

AD-A265 801

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REPORT DOC



3. REPORT SECURITY CLASSIFICATION

none

4. SECURITY CLASSIFICATION AUTHORITY

none

5. DECLASSIFICATION/DOWNGRADING SCHEDULE

none

6. PERFORMING ORGANIZATION REPORT NUMBER(S)

Technical Report # 50

7. DISTRIBUTION/AVAILABILITY OF REPORT

unlimited

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8. MONITORING ORGANIZATION REPORT NUMBER(S)

ONR N00014-89-J-1225

9a. NAME OF PERFORMING ORGANIZATION

University of Southern
Mississippi9b. OFFICE SYMBOL
(if applicable)

10a. NAME OF MONITORING ORGANIZATION

Office of Naval Research

10c. ADDRESS (City, State, and ZIP Code)

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

10b. ADDRESS (City, State, and ZIP Code)

Chemistry Division
800 North Quincy Street
Arlington, VA 22217-500011a. NAME OF FUNDING/SPONSORING
ORGANIZATION

Office of Naval Research

11b. OFFICE SYMBOL
(if applicable)

12. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

13c. ADDRESS (City, State, and ZIP Code)

Chemistry Division
800 North Quincy Street
Arlington, VA 22217-5000

14. SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NOPROJECT
NO.TASK
NOWORK UNIT
ACCESSION NO

15. TITLE (Include Security Classification)

Bis(vinylbenzyl)ether and Bis(vinylbenzyl)thioether: Synthesis, Cure Studies and
Evaluation of Carbon Fiber Composites.

16. PERSONAL AUTHOR(S)

L. J. Mathias, J. Muthiah, C. C. Roberts

17a. TYPE OF REPORT

Technical

17b. TIME COVERED

FROM 6-1-92 TO 5-31-93

18. DATE OF REPORT (Year, Month, Day)

93-6-7

19. PAGE COUNT

20. SUPPLEMENTARY NOTATION

Publication in Press

21. COSATI CODES

FIELD

GROUP

SUB-GROUP

22. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19. ABSTRACT Bis(vinylbenzyl)ether (BVE) and bis(vinylbenzyl)thioether (BVT) have been synthesized from vinylbenzyl chloride in yields greater than 90%. The onset/peak temperatures for thermal cure observed by first-run DSC scans were 80°C/110°C and 120°C/190°C, respectively, for BVE and BVT with no T_g in the second run. FT-IR and solid state NMR data indicated that cure occurred mainly through vinyl addition polymerization with high conversions. Composites formed from these resins had flexural modulus values at room temperature comparable to, or better than, traditional epoxy resins. More importantly, however, the BVE and BVT samples maintained much higher moduli than epoxy samples at temperatures above 200°C and up to 300°C. In addition, thermal cycling to 250°C caused ca 50% loss in epoxy composite properties, while BVE and BVT composites maintained their ambient temperature properties. Thermal decomposition of BVT in air occurred at a higher temperatures than BVE, but once degradation began, it was much faster for BVT than BVE as confirmed by DMA and TGA.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL

Lon J. Mathias

22b. TELEPHONE (Include Area Code)

601-266-4871

22c. OFFICE SYMBOL

Bis(vinylbenzyl)ether and Bis(vinylbenzyl)thioether: Synthesis, Cure Studies and Evaluation of Carbon Fiber Composites

Lon J. Mathias*, Jeno Muthiah and Christopher C. Roberts
Department of Polymer Science, University of Southern Mississippi,
Hattiesburg, MS 39406-0076.
PHONE: 601-266-4871; FAX: 601-266-5504

Abstract

Bis(vinylbenzyl)ether (BVE) and bis(vinylbenzyl)thioether (BVT) have been synthesized from vinylbenzyl chloride in yields greater than 90%. The onset/peak temperatures for thermal cure observed by first-run DSC scans were 80°C/110°C and 120°C/190°C, respectively, for BVE and BVT with no T_g in the second run. FT-IR and solid state NMR data indicated that cure occurred mainly through vinyl addition polymerization with high conversions. Composites formed from these resins had flexural modulus values at room temperature comparable to, or better than, traditional epoxy resins. More importantly, however, the BVE and BVT samples maintained much higher moduli than epoxy samples at temperatures above 200°C and up to 300°C. In addition, thermal cycling to 250°C caused ca 50% loss in epoxy composite properties, while BVE and BVT composites maintained their ambient temperature properties. Thermal decomposition of BVT in air occurred at a higher temperatures than BVE, but once degradation began, it was much faster for BVT than BVE as confirmed by DMA and TGA. Overall, these new resins offer improvements in processing and ultimate composite properties compared to epoxies.

Key words: Chloromethyl styrene ● styrylmethyl ether ● bis(vinylbenzyl) ethers ● phase transfer catalysis ● carbon fiber composites ● composites ● composite resins

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93-13396



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Lon J. Mathias*, Jeno Muthiah and Christopher C. Roberts
Department of Polymer Science, University of Southern Mississippi,
Hattiesburg, MS 39406-0076.

