Aqueous Ring-Opening Metathesis Polymerization of exo-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide

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SYNOPSIS

The aqueous ring-opening metathesis polymerization of the exo-Diels–Alder adduct of furan and maleimide was accomplished using an "activated Ruthenium" catalyst present in the supernatant of a RuCl₃-catalyzed aqueous polymerization of furan–dimethylacetylene dicarboxylate adduct. The polymer was characterized by solution ¹H- and ¹³C-NMR, IR, DSC, and viscometry. Characterization revealed an intact imide group and the possibility of high-temperature applications. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The newly discovered aqueous ring-opening metathesis polymerization (ROMP)[1] of furan adducts offers an opportunity for synthesizing novel polymers with unique properties hitherto not possible. The classical ROMP catalysts, for example, are poisoned by polar functional groups (such as the —OH and —NH groups), whereas aqueous ROMP catalysts do not seem to be susceptible to these groups to the same extent. The Diels–Alder reaction of furan with dienophiles such as maleic anhydride and dimethylacetylene dicarboxylate occurs in high yields to be deemed economically feasible and may play a significant role in the practical application of aqueous ROMP.[2,3] High molecular weight and low polydispersity afforded by the aqueous ROMP technique will lend itself to physical characteristics that may be in the realm of engineering plastics or films. The Diels–Alder reaction of furan takes place only with excellent dienophiles, one of which is maleimide. The reaction yields the kinetic endo-adduct at room temperature and the thermodynamic exo-adduct when the reaction is carried at ≥ 90°C.

This paper discusses the polymerization (via aqueous ROMP technique) of the exo-adduct, as well as the spectral, thermal, and viscometric characterization of the resultant polymer. The spectral characterization of the polymer has not yet been reported. This is probably due to the polymer's lack of solubility in most solvents. The characterization of the related poly(exo-N-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide) has been done earlier.[4] The insolubility of poly(exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide) unlike the N-methyl-derivative has been attributed to interchain hydrogen bonding.[4] The spectral or viscometric characterization was not presented, probably due to this reason.

Figure 1 shows the route undertaken for the synthesis of the polymer of the exo-adduct synthesized in our laboratory.

EXPERIMENTAL

¹H- and ¹³C-NMR spectra were recorded on a Bruker AC-F 200 MHz (50 MHz ¹³C) instrument. Chemical shifts are referenced to residual protons on deuterated solvents. IR spectra was acquired on a Perkin-Elmer ratio recording spectrometer. Samples used for IR data were in the form of pressed KBr disks. Thermal analysis was performed on a Mettler DSC-20 with a scan rate as indicated in Figure 5. TGA
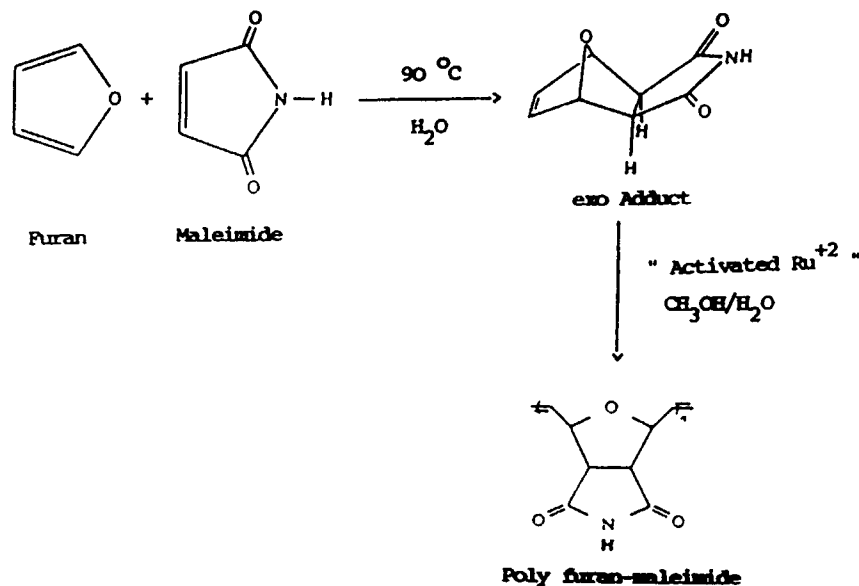

Figure 1 Proposed route for the synthesis of poly(exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide).

was performed using a DuPont 951 thermogravi-metric analyzer. Viscosity measurements were made using Cannon-Ubbelohde viscometer that permitted serial dilutions to be made directly in the viscometer. All reagents were purchased from the Aldrich Chemical Co., Milwaukee, WI.

