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Heterocyclic Poly(bismaleimide)s. I. Synthesis and Characterization of New Poly(amino-bismaleimide)s Containing Parabanic Rings

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NOTES

**HETEROCYCLIC POLY(BISMALEIMIDE)S. I.
SYNTHESIS AND CHARACTERIZATION OF
NEW POLY(AMINO-BISMALEIMIDE)S
CONTAINING PARABANIC RINGS**

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ABSTRACT

New poly(amino-bismaleimide)s containing parabanic rings were obtained by the polyaddition reaction of parabanic bismaleimide III with various aromatic diamines A(1-4). The polymers are partially soluble in aprotic dipolar solvents and showed higher thermal stability than other polymers without parabanic units.

INTRODUCTION

Extensive literature concerning the poly(amino-bismaleimide)s systems, is available [1-7]. Mikroyannidis outlined the significant improvement in the thermal stability and the chemical resistance for maleimide systems, induced by the incorporation of heterocyclic rings such as that of benzimidazole, benzoxazole, benzoxazinone [8]. Polymers carrying parabanic rings such as polyurethanes, polyoxadiazolureas, polyimides, polybarbiturates, polyquinazolindiones etc. [9,10] are known as highly thermally stable polymers with improved chemical resistance in organic solvents. There are a few literature citations available concerning the poly(amino-bismaleimide)s systems containing para-

banic ring [11]. Our previous work has been focused mainly on the synthesis and characterization of new poly(aminobismaleimide)s with aliphatic urethane links as new materials with better processibility [12]. The goal of the present paper is to describe the synthesis and characterization of new poly(amino-bismaleimide)s with parabanic rings possessing higher thermal stability and better chemical resistance than the above discussed polymers.

EXPERIMENTAL

Materials. Acetone, 1,2-dichloroethane (DCE), *m*-cresol and CCl_4 were distilled before use. Acetic anhydride and oxalyl chloride (Aldrich) were used as received. Maleic anhydride (54–56°C) and *p*-phenylenediamine (143–145°C) (Aldrich) were resublimed before use. 4,4'-Oxydianiline, 4,4'-methylenedianiline and 4,4'-ethylenedianiline (Aldrich) were used as received. *N*-(4-Isocyanatophenylene)maleimide (I) was synthesized as described in literature [13].

***N,N'*-Bis(4-maleimidophenylene)urea II.** A 100 mL three-necked flask equipped with a mechanical stirrer, thermometer and condenser was charged with 2.0g (9.338 mmol) I, 50 mL DCE and 3 mL water. After 3 hours of refluxing under stirring a yellow solid precipitated from solution. The solid was filtered, washed with methylene chloride and dried for 18 hours at 60°C in vacuo. Yield 98%, m.p. >300°C. Analysis: Calculated for $\text{C}_{21}\text{H}_{14}\text{N}_4\text{O}_5$ (402.35): C, 62.68%; H, 3.51%; N, 13.92%. Found: C, 63.35%; H, 3.15%; N, 14.08%. IR (KBr, cm^{-1}): 3400 (N-H), 1785, 1725, 1710 (imide I), 1655 (C=O, urea), 695 (imide IV). $^1\text{H-NMR}$ (DMSO- d_6) δ : 8.85 (s, 2H, NH), 7.575 (d, 4H, ortho to imide), 7.225 (d, 4H, ortho to NH).

1,3-Bis(4-maleimidophenylene)parabanic acid III. The same apparatus as above was charged with 2.0g (4.971 mmol) II, 30 mL DCE and 0.6 mL of dry pyridine (Py). The flask was cooled with an ice bath. A solution of 0.63g oxalyl chloride in 10 mL DCE was added carefully in 15 min while temperature was kept in the range -5 to 0°C. The ice bath then removed and the temperature was increased slowly and maintained 3 hours at reflux. After cooling the clear solution, a brown solid separated out, filtered and washed with methylene chloride. The product was dried at 60°C for 18 h. Yield 90%, m.p. >300°C. Analysis.

Calculated for $C_{23}H_{12}N_4O_7$ (456.35): C, 60.53%; H, 2.65%; N, 12.28%. Found: C, 60.39%; H, 3.19%; N, 10.14%. IR(KBr, cm^{-1}): 1750(parabanic ring), 1725, 1700(imide I), 1620, 1515, 840(aromatic), 695(imide IV). 1H -NMR(DMSO- d_6) δ : 7.68(s, 8H, phenyl), 7.20(s, 4H, olefinic imide).

