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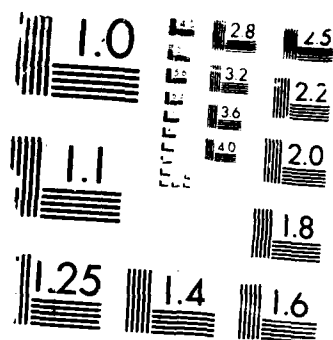
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SYNTHESIS AND CHARACTERIZATION OF 1,2-CYCLOBUTENEDICARBOXAMIDES:
THERMALLY GENERATED POLYMERS AND DIELS-ALDER ADDUCTS

by

Douglas G. Powell and Lon J. Mathias

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Department of Polymer Science
University of Southern Mississippi
Southern Station Box 10076
Hattiesburg, MS 39406-0076

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SYNTHESIS AND CHARACTERIZATION OF 1,2-CYCLOBUTENEDICARBOXAMIDES: THERMALLY GENERATED POLYMERS AND DIELS-ALDER ADDUCTS

Douglas G. Powell and Lon J. Mathias*
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406-0076

ABSTRACT

A series of model diamides were synthesized from mono- and disubstituted amines with the diacid chloride of cyclobutene-1,2-dicarboxylic acid. Yields ranged from 30 to 70%. Melting points of the purified diamides ranged from less than 23°C for N-alkyl and N,N-dialkyl species to 204°C for the N-phenyl model. Relative rates of thermolysis (by DSC) with maxima from 208-224°C at 10°C/min. were dependent on the number and type of substituents, and on intramolecular hydrogen bonding. Thermolysis products were Diels-Alder dimers for N-mono-substituted materials and for bulky tetrasubstituted models, and spontaneously formed polymers for two tetrasubstituted models with at least one methyl group on each nitrogen. Thermal imidization of cycloadducts was possible in some cases with concomitant oxidation to tetrasubstituted aromatic bisimides.

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SYNTHESIS AND THERMOLYSIS OF 1,2-CYCLOBUTENEDICARBOXAMIDES: THERMALLY GENERATED POLYMERS AND DIELS-ALDER ADDUCTS

Douglas G. Powell and Lon J. Mathias*
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406-0076

Introduction

2,3-Disubstituted cyclobutenes and their thermally generated butadiene derivatives undergo a rich variety of reactions. The cyclobutenes can react via cycloaddition with appropriate dienes¹, and thermally ring-open to the corresponding substituted butadienes^{1,2}. The resulting dienes in turn have been found to spontaneously dimerize and polymerize^{3,4}, and to react with dienophiles in typical [4 + 2] cycloadditions⁴. We are currently exploring these compounds for synthesis of polybutadienes, and for curing of thermosetting polymers and composites. The latter application involves the incorporation of relatively non-reactive functionality into tough composite matrix polymers for potential use as one-pot thermally-activated curing systems. The former provides a synthetic pathway to a unique family of 2,3-disubstituted poly-1,4-butadienes which may be converted to the head-to-head polyacrylamides not readily available by other synthetic routes.

We previously described our initial results on the thermal reactions of several model diamides and polyamides⁵. Of three derivatives with two or four nitrogen substituents (1-3), only compound 2 spontaneously polymerized while the others cyclodimerized. In an effort to further understand the factors controlling the spontaneous reactions of the butadienes generated by thermal ring-opening, we have synthesized a number of additional derivatives 4-9 (Figure 1) and examined their properties and behavior. We report here the general synthesis of these compounds, their thermal reaction energetics, and their expected and unexpected reaction products.

Results and Discussion

Substituted Cyclobutene Synthesis

Amide formation traditionally involves thermal dehydration of amine-carboxylic acid mixtures, although this method requires temperatures which, in our case, cause thermolysis of the cyclobutene group. Alternative procedures utilize high-energy intermediates such as acid chlorides, anhydrides or mixed anhydrides, or *in situ*

generated active esters of the carboxylic acid group.^{6,7} The previously reported diacid chloride of 1,2-cyclobutene-dicarboxylic acid was found to provide a facile route to the desired compounds. The general synthesis described previously⁵ was extended to the other derivatives 4-9. Isolated yields, melting points and ¹³C NMR spectral properties of these compounds are given in Table 1.

Table 1. 1,2-Cyclobutenedicarboxylic Diamides Yields, Melting Points and ¹³C NMR Characteristics.

Cmpd	Yd %	T _m °C	Chemical Shift (ppm)			
			1	2	3	alkyl and aryl carbons
1	55	185-187	163.5	144.2	29.3	126-130
2	63	150-152	163.9	143.5	29.3	37.4 37.0 126-131
3*	68	202-204	159.9	144.7	25.5	137.5 128.3 123.9 120.0
4*	46	72-73	169.3	142.2		46.8
5	34	56-57	165.0	146.2	24.7	41.4 34 31.3 31.1 29.0
6*	45	oil	166	148.5	25	49 43 30.1 25 23.8 18.4
7	77	oil	163.5	139.5	28.4	36.3 33.8 (N-CH ₃)
8	40	155-160	161.1	143.7	32.6	
9	32	159-162	164.8	136.5		

*in DMSO-d₆ rather than CDCl₃

Many of the crude compounds contained residual amines which would inhibit radical polymerization. Purification in some cases required chromatography and/or recrystallization. Final purity was established with GC to be greater than 99% in all cases.

Thermal Analysis by DSC

DSC was used to investigate the onset and breadth of the various thermally-induced transitions and reactions, and to determine the enthalpy of the individual or combined processes. Figure 2 gives several typical DSC traces showing multiple exotherms during the heating of compounds that either polymerize exclusively or only cyclodimerize. Table 2 lists the values for the melting points determined by DSC, the exotherm maxima (T_{max}), and enthalpies for the peaks. For a given scan rate, the position of the maximum of a specific peak is an indication of the relative reaction rate⁸. Interestingly, for the cyclobutene ring-opening process, T_{max} varies less than 20°C for the series of derivatives 1-9.