Monomer Synthesis

Synthesis of exo-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (exo-furan maleimide adduct)

The synthesis of the monomer was accomplished by a previously published procedure[5] with slight modifications. To 1.5 g of furan (MW 68.1, 0.022 mol) in 75 mL of water was added 1.42 g of maleimide (MW 97.07, 0.0146 mol), so that furan was 50% in excess. The resulting solution was heated in a sealed bottle for 10 h in a water bath maintained at 90°C. The white crystalline adduct separated from the reaction mixture on cooling. The crystals were filtered and washed with water several times, before being vacuum-dried. The product was obtained in 52% yield (observed mp, 162°C; literature mp,[5] 162°C). The ^{1}H-NMR shift values (d_6-DMSO solvent) of the exo-adduct were 2.9 ppm for the methine protons, 5.1 ppm for allylic protons, 6.5 ppm for the olefinic protons, and 11.1 ppm for the imide proton.

The ^{13}C-NMR shift values were 177.9 ppm for the carbonyl carbons, 136.5 ppm for olefinic carbons, 80.3 ppm for allylic carbons, and 48.5 ppm for methine carbons. No peaks due to the endo-isomer were observed.

Polymer Synthesis

Synthesis of Poly(exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide), i.e., Poly(exo-furan maleimide)

The exo-furan maleimide adduct, 0.3 g (MW 166, 1.81×10^{-3} mol) was dissolved in 2 mL CH$_3$OH. To this was added fresh "activated Ru^{2+} species" (5% mol ratio of catalyst to adduct) that was present in the entire supernatant after the polymerization of 0.1 g of furan–dimethylacetylene dicarboxylate (F-DMAD) adduct in 2.5 mL CH$_3$OH and 0.5 mL of deionized degassed H$_2$O using 0.0187 g (9.04×10^{-5} mol) of RuCl$_3$ (MW 207.42).

The final reaction mixture contained 4.5 mL of CH$_3$OH and 0.5 mL of deionized degassed H$_2$O. This solution was heated under vacuum in a water bath at 55°C. The initiation of polymerization (as evident by polymer precipitation) occurred in about 3–5 min. The reaction was continued for 30–35 min until no more polymer was formed. The off-white polymer was washed several times with water and then with

CH₃OH. It was then washed several times with ace-
tone, and the pure white polymer was finally washed
with water and vacuum-dried. The yield of the poly-
mer obtained was 50%.

RESULTS AND DISCUSSION

We report here the characterization of the polymer
from furan–maleimide adduct using aqueous ROMP.
The characterization of the polymer in the solution
state via NMR and viscometry has been possible

due to the solubility of the polymer in DMSO. The
imide functionality is susceptible to ring opening by
hydrolysis in the presence of several transition metal
salts. The susceptibility of functional groups to ox-
idation and deactivation of catalyst has been a
problem with monomers containing polar functional
groups. Aqueous ROMP catalysts that could over-
come this reaction would offer the possibility of syn-
thesis of novel polymers with unique properties. The
presence of imido groups in a polymer with possible
high-temperature applications is such an example.