1,3-Bis[4-(4-tolylamino)maleimidophenylene]parabanic acid IV. A 50 mL three-necked flask equipped with magnetic stirrer, thermometer and condenser was charged with 1.0g (2.19 mmol) III, 17 mL m-cresol, 0.5 mL acetic acid (AcOH) and 0.469g (4.337 mmol) p-toluidine to form initially a slurry and after the temperature was increased to 100°C became a clear solution. Maintaining the temperature at 100°C for 10 hours while stirring, the reaction mixture was then precipitated with methanol, filtered, refluxed 3 hours in methanol, filtered, washed with Et₂O and dried for 12 hours in vacuo at 60°C to obtain a 80% yield of a white solid with m.p. 280-285°C. Analysis. Calculated for $C_{37}H_{30}N_6O_7$ (670.65): C, 66.26%; H, 4.51%; N, 12.53%. Found: C, 66.05%; H, 3.95% N, 11.95%. IR(KBr, cm^{-1}): 3390(N-H), 1780(sh), 1715(imide I), 1750(parabanic ring), 1650(w, conjugation), 1620, 1520(C=C, aromatic), 1380(imide II), 1140(imide III), 940(ring imide), 1025, 835, 810(aromatic 1,4-disubstituted ring), 690(imide IV). 1H -NMR(DMSO- d_6) δ : 7.725(s, 8H, 4H ortho to imide, 4H ortho to parabanic ring), 7.085(d, 4H ortho to NH), 6.750(d, 4H ortho to -CH₃), 4.875(m, 2H -C=), 3.675, 2.90(m, 4H -CH₂-), 2.275(s, 6H, CH₃).

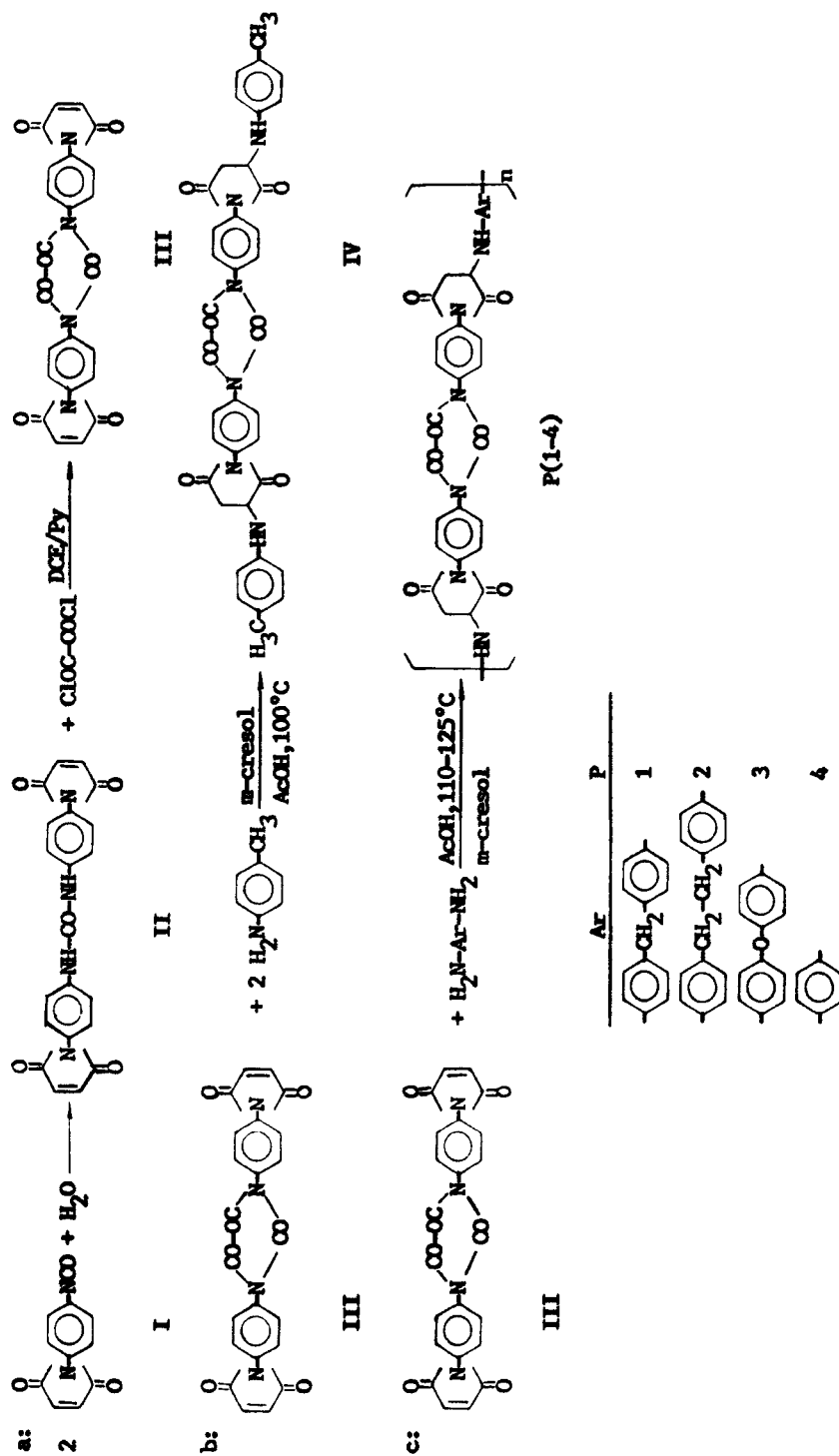
Polymerization. The following were charged into the same apparatus described above: 0.9127g (2.0 mmol) III, 0.396g (2.0 mmol) A-1, 1 mL AcOH and 30 mL m-cresol. The mixture was heated with stirring at 110-125°C for 24 hours. After cooling at room temperature, the polymer was coagulated into methanol, filtered, refluxed in methanol for 2 hours, filtered and dried under vacuum for 24 hours at 60°C.

