



## Synthesis and Characterization of N-Phenyl Citraconimide Homopolymers

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Synthesis and characterization of poly(N-phenyl citraconimide) (PPC), poly(N-*o*-chorophenyl citraconimide) (POC), poly(N-*m*-chorophenyl citraconimide) (PMC), poly(N-*p*-chorophenyl citraconimide) (PCC), poly(N-*p*-tolyl citraconimide) (PPTC) were evaluated by using anionic and controlled free radical initiators.

**Key Words:** N-Phenyl citraconimide, Homopolymers, Citraconic acid, Citraconic anhydride, Citraconimide.

### INTRODUCTION

Polymers derived from maleimides and citraconimide are some of the most important resins used in the aerospace and electronic industries because of their resistance to water, fire, radiation and due to their high stability and high softening temperature. Copolymerization of MMA with N-aryl substituted maleimides has been investigated<sup>1-5</sup> with an aim to improve their thermal performance.

Earlier studies have shown that the position as well as the nature of substituent *i.e.* electron withdrawing or releasing group in maleimides affected the copolymerization and thermal behaviour of MMA copolymers therefore the main focus of present work is to investigate synthesis and characterization of N-(phenyl)citraconimide N-(*o*/*m*/*p*-chorophenyl)citraconimide and N-(*p*-tolyl)citraconimide homopolymers by using anionic and controlled free radical initiators.

### EXPERIMENTAL

Citraconic acid, P<sub>2</sub>O<sub>5</sub>, chloroform, tetrahydrofuran, AIBN, nitrogen gas, methanol and acetone.

**Procedure:** 200 g of Citraconic acid, 144 g of phosphorus pentoxide and 1000 mL of chloroform were taken in a 2 L reaction kettle equipped with mechanical stirrer and reflux condenser. The mixture was allowed to reflux with stirring for 48 h. After refluxing, chloroform solution was decanted from the viscous brown residue at the bottom of the flask and the solution was concentrated to 0.5 L by removing chloroform. A rotary vacuum evaporator was used for this purpose. On cooling the remaining solution to -10 °C, Citraconic anhydride

crystallizes out which was separated by filtration followed by drying in vacuum oven for 3 h at 40 °C. Purity of the crystals was checked by differential scanning calorimetry (Fig. 1) and yield was found *ca.* 80 %.

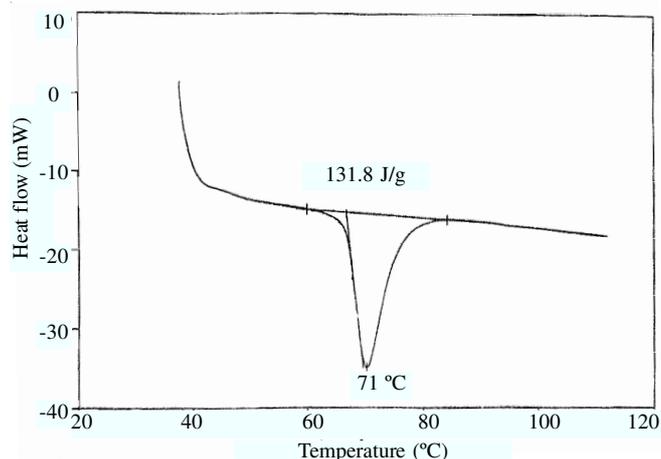


Fig. 1. DSC scan of citraconic anhydride

N-aryl citraconimide monomers was synthesized as per the procedure<sup>6</sup> using acetone as a solvent. Citraconimide have two electron-withdrawing carbonyl groups and therefore may give high-molecular-weight materials by anionic polymerization. By contrast, the anionic polymerization of dialkyl citraconimides yield only cyclic oligomers.

Homopolymerization of N-aryl citraconimides was carried out at 60 °C under nitrogen atmosphere in solution using THF as solvent and AIBN as an initiator. A 25 % (w/v)

solution of monomers in THF was placed in a three-necked round bottom flask equipped with a reflux condenser, CaCl<sub>2</sub> drying tube and a nitrogen gas inlet tube. The polymerization was initiated by adding 0.5 % AIBN (w/w) to the monomer solution. The reaction was stopped at low conversion (up to 15 %) by pouring the contents of the flask into large excess of methanol. The precipitated polymer was washed repeatedly with hot methanol to remove unreacted monomers and dried in vacuum oven.