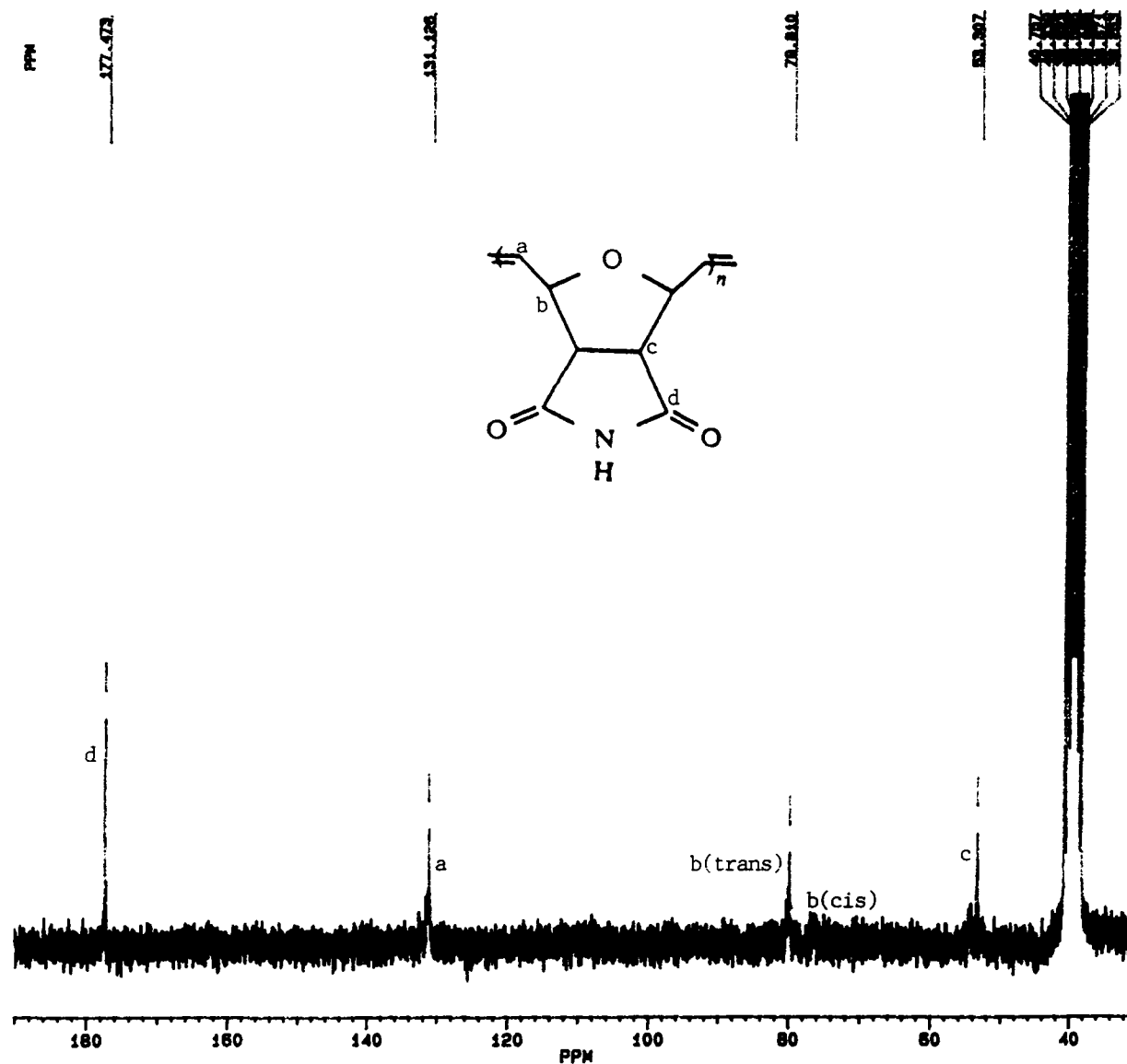Earlier, the polymerization of the Diels–Alder

Figure 2   ¹³C-NMR spectrum of furan–maleimide polymer (d₆-DMSO solvent with TMS
as internal standard).

adduct of furan and maleic anhydride by $RuCl_3$ has been carried out to yield the polyacid derivative.[6,7] The anhydride hydrolyzed to the acid during the polymerization process. The structural similarity of the imide to the anhydride might suggest a similar problem, even though imide linkages are more resistant to hydrolysis.

Since the polymer initiation and propagation might be in competition with the possible hydrolysis and subsequent deactivation of the catalyst, an "activated Ru^{2+}" present in the supernatant of an already polymerized 7-oxanorbornene species might be a better catalyst for the polymerization of a furan–maleimide monomer.