Table 2. Thermal Analysis Results by DSC.

Cmpd	R	R'	T ^m (°C)	T _{max} (°C)	
1	phenyl	phenyl	186.2	224.2	13.6
2	-	methyl	phenyl	151.8	220.6
3	H	phenyl	202.5	(211) ^a	20.5
4	H	n-dodecyl	72.0	208.3	11.4
5	H	n-heptyl	56.4	208.2	23.2
6	H	i-pentyl	--- ^b	208.2	17.4
7	methyl	methyl	--- ^b	214.5	24.6
8	H	cyclohexyl	156.0	208.2	14.7
9	cyclohexyl	cyclohexyl	183.6	228.4	21.4

^aPeak obscured by melt endotherm

^bViscous oils at room temperature

Cyclobutenes substituted in the 3-position, on the other hand, show a wide range of thermolysis rates depending strongly on the type of substituent⁹. It may be that the nitrogen substituents on 1-9 are too far removed from the strained ring to much effect the ring-opening energetics which are controlled mostly by the presence of the two adjacent carboxamide moieties. Within the 20° range observed, however, there does seem to be some correlation with the ability of the amide groups to intramolecularly hydrogen bond, and on whether the substituents are alkyl or aryl. The rate of reaction decreases in the order N-alkyl > N-aryl > N,N-dialkyl > N-alkyl-N-aryl > N,N-diaryl. Hydrogen bonding increases the rate while aryl substituents decrease it.

The experimental heats of reaction (ΔH_r) vary widely but do not appear to relate to the number or type of substituents. This is probably the result of the DSC exotherms being combinations of two or more reactions: ring-opening followed by either or both polymerization and cycloaddition such that

$$\Delta H_t = \Delta H_r + (\Delta H_p + \Delta H_c)$$

Indeed, compounds 4-6 show two overlapping exotherms clearly demonstrating the consecutive nature of the reactions. These three compounds undergo almost exclusive Diels-Alder addition while compounds 2 and 7 give only polymeric products. The DSC scans of the last two compounds show only one exothermic peak, however.

The appearance of a single peak is not exclusive to polymer formation, however, since compound 1 shows only one peak yet undergoes only cycloaddition. The rate of the addition reaction is so much slower than ring-opening that only the latter is detected

by DSC at these scan rates. In fact, NMR analysis of this compound clearly shows the appearance of the butadiene species before gradual disappearance with formation of the cycloadduct (Figure 3).

The polymerizability of the butadiene compounds, as well as the imidization process described later in the text, may be directly related to the occurrence of intramolecular hydrogen bonding in both the cyclobutene and the butadiene. Although the 7-membered cyclic structure required for the hydrogen bond in the former may at first appear strained, the large angle of the sp^2 hybridized carbons¹⁰ of the ring may actually favor this structure (Figure 4a-4c). X-ray analysis has confirmed the existence of strong intramolecular hydrogen bonding in cyclobutene-1,2-dicarboxylic acid¹¹ which has been suggested as the reason for the opposite endo:exo ratio for its cycloaddition adducts compared to non-hydrogen bonding analogs⁵. The dimethyl ester, which is not capable of intramolecular hydrogen bonding, gives only polymer on thermolysis^{12,13}.

The polydiene from **2** was a brittle transparent solid. DSC showed a transition (T_g) at 122.5 °C. The polymer had an intrinsic viscosity of 0.36 dl/g in hexafluoro isopropanol, and is soluble in methylene chloride, acetone and dimethylformamide. GPC analysis showed a broad molecular weight distribution typical of free radical addition polymers with an M_n of 189,000 (based on polystyrene standards). The polydiene from **7** was a brown viscous oil which was soluble both in common organic solvents and in water. This polymer, however, precipitated in THF making GPC analysis impractical on our systems.

Figure 5 shows ^{13}C NMR of the polydiene from thermolysis of **2**. The vinyl and methylene resonances of the polymer backbone are typically broad while the pendent methyl and phenyl groups on the nitrogen are much sharper. The absence of resonances in the region 110-120 ppm indicates little, if any, 1,2-addition in the polymers. Although the polymerization appears to be exclusively by 1,4-addition, the presence of two distinct resonances each for the carbonyl, vinyl, and methylene indicate that the stereochemistry about the double bond is a mixture of E and Z isomers. No attempt was made to assign the resonances to a particular geometrical isomer.

Figure 6 shows the solid state ^{13}C NMR of **3** along with the proposed intramolecular hydrogen bonded structure. The difference in chemical shift seen for the vinyl carbons is consistent with different shielding and deshielding environments that would be experienced by the nuclei in such a structure. This demonstrates a unique solid state interaction which we believe affects the ultimate reactivity of the model compounds and polyamides in the melt and even in solution.

Diels-Alder Cycloaddition Reactions

Various 2,3-disubstituted butadienes have been found to be excellent dienes in cycloaddition reactions despite the fact that they contain electron withdrawing substituents. For example, the dinitrile reacts with a variety of dienophiles when used as a previously generated species^{2,5} or when formed *in situ* by thermolysis of the cyclobutene⁴. The 1,3-butadiene-2,3-dicarboxylic acid has also been reported to undergo Diels-Alder dimerization in solution⁴. The cycloaddition chemistry of the dicarboxamide derivatives offers potential application in composite matrix forming reactions. Model systems were studied to evaluate such reactions with compounds 1-9.

The butadiene derived from 1 was chosen first as an extreme example involving intermolecular steric interactions of the four N-phenyl groups. This diene forms readily by thermolysis in bulk and in N-methylpyrrolidone but does not polymerize. It can be isolated and is stable at room temperature. NMR analysis of a nitrobenzene solution of this diene confirms gradual dimerization at 185° C leading to high yields of the cyclodimer shown in Figure 4.

Cyclobutene 1 was also reacted with N-phenylmaleimide in nitrobenzene at 185° C. NMR monitoring indicated high conversion to the cycloadduct 10 (Figure 7, eq. 1) with no evidence of unreacted starting material or byproducts.