Measurements. Inherent viscosities were measured in a Ubbelohde suspended level viscometer, in DMSO at 30°C at a concentration of 0.5g/dL. The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer using the KBr pellet technique. 1H -NMR spectra were run on a Jeol 60 MHz 1H -NMR spectrometer at 50°C in DMSO- d_6 using TMS as the internal reference. Melting and softening points were determined by using a IOR MC1-type polarizing microscope equipped with a heating stage (magnification 150X). Dynamic weight-loss measurements

were carried out on a F.Paulik Derivatograph in air. The heating rate was 12°C/min. All degradation runs were performed at a sample size of 50 mg. Differential scanning calorimetric (DSC) measurements were run on a Mettler 12E DSC Instrument, in nitrogen, with a heating rate of 12°C/min, using a sample size of 5 mg.

RESULTS AND DISCUSSION

A new bismaleimide monomer containing the parabanic ring was synthesized via a two step reaction (Scheme 1,a). The starting isocyanate I, urea intermediate II, and the final parabanic bismaleimide monomer III were characterized using elemental analysis, IR and ¹H-NMR measurements (Fig.1) which confirmed the expected structures. To facilitate the assignment of the spectral data, a model compound IV was synthesized from monomer III and p-toluidine as shown in Scheme 1,b. Linear poly(amino-bismaleimide)s P(1-4) were prepared by the polyaddition reaction of an equimolar mixture of monomer III with four aromatic diamines A(1-4) in m-cresol as the solvent, using a small amount of AcOH as the catalyst, as described [1] (Scheme 1,c). The structures of the obtained polymers P(1-4) were confirmed using IR spectroscopy (Fig.2). The polymers showed no softening behaviour up to 300°C as observed by optical microscope (Table 1). The inherent viscosities ranged between 0.30 and 0.50 dL/g. All of the polymers are partially soluble in DMSO with heating and the viscosities were determined for the soluble fractions. As can be seen, the higher viscosity value was found for P4 and the smaller one for P1. The solubilities of the polymers (0.5 w/v) showed that all polymers were partially soluble in NMP and DMSO. In contrast, similar polymers without parabanic moieties are soluble [14]. A more detailed study of this behaviour is still underway and will be reported at a later time. The thermal behaviour of the polymers P(1-4) was monitored by TGA and DSC measurements. The temperatures at which 5% weight loss occurred (T5) and the maximum decomposition process all shown in Table 1. The polymers P2 and P4 were more thermally stable than P1 and P3. The higher thermal stability of polymer P4 is not surprising, due to the increased content of aromatic units [14,16]. When comparing T5 values for