The "activated Ru^{2+}" present in the supernatant of $RuCl_3$-catalyzed polymerization of F-DMAD has been used to polymerize other 7-oxanobornene systems.[2,3] We chose to polymerize the furan–maleimide adduct with the same activated catalyst for the reason mentioned above. We wanted to see if polymerization of the monomer occurred in the expected manner with the imido group remaining intact.

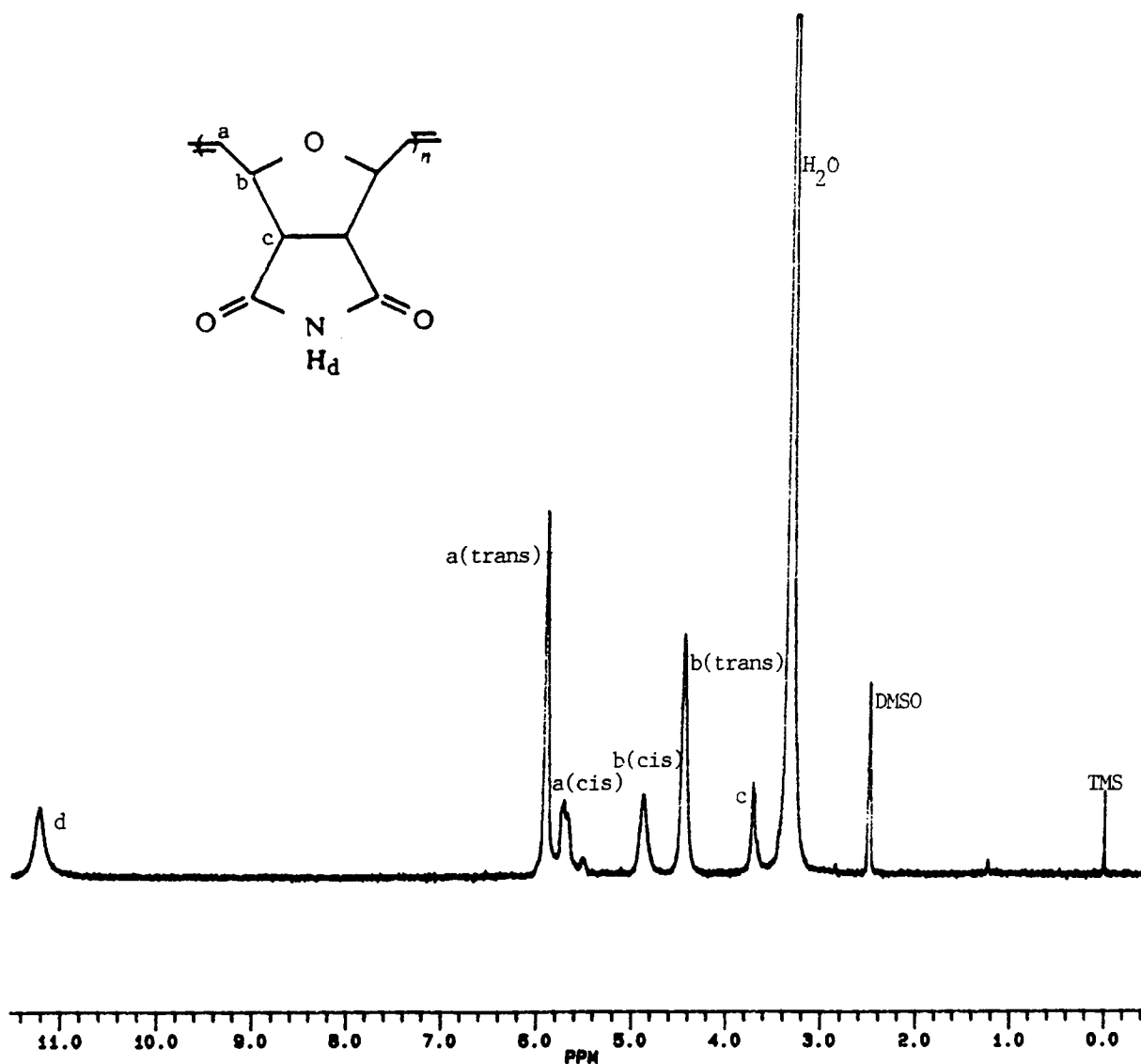The pure (white) polymer obtained was characterized by ^{1}H- and ^{13}C-NMR, IR, DSC, and viscom-