The cycloaddition of N-phenylmaleimide was also carried out with 3 under the same conditions over a 24 h period. Gold platelets precipitated from the homogeneous solution in 11% yield. Microanalysis of these crystals, however, was inconsistent with the expected cycloadduct structure 11. Solution NMR was not possible since the crystals were insoluble even in concentrated sulfuric acid. IR and solid state ¹³C NMR analysis confirmed aromatization of the cyclohexene ring, and disappearance of the amide hydrogens. The reaction process was finally deduced to involve loss of one of the amide nitrogen groups via imide formation, which converts 11 to 12 (Figure 7). Structure 12 is consistent with the data and with a previously reported melting point for this compound of 453°C¹⁴ vs. our value of 452.5°C (determined by DSC).

The remaining soluble fraction from the above reaction was precipitated from nitrobenzene to give a solid that readily dissolved in DMF and DMSO. Heating this solid in air led to gradual formation of an insoluble material that appeared to consist mainly of 12. Conversion of this initial cycloadduct to the 1,2,4,5-benzenetetracarboxylic acid diimide provides a novel synthesis of this material and opens up a new synthetic approach to rigid rod polyimides involving soluble intermediate polymers undergoing thermal cyclization and aromatization.

Experimental

General Procedure for Preparation of Model Cyclobutene Amides

Preparation and purification of cyclobutene-1,2-dicarboxylic acid chloride is described elsewhere⁴. In a typical reaction, the amine was dissolved in 75ml dry chloroform or methylene chloride in a 125ml Erlynmeyer flask with an equimolar amount of triethylamine added as a scavenger for the HCl produced. One equivalent of the acid chloride was added dropwise *via* pipette to the stirred solution. A generous amount of heat was liberated and the addition moderated to prevent the solvent from boiling. The pipette was rinsed with the stirred solution to remove any remaining acid chloride and the solution allowed to stir for 20-30 minutes. The homogeneous solution was taken up in an extraction funnel and washed twice with 10 ml portions of aqueous 1 M NaOH, 1 M HCl, and deionized water. The organic layer was dried over anhydrous MgSO₄. The drying agent was filtered and washed with methylene chloride and the combined solvent layers evaporated from the product.

Purification of the crude product was accomplished by dissolving in a minimal amount of boiling methanol or methanol/water mixture and allowing recrystallization at room temperature. Compounds 1 and 3 were additionally purified by column chromatography (silica gel with a mobile phase of 1:1 chloroform/methanol). Compounds 6 and 7 were viscous oils and failed to crystallize. They were purified by column chromatography and dried *in vacuo* at 70° C.

Polymers derived from the thermolysis of 2 and 7 were purified by dissolving them in methylene chloride and precipitating in n-hexane.

Dimethylamine was purchased from Alfa Chemical as a solution in ether. Other amines were purchased from Aldrich Chemical Company and were used as received. Triethylamine was distilled from NaOH and stored over 4A molecular sieves. All solvents were of reagent grade purity or better and used without further purification.

¹³C NMR high-resolution and solid-state spectra were acquired on a Bruker MSL 200 spectrometer at a frequency of 50.32 MHz. NMR chemical shifts are reported in ppm from TMS (0 ppm). FT-IR spectra were recorded on a Nicolet 5DX FT-IR spectrometer and data station. Microanalyses were performed by Desert Micoranalysis, Tucson, Arizona. Thermal analyses was performed on a DuPont 910 Differential Scanning Calorimeter equipped with a DuPont 9000 controller and data station. GPC of polymers was performed on a Waters 6000A solvent pump, UV detector (250 nm), and Styragel columns (THF solvent).

N,N,N',N'-tetraphenyl cyclobutene-1,2-dicarboxamide (1): Prepared in 55% yield from diphenylamine, m.p. 185-187° C; IR (KBr, cm^{-1}): 3057, 2938, 1659, 1641, 1619, 1593, 1493, 1350, 762, 696; Anal. Calcd. for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_2$: C, 81.06; H, 5.44; N, 6.30%. Found: C, 79.83; H, 5.44; N, 6.10%.

N,N'-diphenyl-N,N'-dimethyl cyclobutene-1,2-dicarboxamide (2): Prepared in 63% yield from N-methyl aniline, m.p. 150-152° C; IR (KBr, cm^{-1}): 3044, 2970, 2919, 1657, 1643, 1632, 1614, 1590, 1372, 1110, 702; Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2$: C, 74.97; H, 6.29; N, 8.73%. Found: C, 74.67; H, 6.33; N, 8.73%.

N,N'-diphenyl cyclobutene-1,2-dicarboxamide (3): Prepared in 68% yield from aniline, m.p. 202-204° C; IR (KBr, cm^{-1}): 3294, 3027, 2937, 1664, 1620, 1595, 1537, 751, 689; Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$: C, 73.95; H, 5.51; N, 9.58%. Found: C, 73.85; H, 5.69; N, 9.61%.

N,N' di-n-dodecyl cyclobutene-1,2-dicarboxamide (4): Prepared from n-dodecylamine in 46% yield, m.p. 72-73° C; IR (neat, cm^{-1}): 3289, 2961, 2921, 2852, 1659, 1616, 1582, 1538, 667; Anal. Calcd. for $\text{C}_{30}\text{H}_{56}\text{N}_2\text{O}_2$: C, 75.37; H, 11.83; N, 5.87%. Found: C, 75.53; H, 12.17; N, 5.97%.

N,N' di-n-heptyl cyclobutene-1,2-dicarboxamide (5): Prepared from n-heptylamine in 34% yield, m.p. 56-57° C; IR (neat, cm^{-1}): 3240, 3036, 2924, 2853, 1658, 1604, 1537, 1241, 695; Anal. Calcd. for $\text{C}_{20}\text{H}_{36}\text{N}_2\text{O}_2$: C, 71.38; H, 10.78; N, 8.32%. Found: C, 71.25; H, 11.16; N, 8.21%.