Introduction

Vinylbenzyl (or styryl) monomers or oligomers terminated with vinylbenzyl groups are a new class of resins which can be cured thermally with no evolution of volatiles. The cured resins have good thermal stability, excellent moisture resistance and low dielectric constant¹ which makes them ideal for applications in electronics.² As shown earlier, vinylbenzyl groups can be cured neat or with added free radical initiator.³ The onset temperature of the curing exotherm varies from 110 to 180°C depending on the connecting group between the vinylbenzyl ether groups.^{4,5} A 4+2 cycloaddition process involving two styrene moieties has been proposed as a major cure reaction,⁶ similar to what has been reported to occur in the bulk polymerization of styrene at 150°C in which up to 20% cyclodimerization was observed.⁷ However, these reports also reference earlier work showing efficient thermal polyaddition of styrene involving initiation with, and chain transfer to, the styrene cyclodimer.^{8,9} We are aware of no reports of spectral confirmation of intermediate or product structures from the reactive styryl group of materials explored to date. Preliminary work in our laboratory suggested that both thermal and free radically induced cure of neat BVE resin occurred almost solely through vinyl polyaddition,¹⁰ and that both ether and thioether dimers give fiber-reinforced composites with excellent physical and thermal properties.¹¹

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This paper describes single-step syntheses of the lowest members of this family of styryl-containing resins, bis(vinylbenzyl)ether (BVE) and bis(vinylbenzyl)thioether (BVT), which were obtained from commercially available vinylbenzyl chloride (VBC). In addition, we describe their bulk cure neat, carbon fiber composite formation, and composite properties. We are aware of only one reference (prior to our communication) to unpublished work on the p,p'-isomer of BVE obtained from p-vinylbenzyl chloride.¹²

Experimental Section

Solvents, reactants and Aliquat 336 were commercially available and used without further purification. A sample of an isomeric mixture of vinylbenzyl chloride (VBC) containing 30% para- and 70% meta-isomers was used as obtained from the Aldrich Chemical Company. AS-4 unsized carbon fibers donated by Hercules Chemical Company were used as the reinforcing component. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR. ¹³C NMR spectra were obtained in CDCl₃ on Bruker AC-300 and AC-200 spectrometers. ¹³C CP/MAS spectra were obtained on a Bruker MSL-200 spectrometer. A DuPont 9900 data station equipped with DSC, TGA and DMA modules was used for thermal characterization.

Flexural modulus values were also calculated from 3-point bending tests using an MTS-810 material testing system with a span-to-thickness ratio of 16:1 and a strain rate of 2 mm/min. Scanning electron micrographs were obtained with an Electroscan environmental scanning electron microscope.

Synthesis of BVE and BVT. BVE was prepared and purified according to the procedure we reported earlier.¹⁰ The following procedure was adopted for the synthesis of BVT. A solution of 140 mL water, 0.4 g Aliquat 336, and 11 g $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (0.046 mol) was prepared in a 250 mL round bottom flask. After purging with N_2 , vinylbenzyl chloride (10 g, 0.066 mol) was added and the solution mixed vigorously with a mechanical stirrer while being heated in a water bath at 60-70°C for 1.5 h. During this time, the mixture changed from an intense yellow to an orange color. The mixture was allowed to react for an additional hour without heat and was then transferred to a separatory funnel using 200 mL hexanes as a transfer aid. The organic layer was washed several times with water, separated and rotary evaporated to yield bis(vinylbenzyl)thioether as a viscous liquid (96% pure by GC). Trace amounts of Aliquat 336 and its degradation products were sometimes found in the crude reaction products (BVE and BVT); these could be removed by silica gel chromatography (50-200 mesh) with hexanes or ether solvent.

Preparation of carbon fiber composites. Composite samples were prepared in a steel mold which has four sections (enclosed by a base) that form a rectangular indentation into which fits a cover plate insert with the same dimensions (width = 13 mm, length = 65 mm). There is side clearance between the indent and the insert so that only the sample area is subjected to load. With this mold, the resin content in the sample is mainly controlled by the applied pressure, and a top load of 7 lbs was used in the preparation of all samples reported here.

Carbon fibers (cut to fit the length of the mold) were weighed and laid unidirectionally one layer at a time into the mold. Just enough resin was added after

every layer using a pipette to wet the surface of fibers completely. The top load was then put in place, causing the excess resin to squeeze out. Each carbon fiber composite was cured in the mold by placing the assembly in a preheated oven with temperature control of $\pm 10^\circ$. BVE samples were cured at 200°C for 10-12 h while BVT samples were cured at 165°C and 205°C for 5 h each. An epoxy control sample made with Epon-828/MDA (4,4'-methylene dianiline) as matrix material was cured for 4 h at 75°C and 2 h at 175°C ¹³. The composites contained approximately 30% resin by weight after cure.

Results and Discussion

Ether synthesis Figure 1 shows the scheme for synthesis of BVE and BVT and the isomer ratio for the starting VBC. Syntheses of both BVE and BVT were facile. Yields of the ether were typically greater than 85-90%, and the compound was obtained crude in ca 90% purity by GC. BVT was obtained in ca 95% yield with comparable purity as crude product. Residual Aliquat 336 was removed by silica gel chromatography. It should be mentioned that, because the starting material consists of a mixture of meta and para isomers, the product contains all three isomer combinations in approximately statistical amounts (ca 50:40:10 of the m,m:m,p:p,p isomers) as determined from close multiple GC peak intensities. The ^1H and ^{13}C NMR spectra also show multiple peaks for many of the peaks consistent with these isomer contents. The formation of BVE and BVT was readily confirmed by ^{13}C NMR by monitoring conversion of the chlorobenzyl carbon at 45 ppm to the ether or thioether carbons with peaks at 71 and 35 ppm, respectively. We typically used the crude product directly in the reactions described below without

removal of residual VBC, although the presence of tertiary amines (from the degradation of Aliquat 336 by base) strongly inhibited polymerization and cure.