Radical polymerization of N-alkyl-citraconimides and N-aryl citraconimides have been carried out in degassed glass tubes or in an inert atmosphere in the presence of suitable initiators at 40-160 °C.

## RESULTS AND DISCUSSION

In the FTIR spectra of the monomers, the characteristic absorption bands due to imide groups were observed at  $1709 \pm 5 \text{ cm}^{-1}$  and  $1770 \pm 5 \text{ cm}^{-1}$ . The absorption band due to  $\text{-C=C-}$  stretch was observed at  $1662 \text{ cm}^{-1}$ . FTIR spectra of N-(*o*-chlorophenyl)citraconimide and N-(*p*-tolyl)citraconimide are shown in Figs. 2 and 3, respectively.

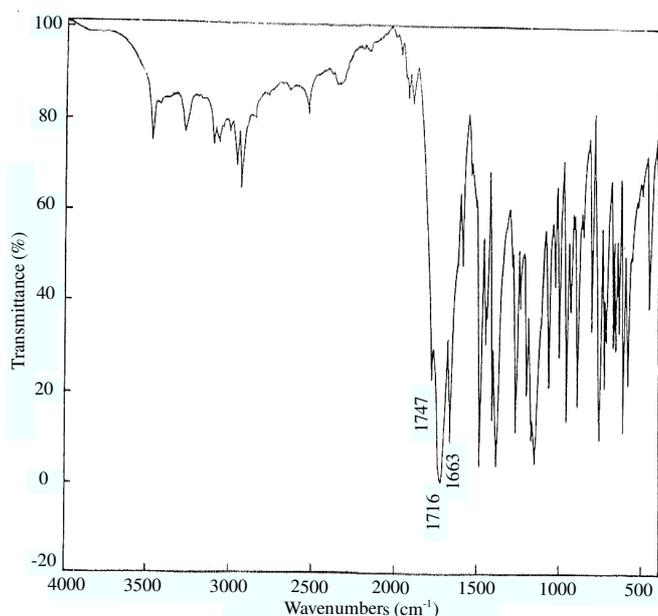


Fig. 2. FTIR spectrum of N-(*o*-chlorophenyl)citraconimide

DSC scans of homopolymers were recorded to study the effect of monomer (N-aryl citraconimide) structure and the glass transition region was characterized by noting the following temperatures.

$T_e$  = Extrapolated onset temperature

$T_g$  = Midpoint temperature (inflection point)

$T_f$  = Extrapolated end set temperature.

In order to have a similar thermal history, second heating scans were used to determine the glass transition temperature. Powdered samples were first heated in a DSC cell from room temperature to 120 °C followed by cooling. The quench cooled samples were used for recording DSC scans at a heating rate of 10 °C/min. The second heating scans were used in all the homo/copolymer samples for characterizing glass transition region.