Figure 3 ^{1}H-NMR spectrum of furan–maleimide polymer (d_6-DMSO solvent with TMS as internal standard).
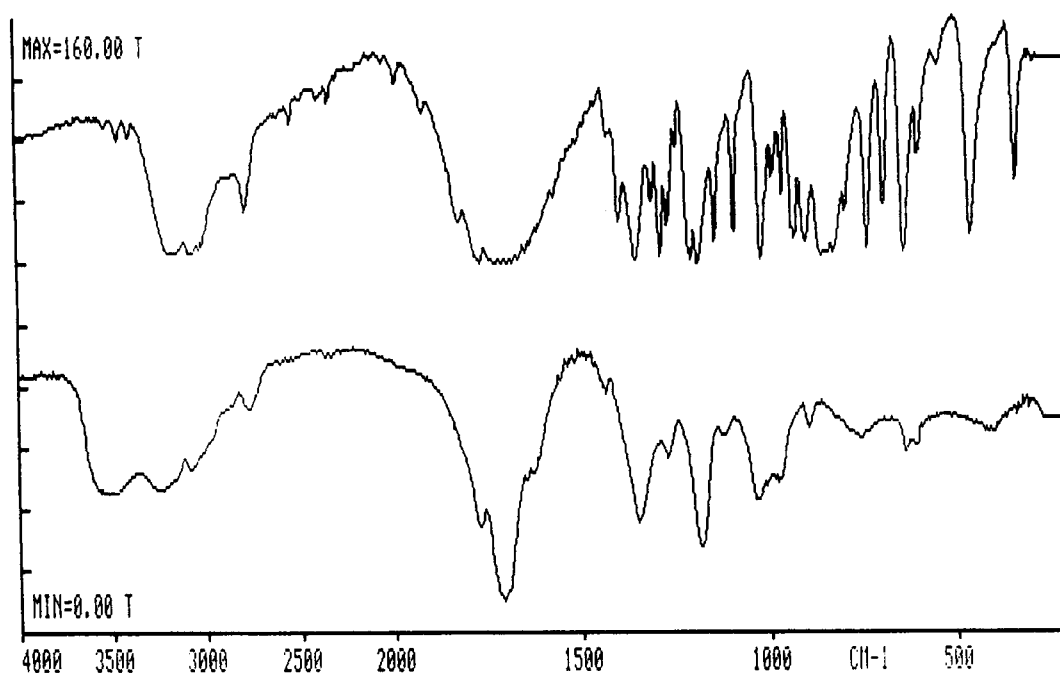
Figure 4 IR spectrum of furan–maleimide monomer (top) and polymer (bottom) in KBr pellet.

etry. We found that the polymer was soluble in DMSO upon slight heating, with a noticeable increase in viscosity at 0.5 g/dL. Viscometry showed an intrinsic viscosity of 2.27 dL/g at 25°C with DMSO as solvent.

The ^{13}C-NMR (50 MHz ^{13}C) in d_6-DMSO (TMS internal standard) is shown in Figure 2. In comparison to the monomer, the chemical shifts of olefinic carbons and to a lesser extent the allylic carbons shift upfield while the methine carbons shift downfield. The trans-isomer predominates in the spectrum with small amount of cis-isomer showing up. The peak at 177 ppm corresponds to the carbonyl carbons.

The absence of hydrolysis of the imido group is seen more clearly in the ^{1}H-NMR (200 MHz) of the polymer in Figure 3. The peak at 11.3 ppm corresponds to the N — H peak and correlates well with the N — H peaks of other symmetrical imides.

The IR spectrum of the solid polymer in KBr shown in Figure 4 corroborates with the presence of the intact imide as seen by the asymmetric stretch close to 1800 cm^{-1}, a peak that is also seen in intact anhydrides. Two peaks due to secondary N — H is also seen at $\approx$ 3000 and 3200 cm^{-1}.