Neat resin thermal cure results Resins were scanned in the DSC at 10°C/min under nitrogen. The onset and peak temperatures observed for BVE in the first scan (taken up to 300°C) were ca 80°C and 110°C, respectively. The total heat of curing observed was ca 600 J/g. The second scan (up to 350°C) did not show any glass transition or melting point, consistent with a high degree of crosslinking and lack of crystallinity. NMR and FT-IR spectroscopic evidence showed that the thermal curing of BVE occurred mostly through vinyl addition polymerization which may also involve or be initiated by small amounts of the 4+2 cycloaddition product.⁹

BVT showed similar cure behavior with heat of curing of ca 400 J/g. The thermogram (Figure 2) showed onset temperature of ca 120°C and peak temperatures of ca 150°C and 190°C, respectively. The presence of two exotherm peaks is probably due to an initial crosslinking reaction which leads to formation of a network with a T_g of ca 160-180°C; further cure takes place as the temperature rises above this value. A second DSC scan on the same sample after cooling did not exhibit any transition until degradation began around 350°C.

FT-IR and solid state NMR were used to monitor the extent of vinyl group reaction. Figure 3 gives the FT-IR spectra of neat BVT resin and thermally cured product. Disappearance of the vinyl peaks at 3084, 1626, 989 and 907 cm^{-1} (starred in Figure 3) is consistent with virtually complete vinyl reaction. Similar loss of vinyl peaks was observed in the polymerization of BVE.¹⁰ Based on these results, it is clear that BVT and

BVE both show very high conversions during thermal polymerization in the absence of initiator.

The ^{13}C CP/MAS spectrum of the cured BVT (Figure 4) shows only a trace of residual vinyl carbons (the unique, intense peaks at 114 ppm in the spectrum of the neat resin). The broad peak around 40 ppm is due to the methylene units next to sulfur atoms overlapping some of the backbone carbon peaks formed during polymerization. Both the aromatic and aliphatic regions of the cured BVT resin are very similar in peak positions and intensities to those previously described for cured BVE¹⁰ and seen in the spectrum of polystyrene. ^{13}C dipolar dephasing experiments (which can emphasize quaternary peaks over peaks of carbons with hydrogens) did not show any evidence for 4+2 cycloaddition products which should possess quaternary carbons. These results indicate that the predominant mode of cure for these materials involves vinyl polymerization rather than cycloaddition reaction.

Mechanical testing results Dynamic mechanical analyses were carried out at 4°C/min in air. Figure 5 gives the flexural moduli of carbon fiber composites of BVE, BVT and the epoxy control sample measured to 250°C. The BVT resin gave the highest modulus over the entire temperature range. The modulus of the epoxy sample was somewhat higher than the BVE sample up to ca 200° after which it dropped sharply. Both the BVT and BVE samples retained about 87% of initial modulus values at 200°C and showed no catastrophic drop up to 250°C. Table 1 gives the modulus values at different temperatures plus the temperatures corresponding to $\tan \delta_{\text{max}}$ values of each sample from the first-run measurements. The latter were higher for BVE and BVT than for epoxy.

Cure temperature had a significant effect on the DMA properties of BVE composites. Samples cured at 170°C and 250°C gave flexural modulus values of about 29 GPa and 43 GPa, respectively, compared to 34 GPa for a sample cured at 200°C. However, a BVE Sample cured at 200°C and then post-cured at 250°C did not show any increase in modulus. This seems to indicate that the rate of cure directly effects the extent of cure (and ultimate properties) or faster cure changes the molecular composition in some other way to directly effect modulus, but only during the initial cure process.

Cure temperature had less effect on the properties of BVT composites. When BVT composites were prepared with two different protocols (5 h at each temperature of the pairs 185/225°C or 145/185°C), the moduli were 43 GPa and 45 GPa, respectively.

Figure 6 shows the DMA plots of the same samples shown in Figure 5 that were taken up to 250°C, cooled down to room temperature, and re-analyzed. The reduction in room temperature properties was highest for the epoxy sample and least for the BVE material. Table 2 gives the modulus values at different temperatures plus $\tan \delta_{\max}$ temperatures for these second run analyses. The performance of BVT composites is better than BVE materials up to 300°C in the second run also with BVT maintaining 80% of its room temperature modulus while the BVE sample showed a 40% drop in modulus.

At 350°C, the flexural modulus of the BVT composite dropped to 22% of the initial value whereas that of the BVE composite decreased by only 50%. This shows that even though the BVT resin has higher modulus up to 300°C, and has a higher $\tan \delta_{\max}$ temperature, its decomposition and loss of properties begins at somewhat lower temperatures than BVE materials.

The TGA curves for BVE and BVT are given in Figure 7. Both resins showed a weight loss of only 4-5% up to 350°C. Between 350 and 375°C, BVT lost 11% while BVE showed only 7% weight loss. This is the same trend as seen in the DMA data, and confirms the better overall thermal stability for the BVE composites than for the BVT materials.

Scanning electron micrographs of the broken composite samples (after being tested for flexural strength in 3-point bending analyses) showed poor adhesion of resin to the surface of the fibers. This is not surprising since we did not attempt optimization of the composite properties through surface treatment of the carbon fibers, interface generation or toughening with elastomeric additives.

Conclusions

Bis(vinylbenzyl ether) and bis(vinylbenzyl thioether) are easily synthesized from a commercial meta/para mixture of vinylbenzyl chloride. Crude yields and purities of greater than 90% were obtained for both BVE and BVT dimers. The onset and peak temperatures for thermal cure observed by first-run DSC scans were 80°C/110°C and 120°C/190°C, respectively. Neither resin exhibited any T_g or exotherms in the second DSC run due to high conversion and crosslink density. FT-IR and solid state NMR data indicate that cure and crosslinking occurred through vinyl addition polymerization with high conversions achieved under thermal cure of both neat samples and carbon composites.

