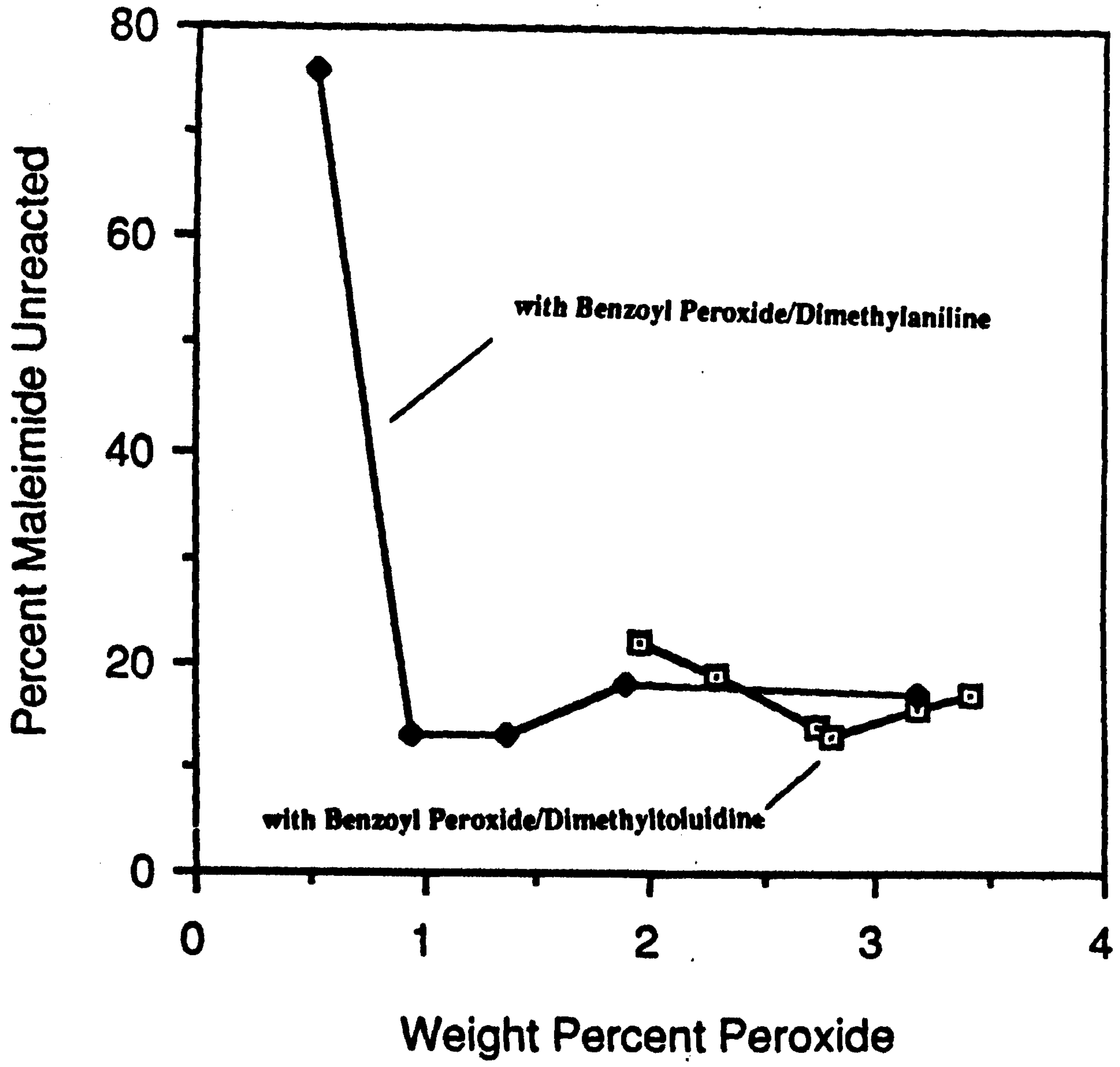


Figure 38. Copolymerization of N-Ethylmaleimide and n-Butylvinylether

from 0 - 4 weight percent, and it became evident that a maximum degree of reaction (cure) could be obtained for both initiator systems when the weight percent benzoyl peroxide equaled at least 1 percent. Under these conditions, the extent of cure approaches 90 percent, which is excellent, if in fact such a system is properly images vitrification in network polymer systems.