The DSC of the polymer in Figure 5, in the first run, indicates several exotherms with one peak as high as 600°C. The same sample was cooled to room temperature and was run again. In second run, the DSC indicated only one exotherm at 458.7°C. This exotherm suggests a possibility of either cross-linking within the polymer or degradation of the polymer. The same sample was again cooled to room temperature and run for a third time. A look at this DSC showed no thermal transitions in the polymer, indicating probable decomposition of the polymer.

The TGA of the polymer, shown in Figure 6, indicates weight loss after reaching 325°C, suggesting that the first exotherm at 280°C in the DSC run is not associated with loss of volatiles but is, rather, a true transition. The polymer completely oxidizes and disappears by $\sim$ 405°C in the TGA apparatus. However, since the DSC was run in an enclosed system (aluminum capsule), we continue to see other transitions/exotherms upon heating of the degradation products.

The intact imido group in the polymer side chain and the solubility in DMSO offers the possibility of cross-linking with polyisocyanates to yield high-

TEMPERATURE °C

HEAT FLOW
EXOTHERMAL ---▶

50.000 mW

100.00

200.00

300.00

400.00

500.00
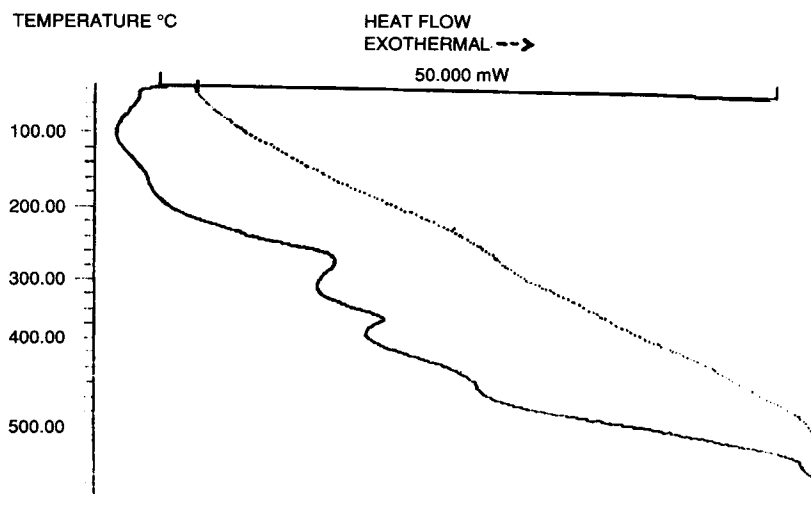
AH ENDO mJ	23678
AH J/G	5919.5
PEAK TEMP. °C	194.7
REACT. ORDER	−0.23
CONF. LIMIT	0.37
E A KJ/MOL	1.19
CONF. LIMIT	3.91
LN Ko	−7.06
CONF. LIMIT	1.09

TEMPERATURE °C

HEAT FLOW
EXOTHERMAL ---▶

20.000 mW

100.00

200.00

300.00

400.00

500.00
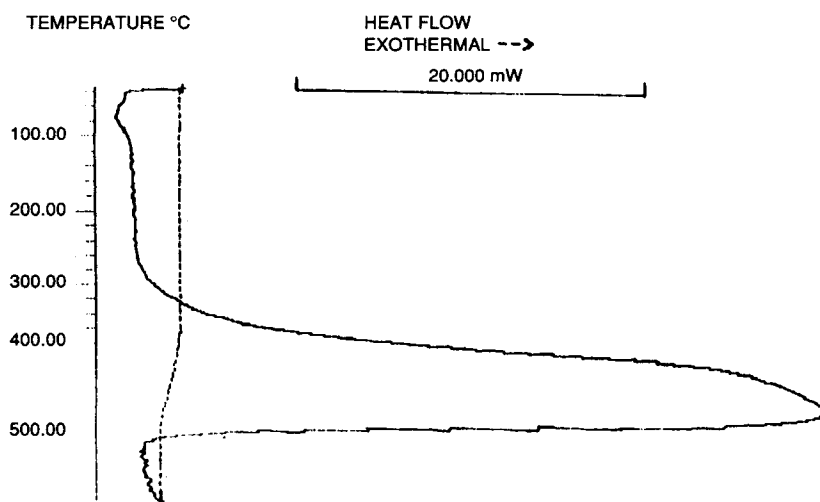
AH EXO mJ	9457.1
AH J/G	2364.3
PEAK TEMP. °C	458.7
REACT. ORDER	0.19
CONF. LIMIT	0.04
E A KJ/MOL	30.08
CONF. LIMIT	3.32
LN Ko	−0.40
CONF. LIMIT	0.58

Figure 5   (Top) DSC of furan–maleimide polymer (scan rate of 20 K/min) (first run). (Bottom) DSC of the same sample after cooling to room temperature (scan rate of 20 K/min) (second run).