Composites formed from these resins had flexural modulus values at room temperature comparable to, or better than, traditional epoxy resins. More importantly,

however, the BVE and BVT samples had much higher moduli than epoxy samples at temperatures above 200°C and maintained significant performance to much higher temperatures. In addition, the loss in modulus upon heating to 250°C a second time was almost 50% for the epoxy samples and almost nil for composites made with the new resins. While BVT had a higher modulus than BVE to begin with, and maintained this difference up to 300°C, the flexural modulus of BVT dropped by 78% of its initial value while that of BVE dropped by only 50% above 350°C. Similarly, the decomposition of BVT by TGA began at a higher temperature than BVE, but once degradation began, it was much faster for BVT than BVE. The DMA results, 3-point bending measurements and TGA analyses all confirm the much better ambient and high temperature performance of the BVE and BVT composites compared to the epoxy samples. When combined with facile syntheses by phase transfer processes, these materials offer excellent potential as stand-alone or synergistic components in composites, especially if interfacial adhesion and interphase formation can be enhanced through fiber pre-treatment.

Acknowledgements

This research was supported in part by a grant from the Office of Naval Research. We also would like to acknowledge a Department of Defense instrumentation grant from the Office of Naval Research for the Bruker MSL-200 solid state NMR spectrometer used in this project.

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Table 1. First-run flexural modulus values and $\tan \delta_{\max}$ temperatures for BVT composite cured for 5 h each at 165°C and 205°C, BVE composite cured for 12 h at 200°C, and epoxy composite cured for 4 h at 75°C and for 2 h at 175°C.

Resin	Flexural Modulus in GPa at:				$\tan \delta_{\max}$ (°C)
	50°C	100°C	150°C	200°C	
BVT	47	46	44	41	220
BVE	34	33	33	30	242
Epon-828/MDA	40	38	35	11	200

Table 2. Second run flexural modulus values and $\tan \delta_{\max}$ temperatures for the same samples as in Table 1 cooled to ambient and re-analyzed.

Resin	Flexural Modulus in GPa at:							$\tan \delta_{\max}$ (°C)
	50°C	100°C	150°C	200°C	250°C	300°C	350°C	
BVT	38	37	36	35	32	30	8	270
BVE	33	32	31	28	24	20	17	248
Epon-828/MDA	23	22	20	10	3	-	-	220

List of figures

- Figure 1. Synthesis of bis(vinylbenzyl) ether and bis(vinylbenzyl) thioether.
- Figure 2. DSC thermogram of BVT at a heating rate of 10°C/min.
- Figure 3. FT-IR spectra of BVT (lower trace) and resin cured for 5 h each at 165 and 205°C.
- Figure 4. ¹³C NMR solution spectrum of BVT (lower trace) and ¹³C CP/MAS spectrum of resin cured for 5 h each at 165 and 205°C.
- Figure 5. DMA spectra at a heating rate of 4°C/min in air up to 250°C (first run) of BVT composite cured for 5 h each at 165 and 205°C [— — —], BVE composite cured for 12 h at 200°C [- - - -] and epoxy composite cured for 4 h at 75°C and for 2 h at 175°C [- · · · · -].
- Figure 6. DMA spectra of at a heating rate of 4°C/min in air up to 300°C (second run) on the same samples as in Figure 5.
- Figure 7. TGA analysis (heating rate of 10°C/min in air) of neat BVT resin cured for 5 h each at 165°C and 205°C [— — —] and BVE resin cured for 12 h at 200°C [- - - -].