Scheme 1

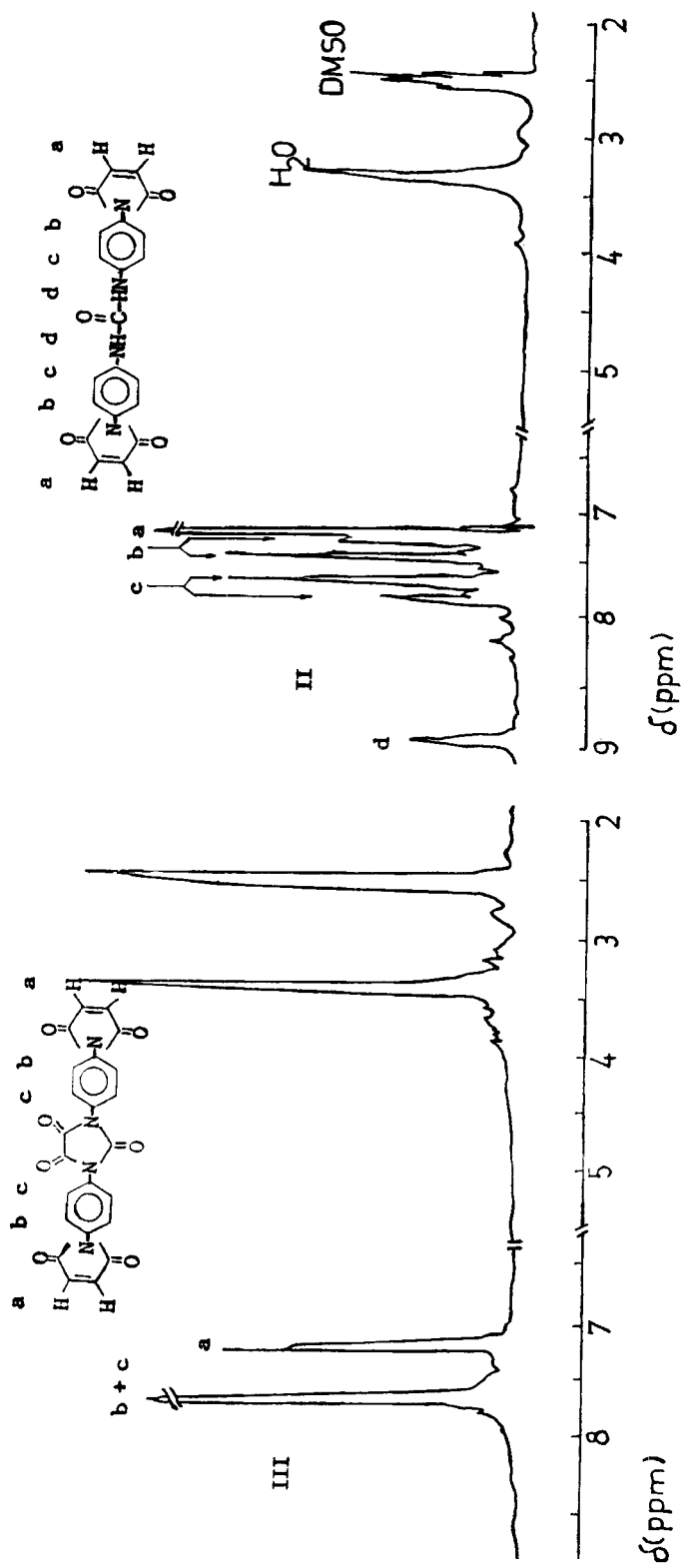


Fig. 1. $^1\text{H-NMR}$ spectra of monomers II and III.