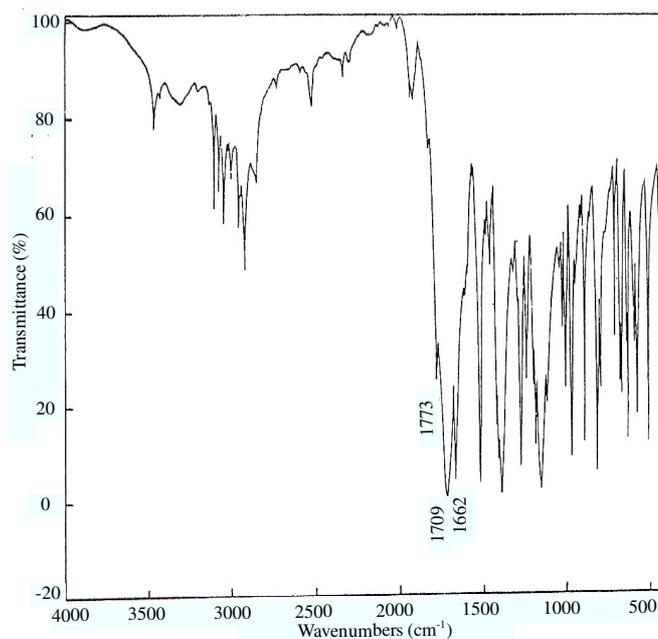


Fig. 3. FTIR spectrum of N-(*p*-tolyl)citraconimide

DSC traces of all homopolymers are shown in Fig. 4 and the results are summarized in Table-1. Homopolymers of citraconimide had glass transition temperature ( $T_g$ ) in the range of 220-240 °C and was dependent on the structure *i.e.* nature and position of the substituent. PMMA prepared under similar conditions had  $T_g$  of 108.4 °C. Homopolymers of N-aryl citraconimides having electron-withdrawing group at *p*-position, poly(N-phenyl citraconimide) (PPC) showed higher  $T_g$  (239.3 °C) as compared to phenyl citraconimide (PC) (220.4 °C) and poly(N-*p*-tolyl citraconimide) (PPTC) (232.4 °C) homopolymers. Position of the substituent also affected the glass transition temperature of homopolymers.

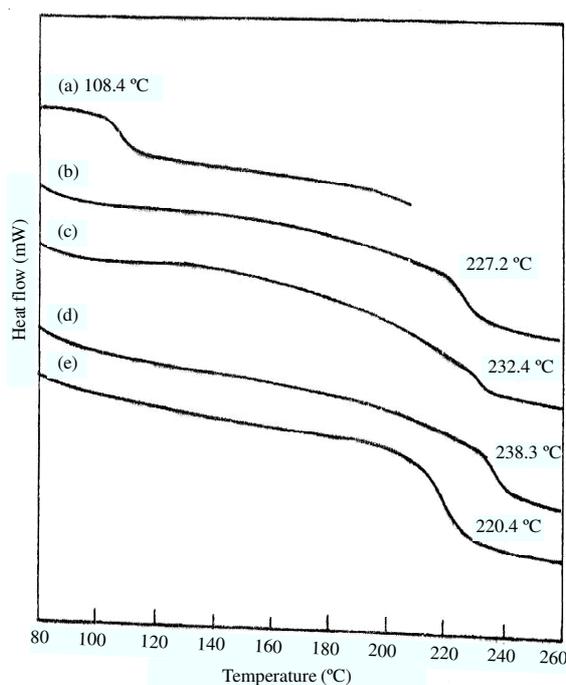


Fig. 4. DSC traces of homopolymers (a) PMMA (b) PMC (c) PPTC (d) PPC (e) PC

TABLE-1  
RESULTS OF DSC SCANS OF HOMOPOLYMERS  
(HEATING RATE 10 °C/min)

Samples	T <sub>c</sub> (°C)	T <sub>g</sub> (°C)	T <sub>f</sub> (°C)
PC	209.3	220.4	223.7
PPC	228.2	239.3	247.1
PMC	221.9	227.2	233.8
POC	—	—	—
PPTC	213.4	232.4	236.7

In the DSC scans of citraconimide monomers, an endothermic transition due to melting was observed. The melting points noted from the endothermic peak position are given in Table-2.

TABLE-2  
MELTING POINT OF N-ARYL CITRACONIMIDE  
MONOMERS OBTAINED BY DSC

Monomers	Melting point (°C)
Citraconimide	115
PC	128
MC	116
OC	91
PTC	118

Thermal stability of the monomers was determined by recording TG/DTG traces in the nitrogen atmosphere. The relative thermal stability of the monomers was compared by comparing the initial decomposition temperature (T<sub>i</sub>), temperature of maximum rate of weight loss (T<sub>max</sub>), final decomposition temperature (T<sub>f</sub>) and percent char yield at 600 °C. TGA scans of N-aryl citraconimide monomers are shown in Fig. 5. Results of the TG/DTG traces are given in Table-3. All monomers show two step degradation except N-phenyl citraconimide which shows three steps degradation. All the monomers were stable up to temperature 135 °C and showed sharp weight loss above the melting point of the monomer. This could be due to the volatilization of the sample above the melting point.