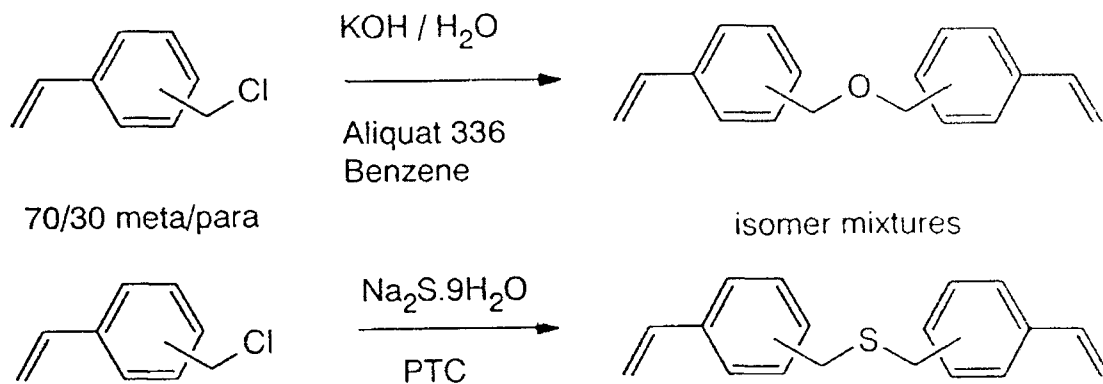


Fig 1

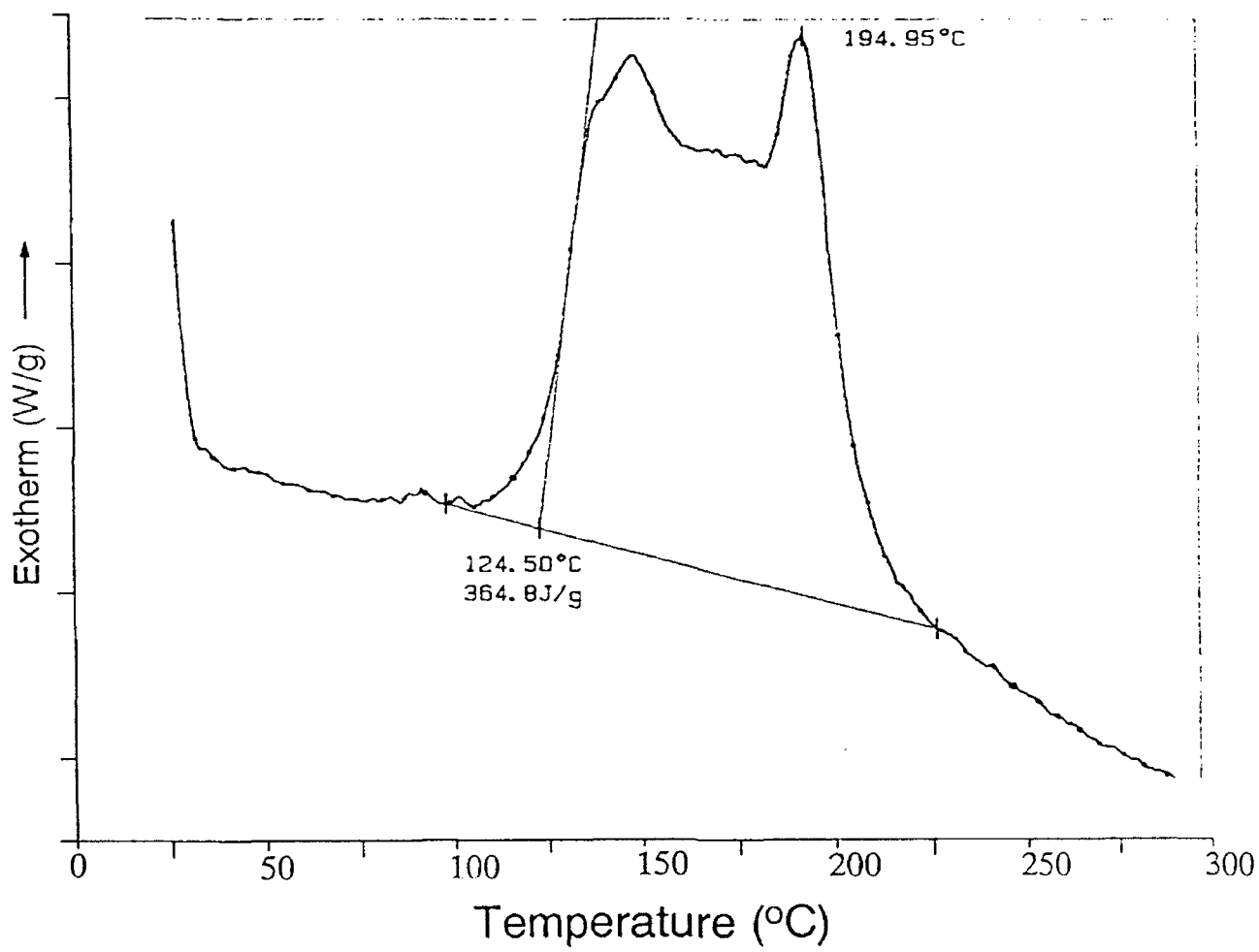
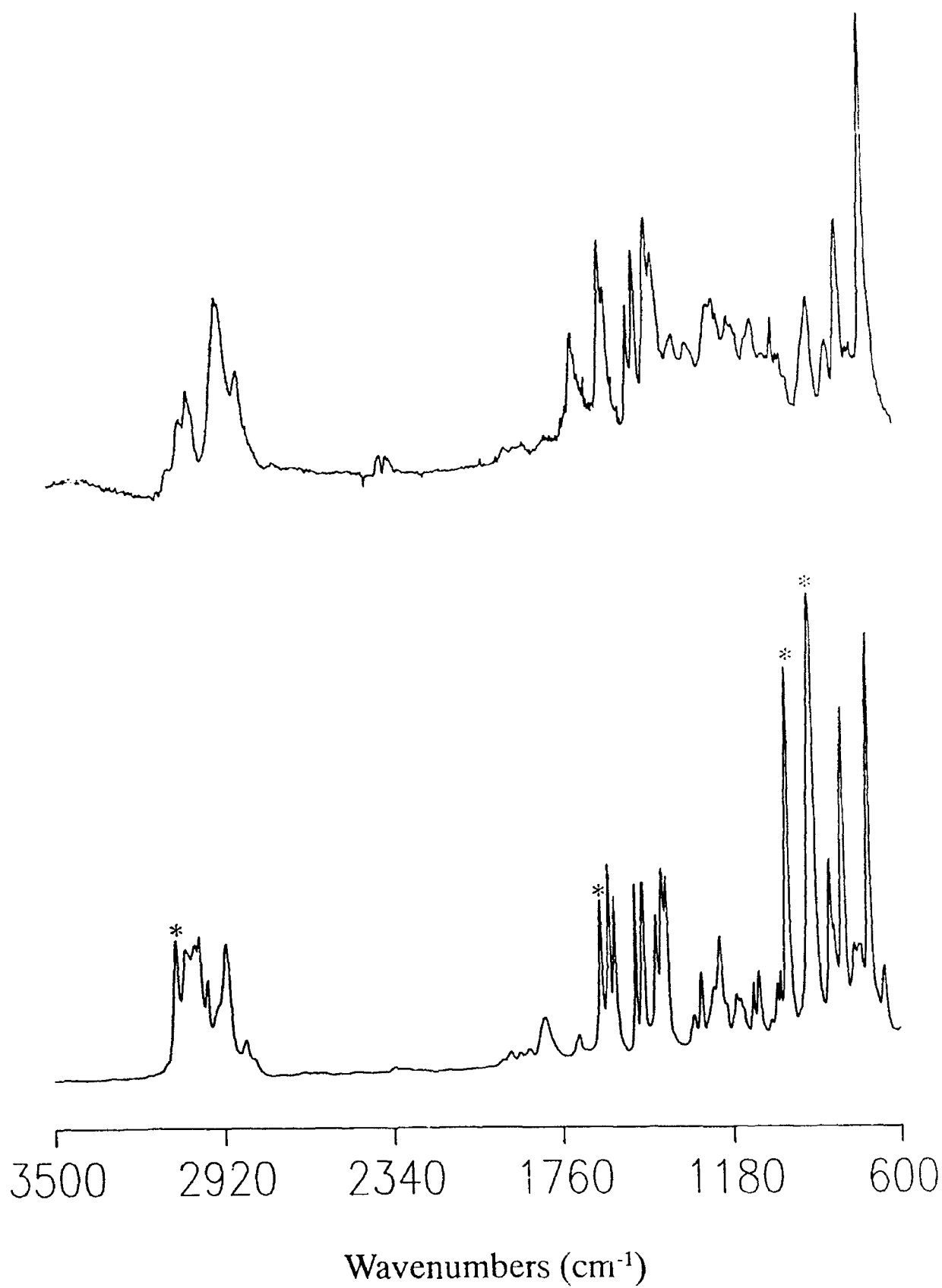