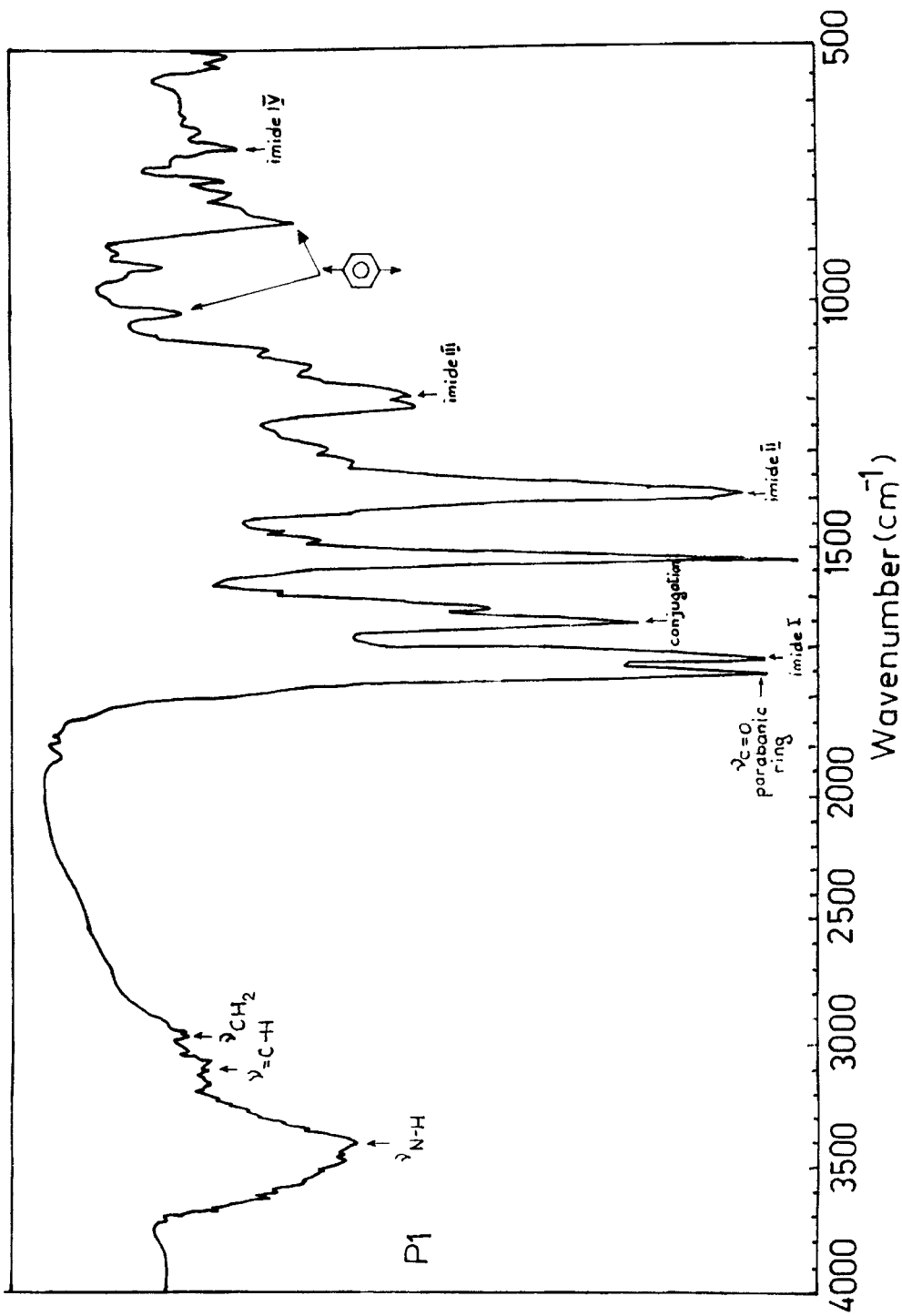


Fig.2. IR spectra of polymer P1.

Table 1. Properties of polymers P(1-4).

Polymer	Yield (%)	M.p. (°C)	η_{inh}^a (dL/g)	TGA ^b (°C)			DSC ^c (°C),Td
				T5	T5 ^d	Tmax	
P1	88	>350	0.30	310	300	380	235
P2	90	>300	0.35	340	-	395	260
P3	82	>300	0.35	328	315	382	256
P4	92	>300	0.50	336	325	400	227

^aMeasured at a conc. of 0.5 g/dL in DMSO at 30°C.

^bTGA measurements at a heating rate of 12°C/min, in air.

^cDSC scans, first heating cycle at a heating rate of 20°C/min, in nitrogen.

^dValues for similar polymers without parabanic units[14].

the polymers P1,P3,P4 with similar values for the polymers without parabanic units[14](Table 1),one see clearly that all values of the former are higher;the parabanic units provided an improvement in the thermal stability for these poly(amino-bismaleimide)s. The DSC curves (first heating cycle at a heating rate of 12°C/min (Fig.3) showed similar thermal behaviour for all of the studied polymers. No glass transition temperatures (Tg) or melting endotherms were detected up to about 250°C,where a large exotherm was observed. Samples analyzed under optical microscope showed no melting or softening behaviour up to 300°C. Probably the rigid character of the polymers chains and the increased content of hydrogen bonds has lead to values of Tg exceeding the polymers decomposition temperatures.