TABLE-3  
RESULTS OF THERMOGRAVIMETRIC ANALYSIS IN  
NITROGEN ATMOSPHERE (HEATING RATE 10 °C/min)

Samples	T <sub>i</sub> (°C)	T <sub>max</sub> (°C)	T <sub>f</sub> (°C)	% Char yield at 600 °C
C	138	207	328	2.8
	326	401	503	
	501	567	621	
PC	151	232	281	2.0
	283	354	398	
MC	135	218	301	2.6
	300	401	479	
OC	125	235	301	2.6
	301	351	472	
PTC	130	237	313	3.1
	310	375	475	

Theoretically from the knowledge of copolymer composition and homopolymer T<sub>g</sub> value, the T<sub>g</sub> of a random copolymer can be predicted using Fox equation<sup>7</sup>.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

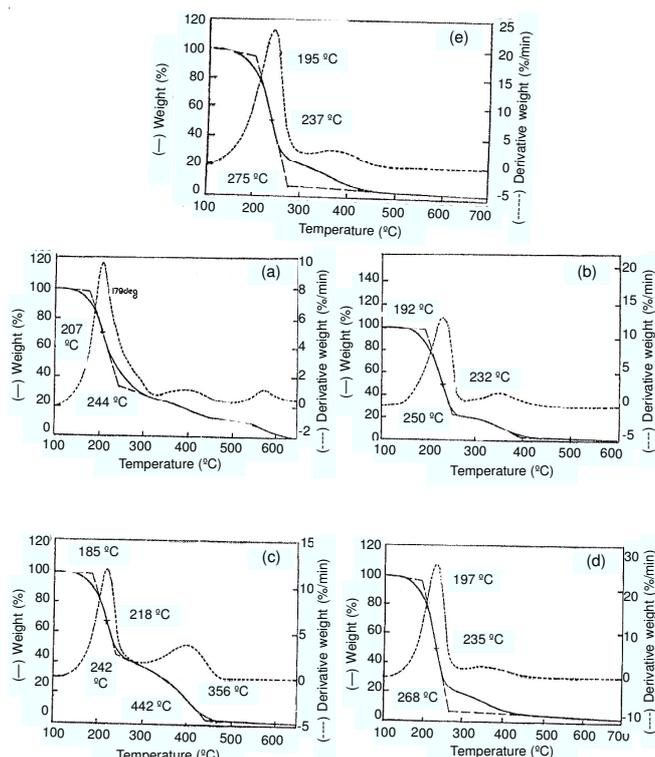


Fig. 5. TG/DTG traces of N-aryl citraconimide monomers (a) C (b) PC (c) MC (d) OC and (e) PTC

where, T<sub>g1</sub> and T<sub>g2</sub> are the glass transition temperature of homopolymer 1 and 2, w<sub>1</sub> and w<sub>2</sub> are their fraction, respectively. The result of the T<sub>g</sub> values obtained by Fox equation are given in Table-4.

TABLE-4  
RESULT OF THE GLASS TRANSITION  
TEMPERATURE OF THE COPOLYMERS

Samples	T <sub>g</sub> (°C) (Experimental)	T <sub>g</sub> (°C) Calculated by Fox equation
PC-1	147.1	131.8
PC-2	166.0	145.2
PC-3	171.9	159.3
PC-4	185.1	166.3
PC-5	185.6	180.4
PPC-1	142.6	136.9
PPC-2	149.1	155.7
PPC-3	177.2	168.7
PPC-5	190.7	189.3
PMC-1	123.3	136.3
PMC-2	142.1	154.4
PMC-3	144.2	165.7
PMC-4	151.6	174.3
PMC-5	155.1	184.4
PPTC-1	150.5	143.1
PPTC-2	167.1	150.1
PPTC-3	167.6	167.3
PPTC-4	187.2	181.7
PPTC-5	204.2	187.8

TG/DTG traces of PMMA, PPC, PMC, POC, PC and PPTC are shown in Fig. 6. In case of PMMA, three-step degradation was observed. The first step degradation (168-264 °C) is attributed to head to head linkages; second step (264-339 °C) due to end unsaturation and the third step (339-