Fig 2



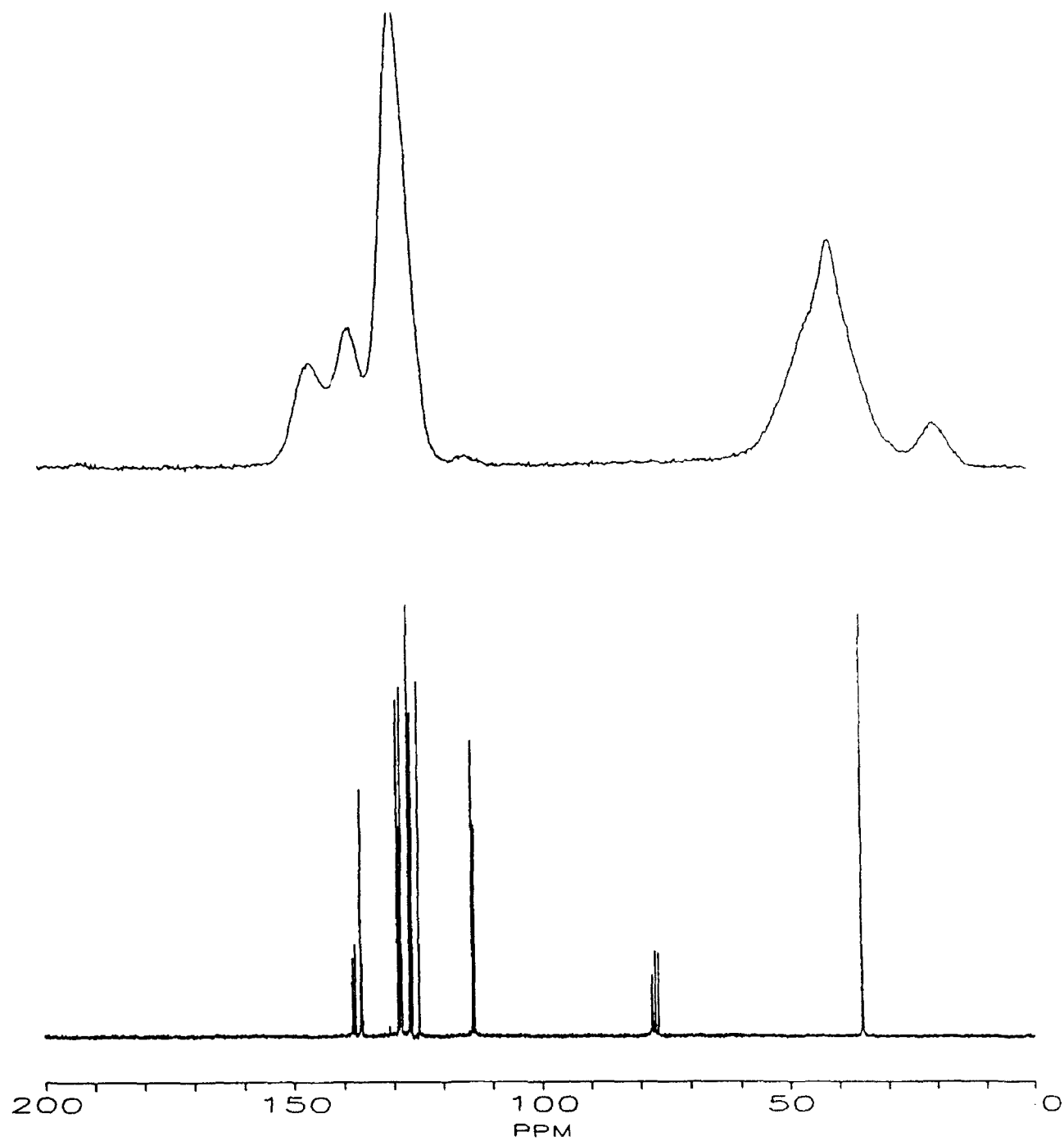


Fig 4