Figure 39 shows the data for these two initiator systems in comparison with two other systems, t-butylperoxypivilate/dimethyltoluidine and t-butylperoxymaleic acid/dimethyltoluidine. Again, the extent of reaction (cure) was determined accurately using high resolution, solution NMR spectroscopy of the linear polymers formed in the bulk state. These data show that the peroxide of choice is benzoyl peroxide. The latter two initiator systems acted very poorly under ambient temperature conditions, where cures were less than 50 percent in all cases, and in some cases were less than 20 percent. It is clear from these data that using bulk polymerization conditions for linear polymers provides an accurate tool to predict the utility of various initiator systems for network polymerization, and on the basis of this data, benzoyl peroxide/dimethyltoluidine was chosen as the initiator for optimal performance.

As a matter of adjusting the ratio of benzoyl peroxide and dimethyltoluidine, a series of experiments were conducted using N-methylmaleimide and isobutyl vinyl ether as the linear copolymerizing donor acceptor pair. The dimethyltoluidine benzoyl peroxide molar ratio was varied from 0 to approximately 6, and these data are presented in Figure 40. The conclusion drawn from the results suggest that the molar ratio of DMT to DP should be a value of one or less.

8. EVOLUTION OF THE 2-TG CONCEPT FOR HIGH TG POLYMERS

One of the objectives defined in the original proposal submitted three years ago provides the genesis for the 2-Tg concept, which has evolved in the course of this research. The proposal suggested that polyethers could be used as comonomers during

Copolymerization of N-Ethylmaleimide and n-Butylvinylether with Benzoyl Peroxide/Dimethyltoluidine

Sample	Weight Percent Peroxide	Percent Maleimide Unreacted
3-14A	0.52	76
3-14B	0.95	13
3-14C	1.37	13
3-14D	1.90	18
3-14E	3.17	17

Copolymerization of N-Ethylmaleimide and n-Butylvinylether with Benzoyl Peroxide/Dimethylaniline

Sample	Weight Percent Peroxide	Percent Maleimide Unreacted
3-13A	1.96	22
3-13B	2.30	19
3-13C	2.73	14
3-13D	2.80	13
3-13E	3.17	16
3-13F	3.40	17

Copolymerization of N-Ethylmaleimide and n-Butylvinylether with t-Butylperoxypivalate/Dimethyltoluidine

Sample	Weight Percent Peroxide	Percent Maleimide Unreacted
3-20A	0.32	56
3-20B	0.56	82
3-20C	0.63	53
3-20D	1.03	79
3-20E	1.58	88
3-20F	1.99	54

Copolymerization of N-Ethylmaleimide and n-Butylvinylether with t-Butylperoxy maleic acid/Dimethyltoluidine

Sample	Weight Percent Peroxide	Percent Maleimide Unreacted
3-24A	0.51	59
3-24B	1.01	87
3-24C	1.37	65
3-24D	1.98	68
3-24E	2.43	64
3-24F	2.92	74