N,N' di-i-pentyl cyclobutene-1,2-dicarboxamide (6): Prepared from 1-methyl butylamine in 45% yield as a viscous oil. Anal. Calcd. for $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_2$: C, 68.53; H, 10.06; N, 9.99%. Found: C, 67.03; H, 9.94; N, 9.38%.

N,N,N',N'-tetramethyl cyclobutene-1,2-dicarboxamide (7): Prepared from a solution of dimethylamine in ether in 77% yield as a viscous oil. IR (neat, cm^{-1}): 2926, 1712, 1620, 1504, 1404, 1195, 875.

N,N'-dicyclohexyl-1,2-dicarboxamide (**8**): Prepared from cyclohexylamine in 40% yield as a white, crystalline solid, mp 155-160° after recrystallization from methanol. IR (KBr, cm^{-1}): 3276 (broad), 3045, 2927.7, 2854.5, 1657.8, 1619.6, 1562.3, 1535.6, 1449.6, 1350, 1245, 1168.8, 893.71, 700.77.

N,N,N',N'-tetracyclohexyl-1,2-dicarboxamide (**9**): Prepared from dicyclohexylamine in 32% yield as a white, crystalline solid, mp 159-162 after recrystallization from methanol. IR (KBr, cm^{-1}): 2934, 2853.5, 1713, 1626.7, 1546.1, 1439.8, 1366.2, 1313.6, 1227, 1182, 1126.7, 896.5, 750.5.

1,2-N,N,N',N',-tetraphenyl diamido-4,5-N''-phenylimido cyclohexene (**10**): 0.0578 g **1** (0.118 mmol) and 0.0247 g N-phenyl maleimide (0.142 mmol) were dissolved in 1 ml nitrobenzene in a screw-cap vial. The vial was heated in an oil bath at 185-190° C for 6 hrs. The nitrobenzene was evaporated under vacuum yielding 0.063 g of crude product. The product was purified by liquid chromatography (1:1 MeOH/ CHCl_3 on silica gel) and the solvent evaporated to give 0.037 g (51%) of **8**, m.p. 145-148° C; IR (KBr, cm^{-1}): 3060, 2931, 1710, 1650, 1490, 1381, 1176, 759, 695; ^{13}C NMR (nitrobenzene) 177.5, 168.8, 143, 40.2 (d), 27.9 (t).

1,2-N,N'-diphenyl diamido-4,5-N''-phenylimido cyclohexene (**11**): 0.0814 g of **3** (0.28 mmol) and 0.05 g N-phenyl maleimide (0.29 mmol) were dissolved in 1 ml nitrobenzene in a screwcap vial. The vial was heated in an oil bath at 180-190° C for 24 hrs. During this time, a small amount of precipitate formed. The crude mixture was dissolved in 50 ml of hot methanol and insoluble precipitate filtered from the solution. The methanol and residual nitrobenzene were evaporated to give 0.067 g (52%) crude **9**, m.p. 138-142° C; IR (KBr, cm^{-1}): 3360, 3057, 2931, 1722, 1500, 1384, 1129, 742, 658; ^{13}C NMR (d_6 -DMSO) 170.7, 168.9, 51.8, 28.9, 22.1, 21.5. This material was readily soluble in DMSO, DMF, and methanol. On heating, the product became insoluble in these solvents perhaps due to aromatization of the cycloadduct. The NMR spectra indicates a mixture of the cycloadduct and other unidentified compounds.

N,N'-diphenyl-1,2,4,5-benzene tetracarboxylic diimide (**12**): The precipitate from purification of **11** was washed with a 4:1 methanol/DMF solution and dried at 120° C for 24 hrs. to yield 0.015 g (11.7%) of **10** as gold colored plates, m.p. 452.5° C (lit. 453° C⁹); IR (KBr, cm⁻¹): 3060, 1722, 1502, 1129, 742, 720 (lit. ¹⁵ 1720, 1132, 752, 730). Anal. Calcd. for C₂₂H₁₂N₂O₄: C, 71.74; H, 3.28; N, 7.60%. Found: C, 71.53; H, 3.09; N, 7.45%.

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LIST OF FIGURES

Figure 1: Structure of cyclobutene-1,2-disubstituted amides **1-9** and their corresponding substituents.

Figure 2: DSC traces of compounds **1-3** (bottom to top) showing melt endotherms and thermolysis exotherms.

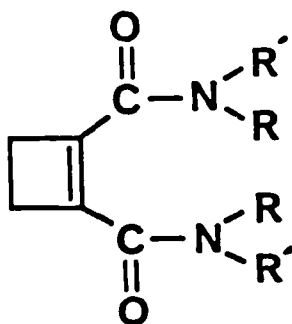
Figure 3: ^{13}C NMR of the thermolysis products of compound **1**: Upper trace shows formation of the substituted butadiene in nitrobenzene solution (R indicates residual cyclobutene resonances) while the lower trace shows the cyclodimer formed after prolonged heating.

Figure 4: Relative angles of sp^2 hybridized carbons in alkenes: a) normal angle of 120° in acrylamide, b) extended angle found in substituted cyclobutenes, c) hypothetical intramolecular hydrogen bonding facilitated by the extended angle.