CONCLUSIONS

New poly(amino-bismaleimide)s containing parabanic rings in the backbone were obtained by a polyaddition reaction. The structures of polymers were confirmed by elemental analysis and IR spectra. Inherent viscosities,solubilities DSC and TGA measurements were also perfor-

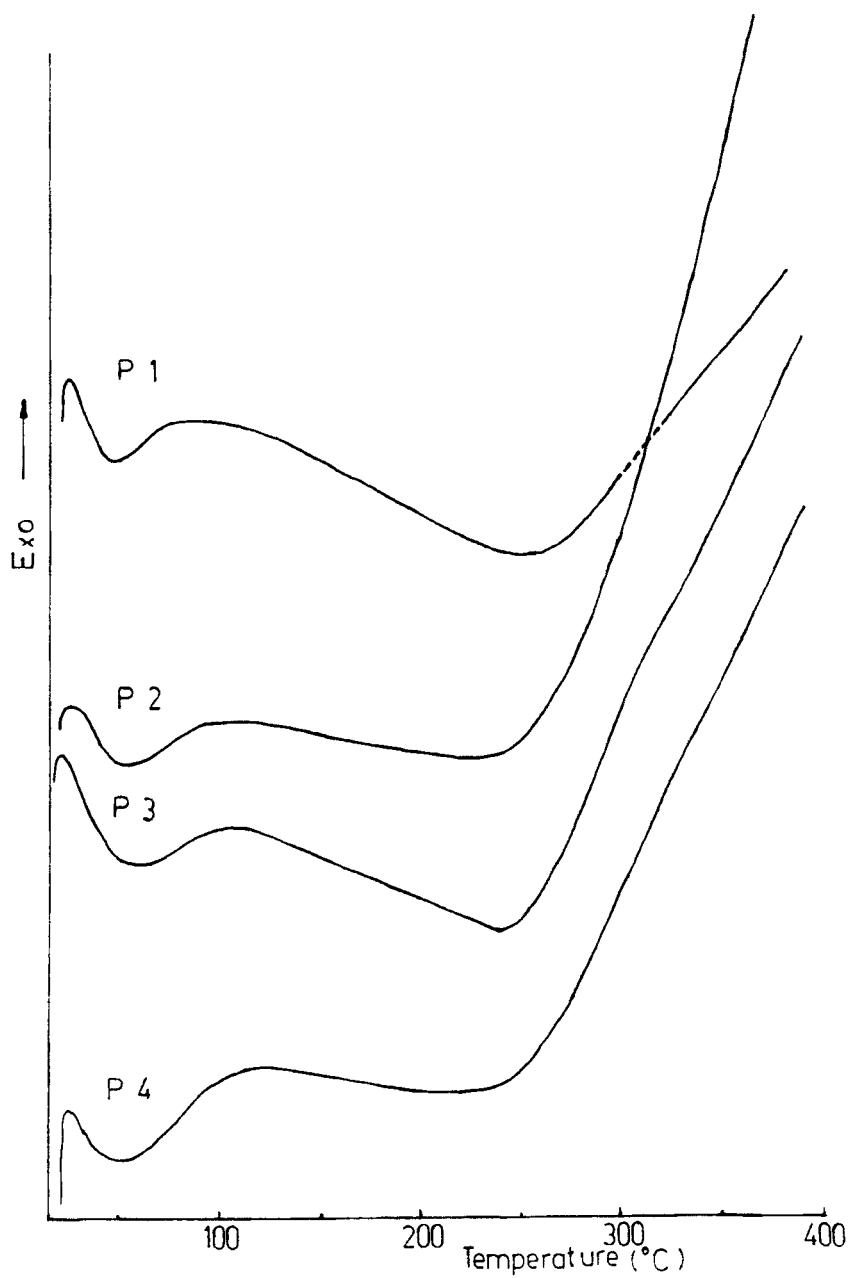


Fig.3. DSC scans of polymers P(1-4), first heating cycle at a heating rate of 12°C/min, in nitrogen.

med. The obtained polymers showed higher thermal stability than other polymers without parabanic units [12,14].

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