Figure 39. Measurement of Extent of Cure in Linear Polymers by Proton NMR

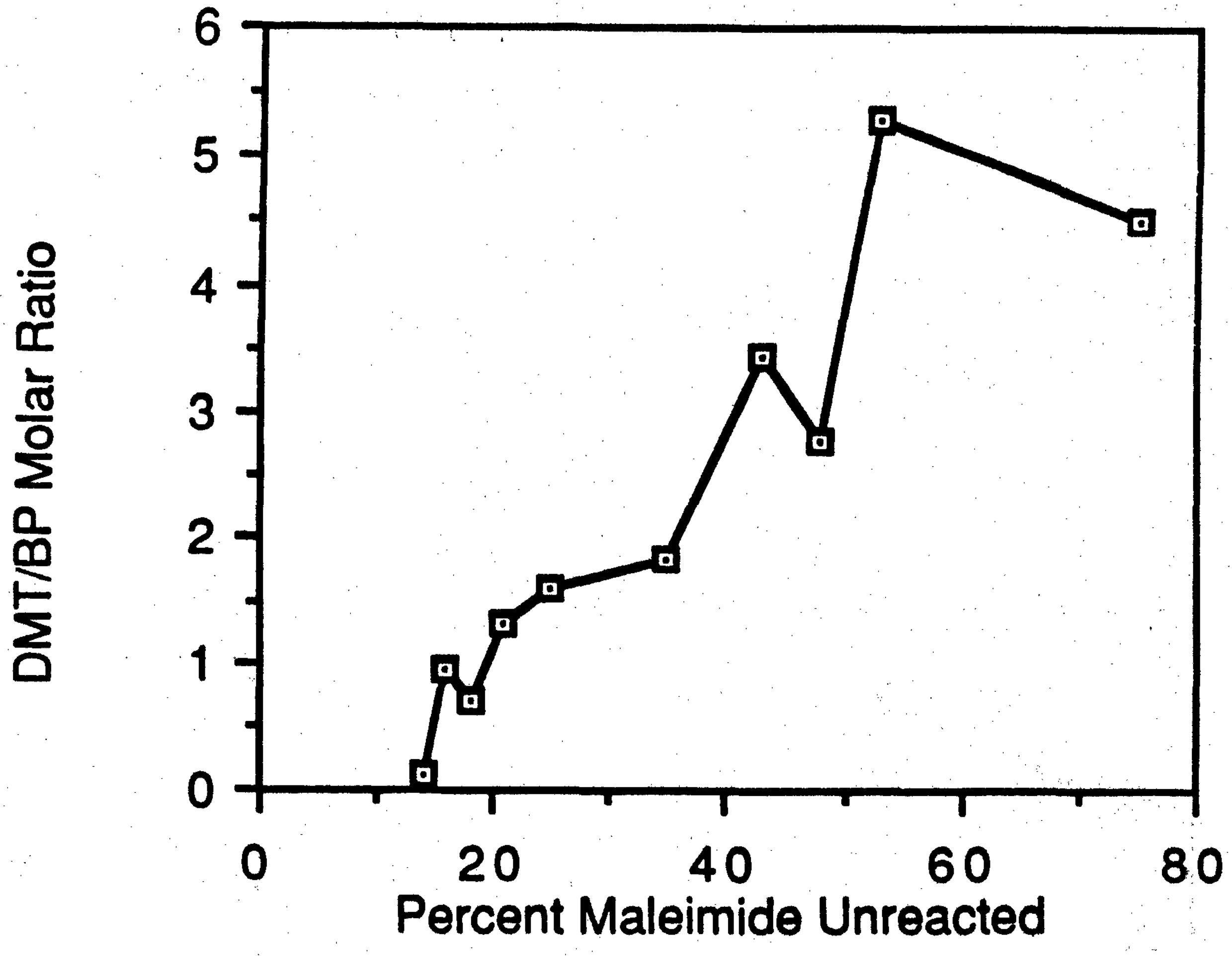


Figure 40. Copolymerization of N-Ethylmaleimide and i-Butylvinylether with Benzoyl Peroxide/Dimethyltoluidine

donor acceptor network copolymerization, such that the polyether would permit the network to relax and also would phase separate to serve as an energy absorbing phase. As our research progressed, it became clear that the polyether could serve another purpose, that being to act as the solvent to permit attainment of the highest possible glass transition temperature during formation of network polymer at room temperature. Figures 41 and 42 demonstrate that the 2-Tg concept indeed can be verified experimentally.

The 2-Tg concept requires that both a high Tg and a low Tg phase exist in the network polymer itself, wherein the low Tg component acts as a solvent permitting full relaxation, and the high Tg phase forms the "working" network. In our case, the low Tg component has been polyoxyethylene or polydimethylsiloxane terminated with required functionalities. For example, in Figure 41 the copolymerization of low molecular weight and high molecular weight tetrafunctional vinyl ethers with tetrafunctional bismaleimides shows that a distinct increase in the glass transition temperature is apparent even with as low a weight percentage as 2.5 percent polyether. Stated differently, the glass transition of the copolymer in the absence of the low Tg component is 236°C, whereas the glass transition temperature of the copolymer containing a low Tg component increases to 252°C. This increase in glass transition temperature can be attributed directly to the presence of the low Tg component solvent which permits natural relaxation of the network as it is being formed. Note also in Figure 41 that the TGA data show acceptable values.