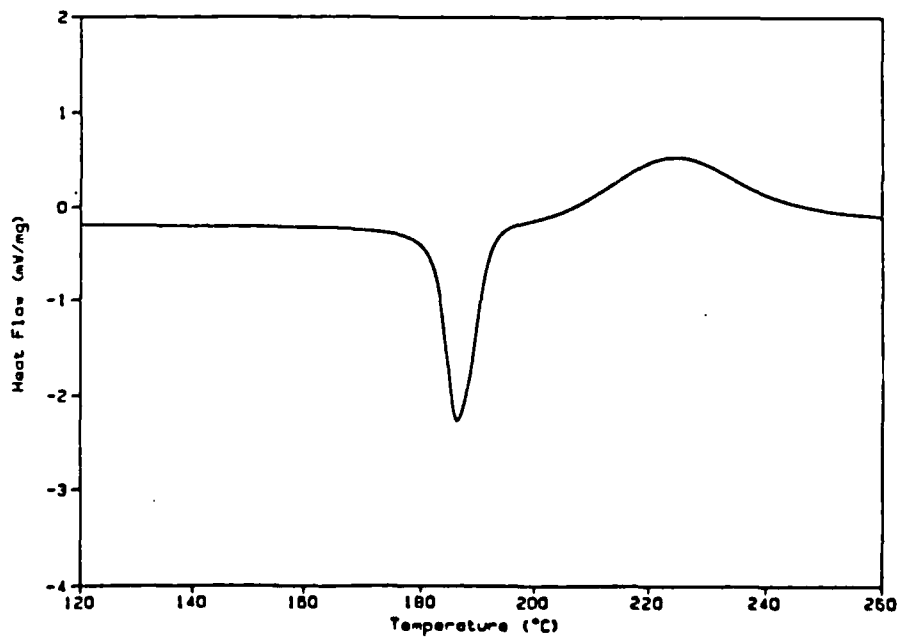
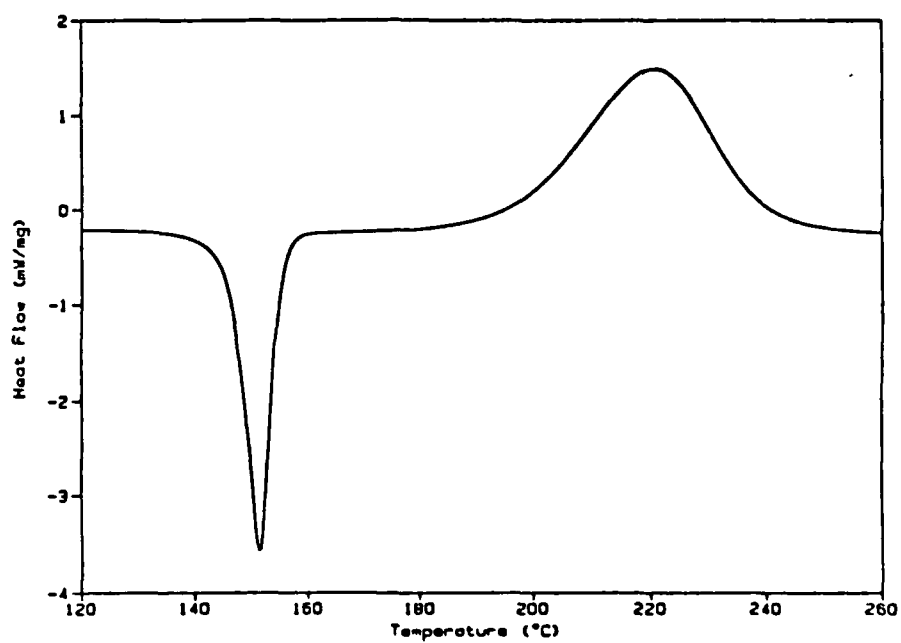
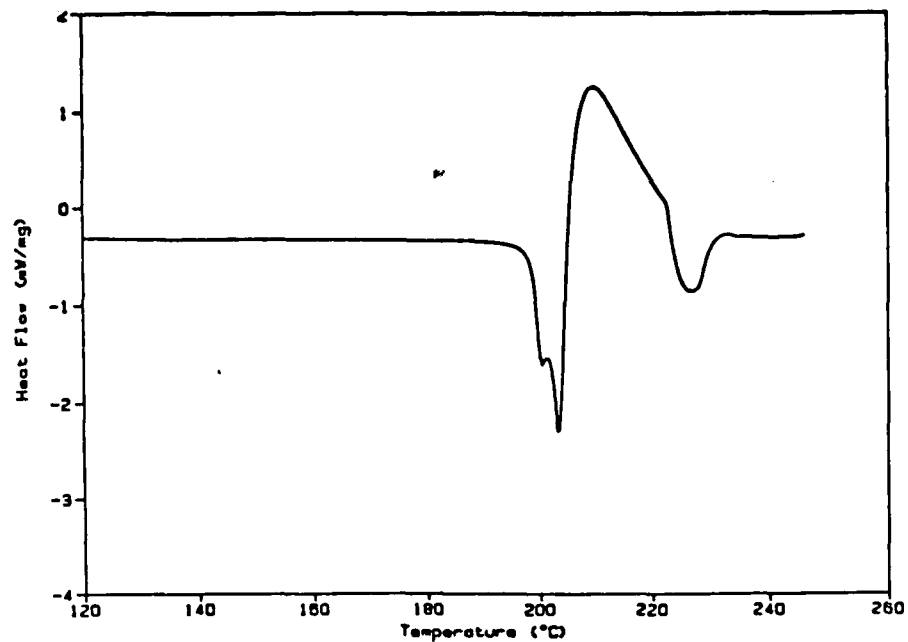
Figure 5: ^{13}C NMR (in CDCl_3) of the polymer from **2** with peak assignments.