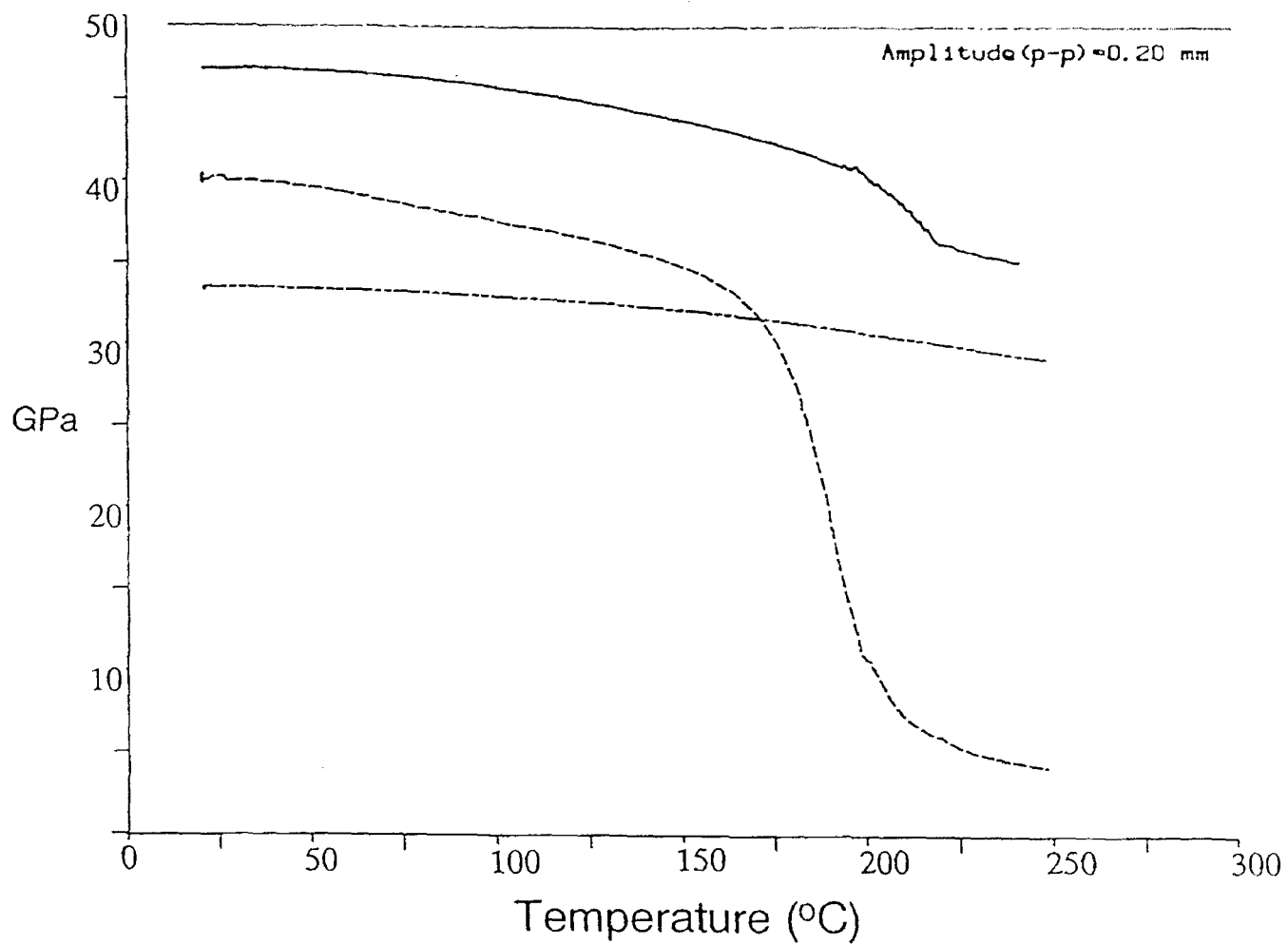
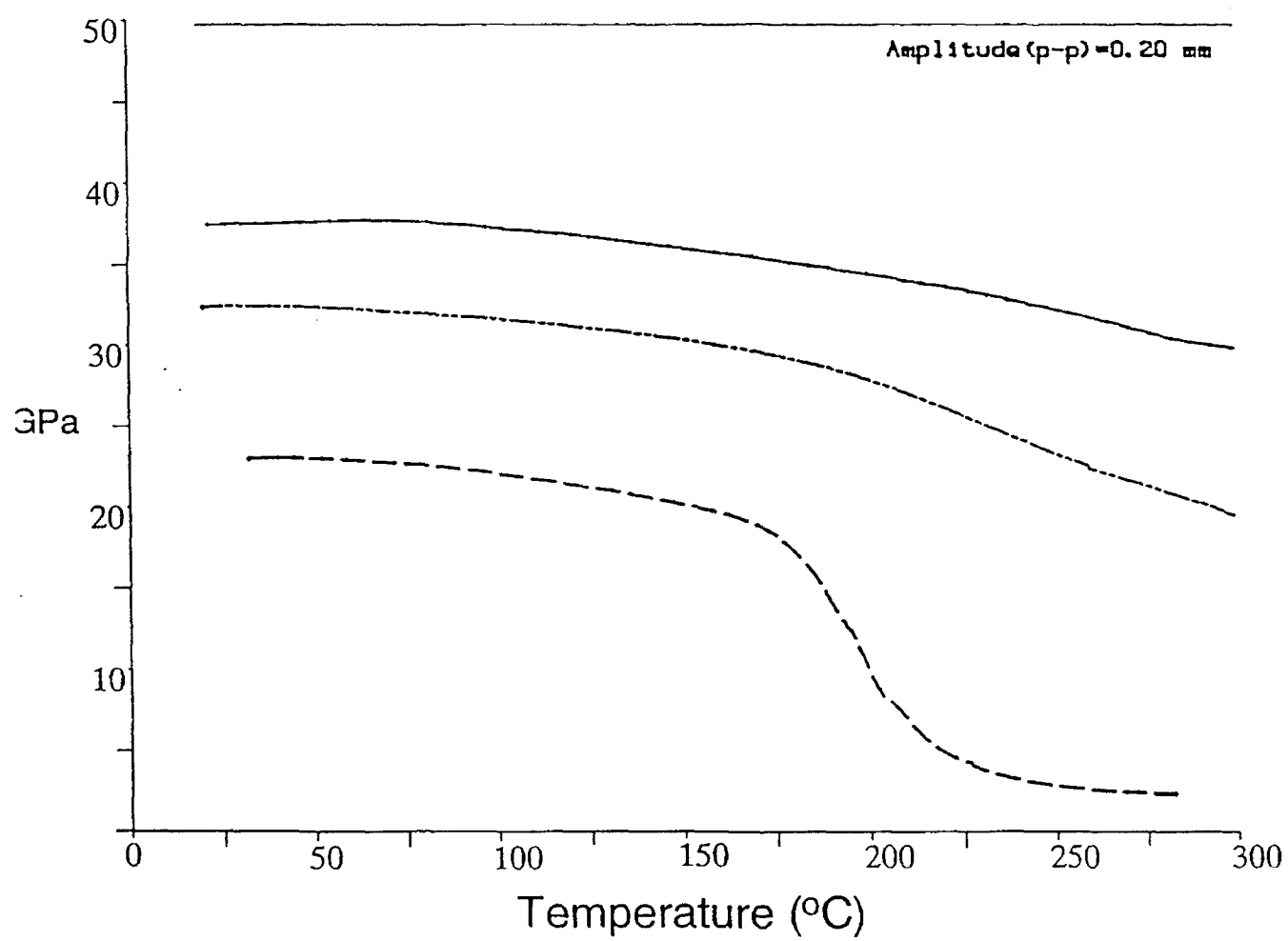