Sample: POLY (FURAN-MALEIMIDE)
Size: 2.3440 mg
Method: HEAT 20C/MIN TO 500C

TGA

File: A: DATA.100
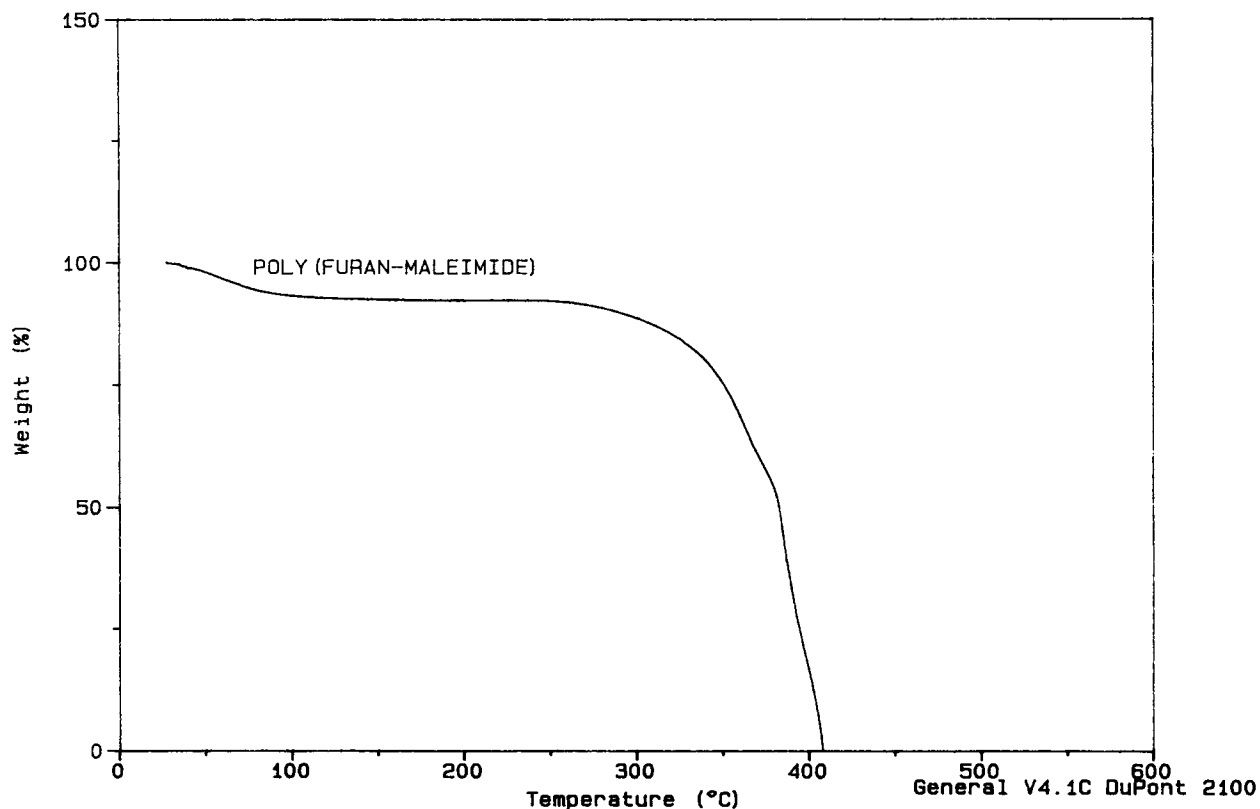Operator: AKR
Run Date: 17-Jul-92 11: 11

Figure 6   TGA of furan–maleimide polymer (rate of 20°C/min) in air.

temperature coating materials. Such work is under-way in our laboratory.

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