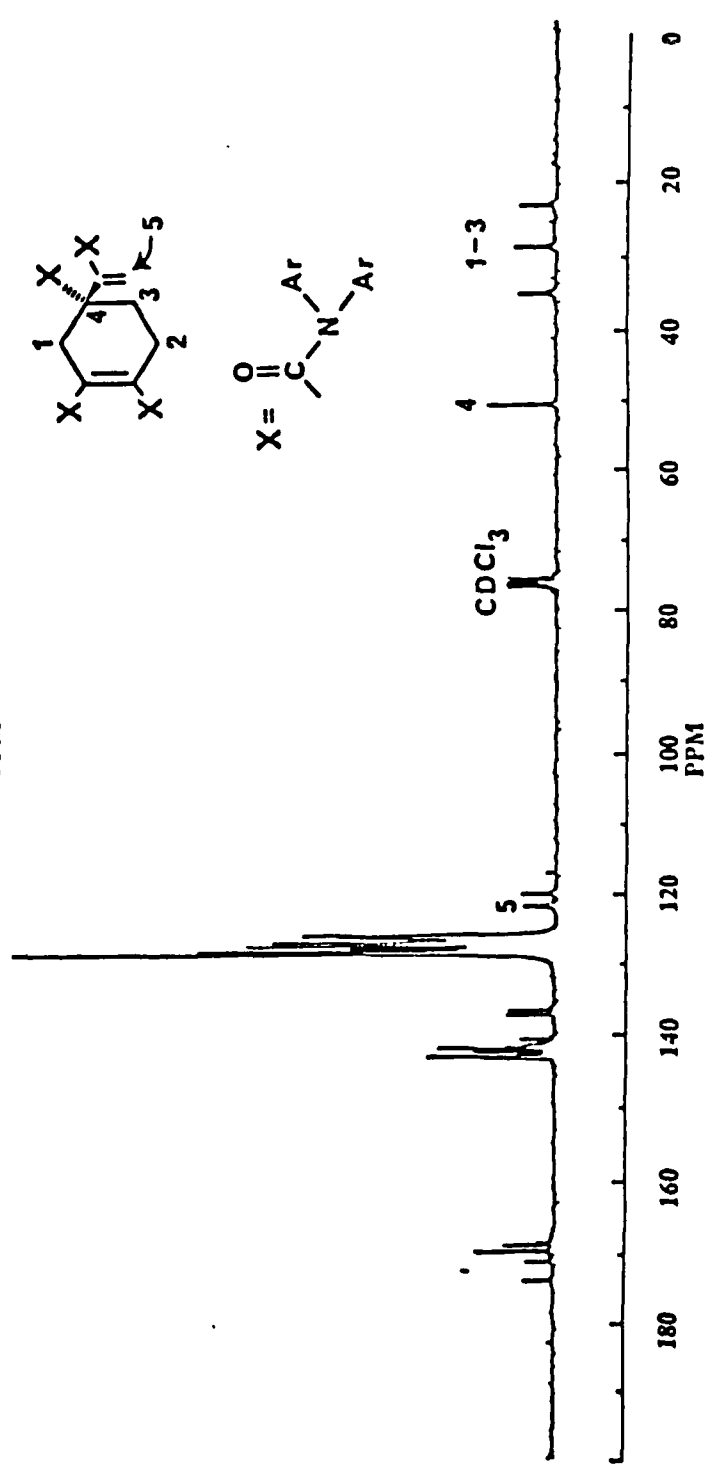
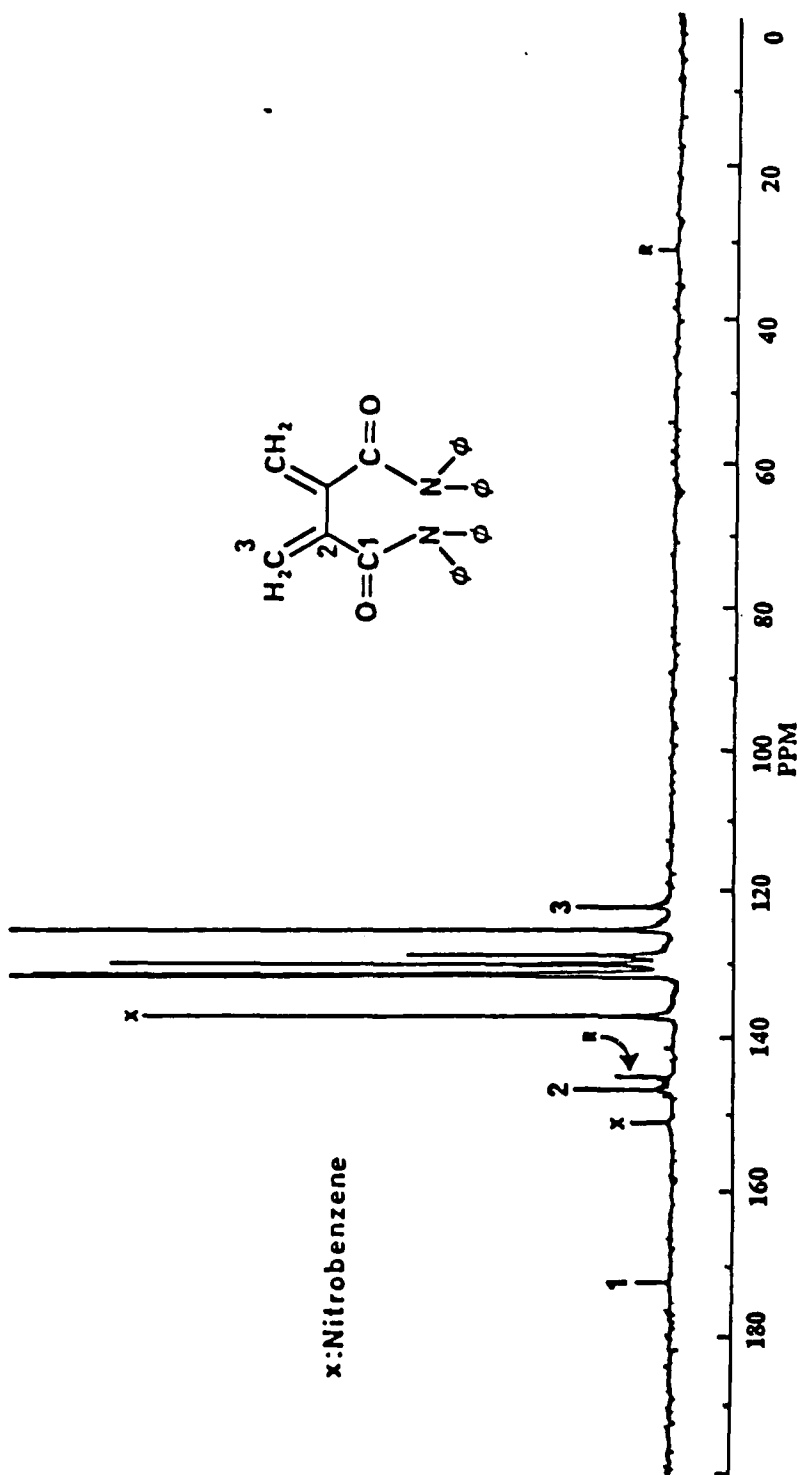
Figure 6: ^{13}C CP-MAS NMR of **3** showing peak assignments and chemical shift differences in the cyclobutene vinyl resonance.