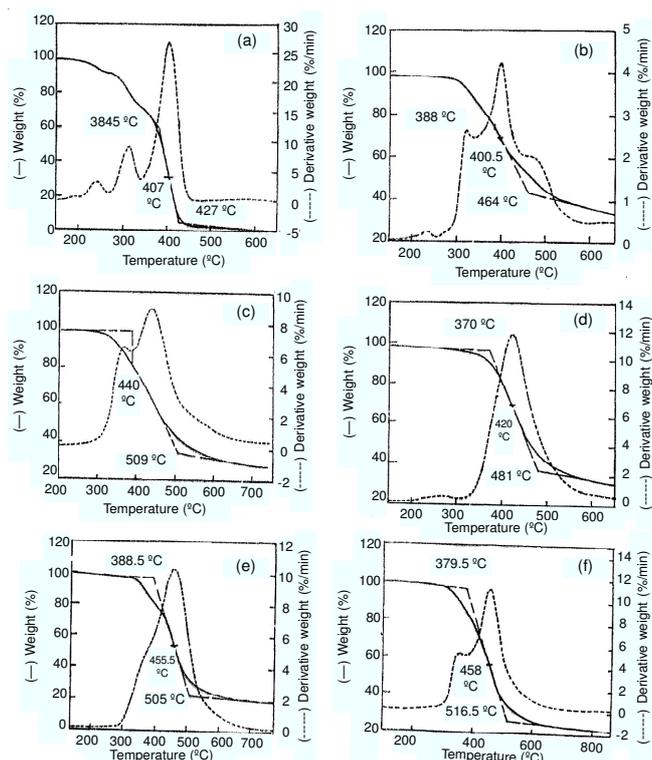


Fig. 6. TG/DTG traces of homopolymers (a) PMMA (b) PPC (c) PMC (d) POC (e) PC (f) PPTC

457 °C) due to depropagation. Major weight loss (~70 %) in case of PMMA was observed in the temperature range of 339–457 °C. Thermal degradation in case of poly (N-aryl citraconimide) was dependent on the structure and it shows single step degradation in case of POC and PC, PPTC and PMC shows two step degradation whereas three step degradation was observed in case of PPC. Poly(N-aryl citraconimide) leave behind a char of 23.2–35.5 % at 700 °C. Char yield (%) in case of poly(N-chlorophenyl citraconimide) *i.e.* samples PPC/PMC/POC was higher as compare to PC/PPTC homopolymers. Results of TG/DTG traces for homopolymers are summarized in Table-5. Integral procedural decomposition temperature (IPDT) for all homopolymers of N-aryl citraconimide was found to be in the range of 500–531 °C whereas PMMA had IPDT value of 376 °C. In case of PPC and POC samples although weight loss started at a lower temperature, the thermal stability over the temperature range of 50–800 °C was higher as compared to other homopolymers. Char yield was also maximum *i.e.* 35.5 % in the case of PPC and POC homopolymers.

TABLE-5  
RESULTS OF THERMOGRAVIMETRIC ANALYSIS OF  
HOMOPOLYMERS IN NITROGEN ATMOSPHERE  
(HEATING RATE 10 °C/min)

Samples	T <sub>i</sub> (°C)	T <sub>max</sub> (°C)	T <sub>f</sub> (°C)	% Weight loss	% Char yield at 700 °C	IPDT (°C)
PC	307.2	447.8	700.6	76.90	23.2	501.4
PPC	255.0	324.0	345.0	10.30		
	347.0	398.0	456.0	31.20	35.5	531.00
	455.0	471.0	595.0	17.30		
PMC	278.0	363.0	385.0	17.10		
	385.0	432.0	656.0	51.90	31.7	511.25
POC	193.0	269.0	307.0	2.98		
	319.0	415.0	591.0	61.90	35.5	519.02
PPTC	305.2	352.9	374.3	12.50		
	375.0	450.6	654.8	60.8	25.6	509.95

## Conclusion

PPC homopolymer had a higher T<sub>g</sub> (239.3) than PMC (227.2) homopolymer whereas the DSC scan of POC homopolymer recorded up to 300 °C showed no visible transition in the temperature range.

The position of chloro-substituent in N-aryl citraconimide affects the melting point. Melting point is higher in case of para substituent and lowest in case of *ortho* substituent.

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