Fig 5



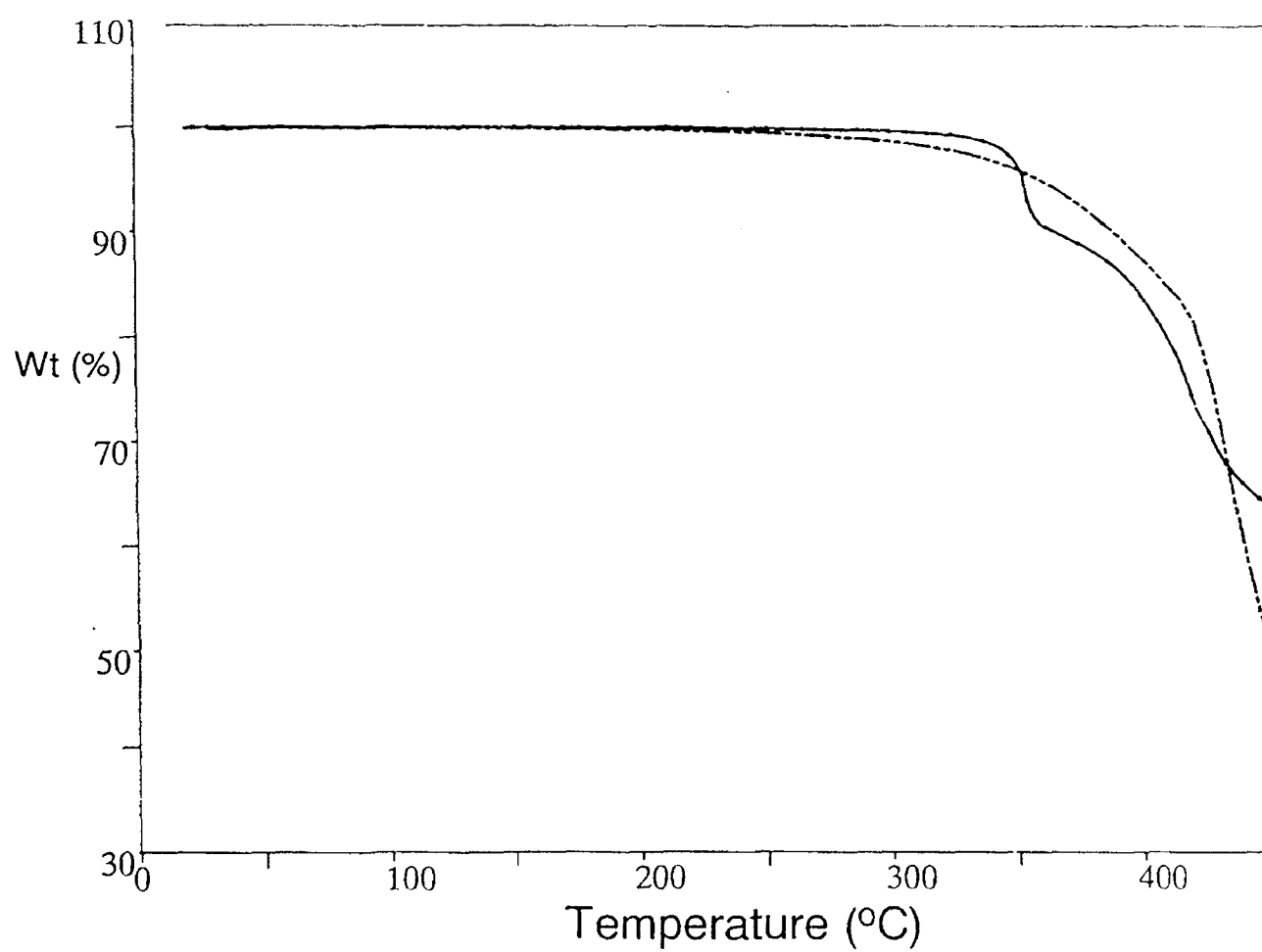


Fig 7