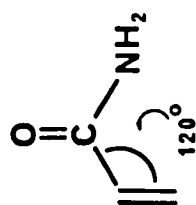
Figure 7: Diels-Alder reactions of *in situ* generated dienes with N-phenyl maleimide: eq. 1) reaction of **1** to give adduct **10**; eq. 2) reaction of **3** to give **11** followed by imidization and aromatization to give the diimide **12**.



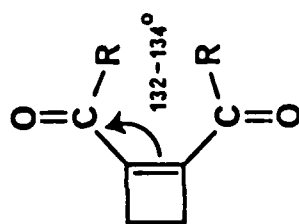
Cmpd	R	R'
1	phenyl	phenyl
2	methyl	phenyl
3	H	phenyl
4	H	n-dodecyl
5	H	n-heptyl
6	H	i-pentyl
7	methyl	methyl
8	H	cyclohexyl
9	cyclohexyl	cyclohexyl



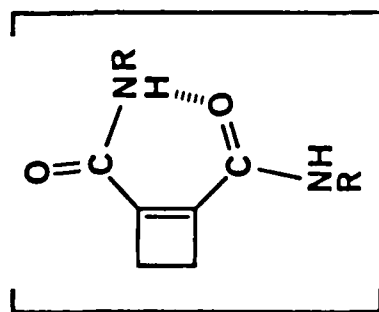




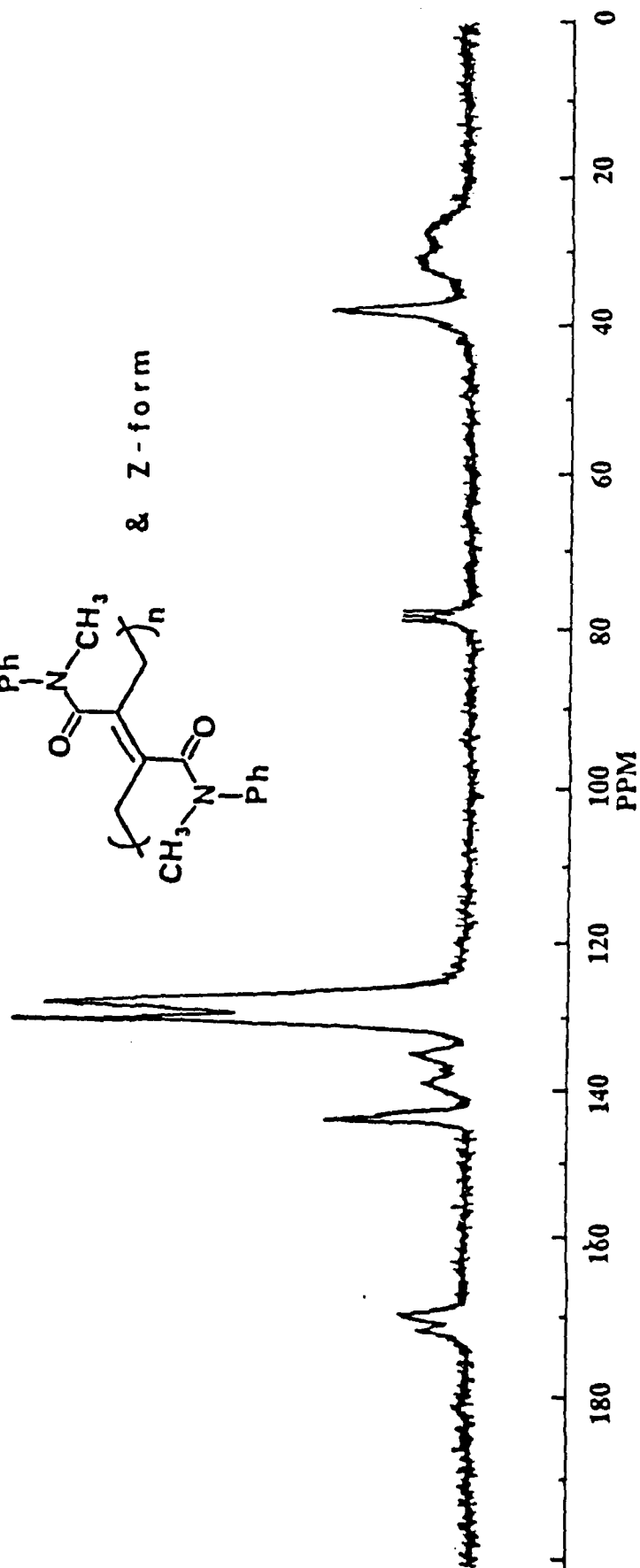
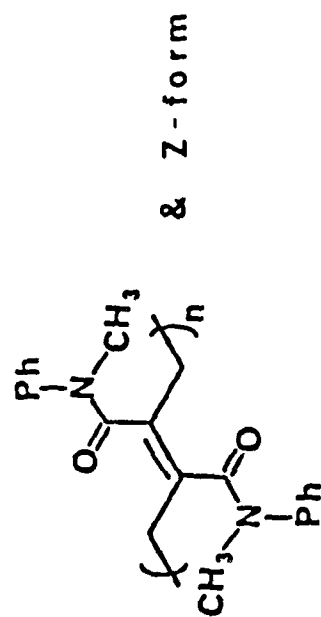
a