Further verification for the viability of the 2-Tg concept can be seen in Figure 42 where two network copolymerizations are illustrated graphically. In this case, N-methylmaleimide is copolymerized with the tetrafunctional vinyl ether butene diol with increasing percentages of two different types of polyethers. For comonomer B, the polyether has a number average molecular weight of roughly 1200, and for polymer D, the number average molecular weight is approximately 2200. Both polymerizations were conducted

$CH_2=CHO(C_4H_8)OCH=CH_2$ +

+ $CH_2=CHO(C_2H_4O)_{22}CH=CH_2$

Weight Percent Polyether	Onset of Weight Loss	T_g
0	431 °C	236 °C
2.5	448	252
5	422	
15	428	
25	437	

Figure 41. Thermal Data Verifying the 2-Tg Concept

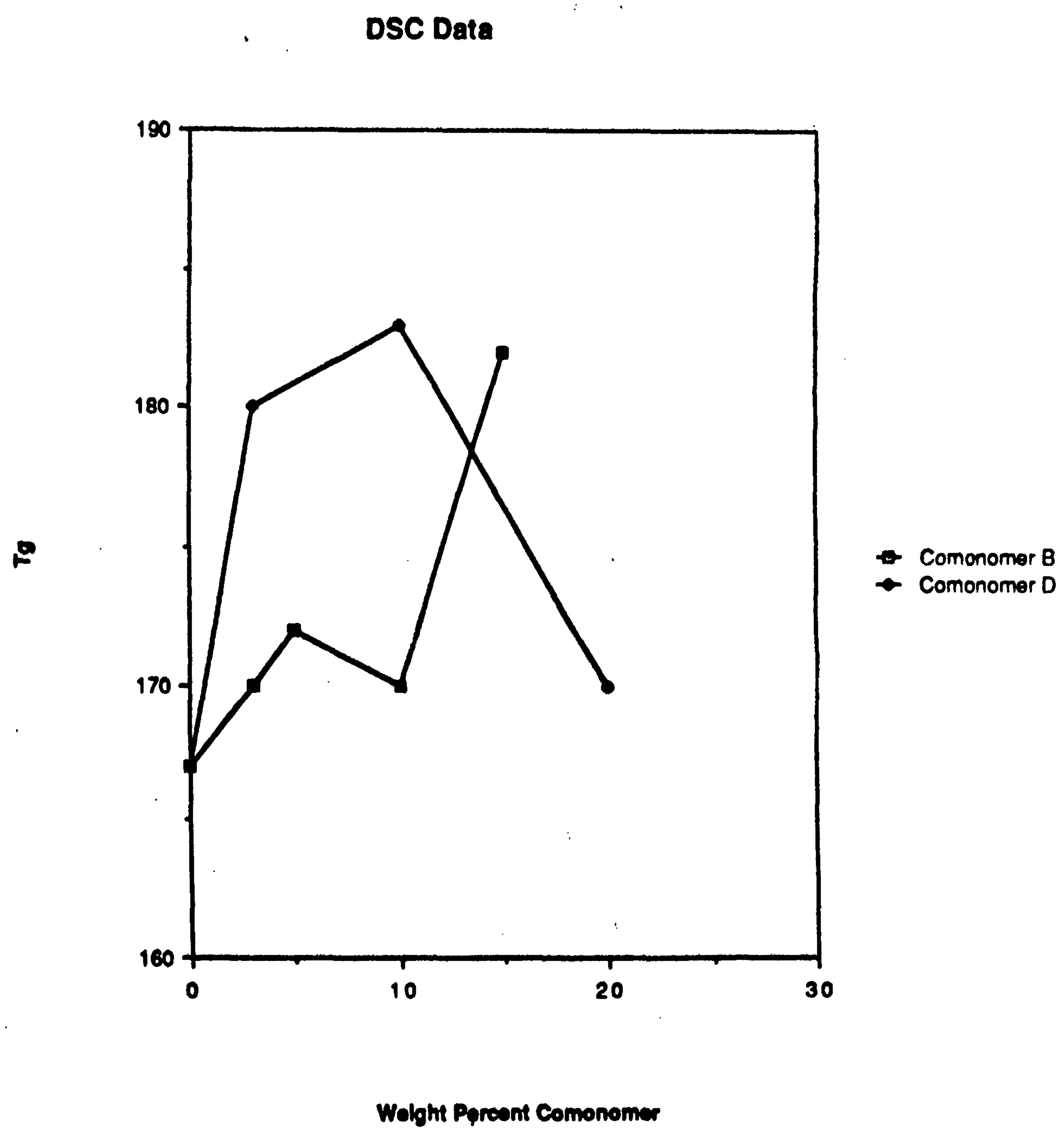


Figure 42. DSC Data Verifying the 2-Tg Concept

in essentially the same fashion using the benzoyl peroxide as the initiator system. Polymerizations were conducted at 70°C for two hours in 40 ml thick silicone molds to produce "dogbones".

The data clearly indicate an increasing trend in glass transition temperature as a function of increasing the weight percentage of the low Tg component. Figure 43 also illustrates that for a variety of copolymers of a similar nature the thermal decomposition temperatures are sufficiently high.

Finally, while the mechanical performance of these polymers was not determined, one would anticipate that the low Tg phase would enhance the impact resistance of the networks.

9. CONCLUSION - WHAT NEEDS TO BE DONE

The 2-Tg concept to high Tg polymers represents a novel approach to solving an old problem, that being how to create high temperature performance polymers under ambient temperature polymerization conditions. The solution to this problem would provide ample opportunity for applications, not only in the aerospace arena, but in other areas where high performance polymers are required under routine polymerization conditions. Figure 44 summarizes a series of polymerizations done at 70°C, and represents data roughly equivalent to that expected for ambient temperature conditions. These data show that glass transition temperatures can be enhanced by choosing comonomers that act as "solvents", and that the "onset of decomposition" temperature as measured by TGA analysis under nitrogen is sufficiently high to make the polymers themselves interesting. The data also show that the reaction systems exhibit small exotherms at temperatures around 200°C, indicating that extent of cure is not complete, though these exotherms in almost every case are relatively small and are occurring at temperatures higher than anticipated use temperatures.