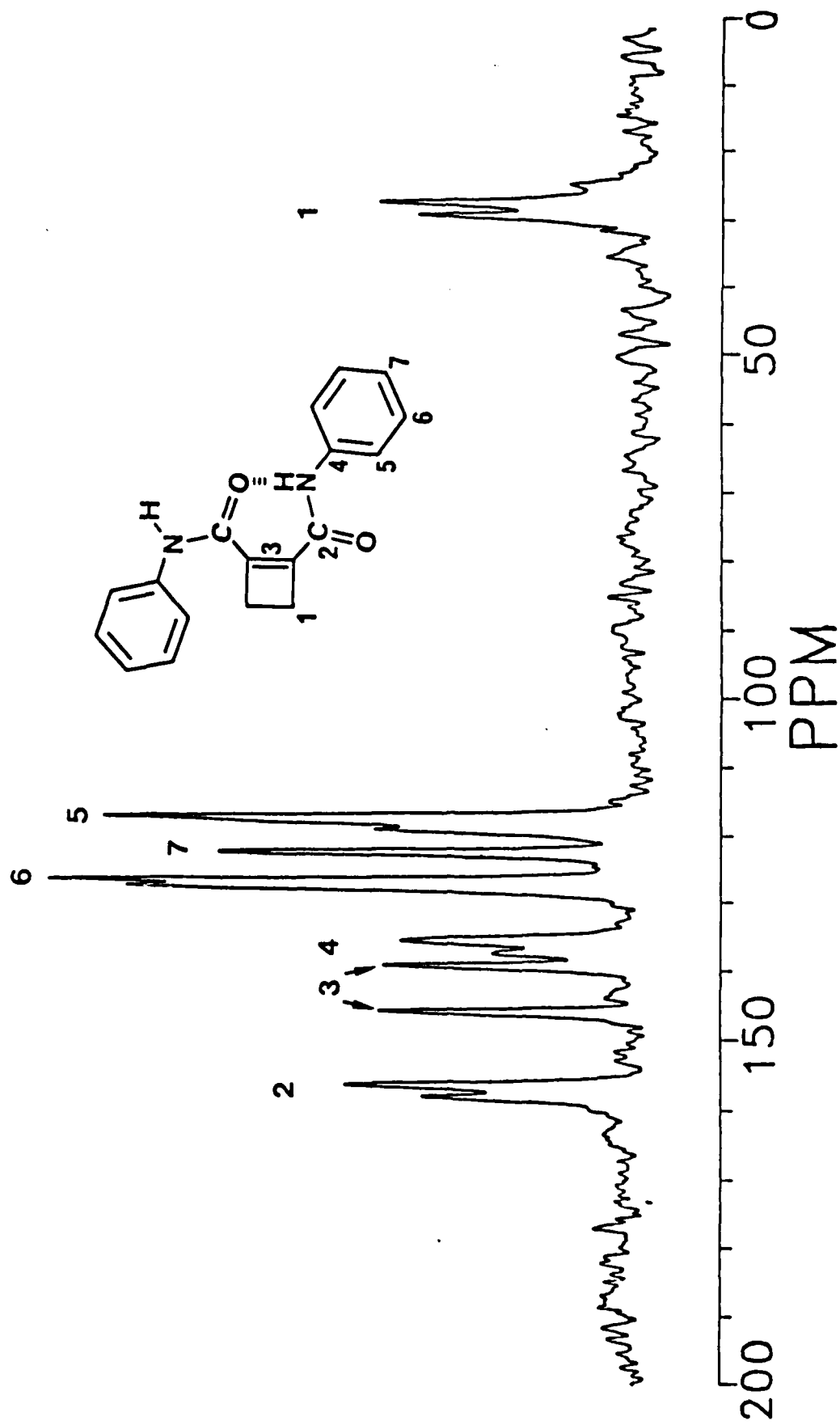


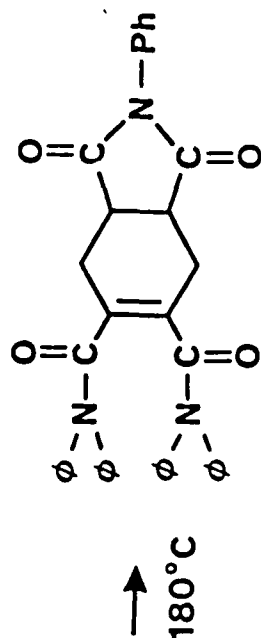
b



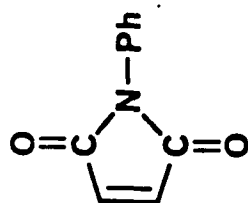
c







→ 180°C

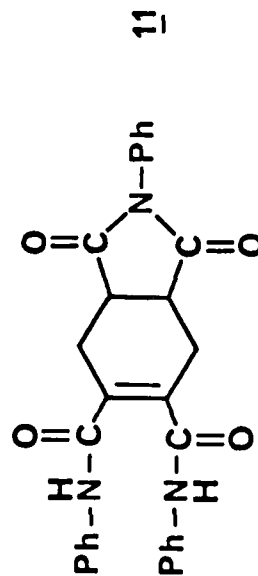


+

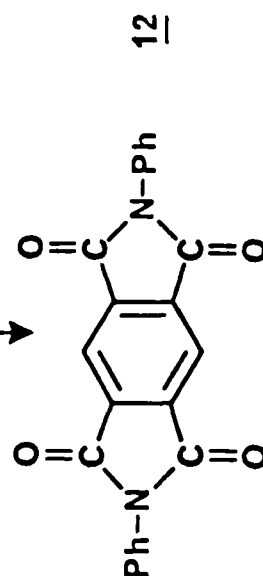
1

(eq.1)

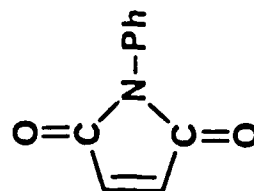
10



11



12



+

3

(eq.2)

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