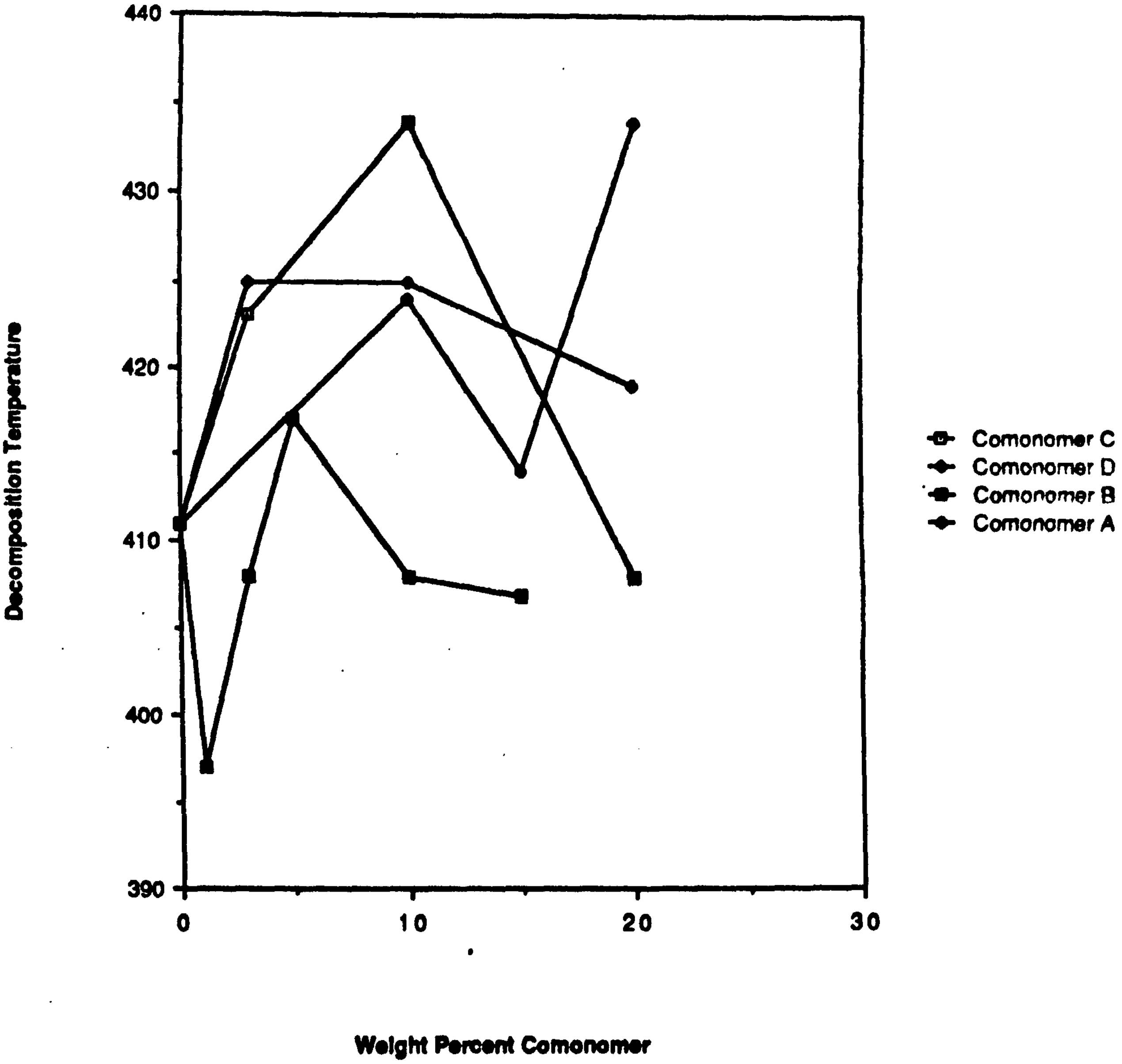


Figure 43. TGA Data

Sample	Comonomer[b]	Weight %[c]	Onset of Decomposition[d]	T_g	Exotherm
2-74	---	---	411°C	167°C	---
3-6A	A	20	434		---
3-6B	A	15	414		---
3-6C	A	10	424		180°C(s)
3-7B	B	15	407	182	199(s)
3-7C	B	10	408	170	195(s)
3-7D	B	5	417	172	135(s)
3-7E	B	3	408	170	---
3-7F	B	1	397	162	---
3-73A	C	20	408	177	195(l)
3-73B	C	10	434		132(s) 188
3-73C	C	3	423		127(s) 215(s)
3-74A	D	20	419	170	120(l)
3-74B	D	10	425	183	123(l) 210(s)
3-74C	D	3	425	180	128
3-75B[e]	B	10	412		128 190(l)
3-75C	B	3	415		132 190(l)

---

[a] Polymerized with lauryl peroxide at 70° for 2 hours in 40 mil thick silicone rubber molds.

[b] A: divinylether of PEO/PDMS ABA block copolymer (mol.wt. 2400)
B: divinylether of PEG 1000
C: divinylether of PEG 600
D: divinylether of PEG 2000

[c] Percentage of weight of copolymer.

[d] Measured in air atmosphere.

[e] Polymerized with benzoyl peroxide/ dimethyltoluidine at room temperture in 40 mil thick silicone rubber molds.

Figure 44. Thermal Characterization of Modified Copolymers of N-Ethylmaleimide and the Divinyl Ether of Butanediol[a]

The 2-Tg concept is only two years old and needs to be explored further in order to develop useful materials from such a novel approach. A systematic investigation of the correct volume percentage of "solvent" required, the nature of the "solvent" itself, and the structure of an appropriate ambient temperature initiator system, could yield materials of practical value.

For example, our preliminary research suggests that only low volume percentages of "solvent" are required in order to fully relax the high Tg network to an optimum value for its glass transition temperature. This needs to be investigated in more detailed fashion. Second, the nature of the "solvent" itself needs to be investigated since it would appear that the Tg of "solvents", such as polyoxyethylene or polydimethylsiloxane, may in fact be much lower than needed. Selecting a "solvent" whose glass transition temperature is just slightly lower than the polymerization temperature may be all that is actually required, in which case its negative effect, if any, on overall properties of the polymer will be reduced to a much larger extent. Finally, the research designed to determine optimal cure under various initiator conditions suggests that a broader study of such initiator systems is merited. We recommend that this research be actively pursued.

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