

# Copolymerization of Acrylonitrile with *N*-(Substituted phenyl)itaconimide

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Received 30 May 2010; accepted 27 September 2010

DOI 10.1002/app.33507

Published online 17 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Acrylonitrile was copolymerized with four *N*-(substituted phenyl)itaconimide in dimethyl formamide using azobisisobutyronitrile as initiator. The structural characterization of the copolymers was done using FTIR, UV/vis, and elemental analysis. Thermal characterization of the copolymers was done using thermogravimetry (TG) and differential thermal analysis (DTA) data, which showed a remarkable improvement in the thermal behavior of the investigated copolymers. The acrylonitrile/

bromophenyl itaconimide copolymer possessed the best thermal property. The investigation of the dyeing properties of the acrylonitrile-*N*-(substituted phenyl)itaconimide showed good affinity toward basic dyes as well as appreciable improvement in their color fastness toward UV light. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 169–175, 2011

**Key words:** copolymerization; thermogravimetry; fibers

## INTRODUCTION

The technological importance of polyacrylonitrile (PAN) is known to suffer from several disadvantages: weak moldability, color instability, and weak dyeability. Copolymerization of acrylonitrile with different comonomers has been used as an effective way for improving the polymer's properties.<sup>1,2</sup> The introduction of *N*-substituted maleimides into PAN backbone is reported to improve the modability, while keeping the excellent mechanical properties of the polymer.<sup>3,4</sup> Moreover, an improvement of the thermal properties of acrylonitrile-*N*-aryl maleimides copolymers is also reported.<sup>5</sup>

As polymaleimides have intensively characterized as thermal stable polymers, polyitaconimide are also candidates for thermally stable vinyl polymers, but there have been very few studies on their polymerization reactivity and on the characterization of the polymer including its thermal stability.<sup>6–9</sup> *N*-substituted itaconimide have been used as comonomers for the production of methyl methacrylate copolymers with improved properties.<sup>10–14</sup>

This article deals with the synthesis, characterization, and radical copolymerization of *N*-(phenyl)itaconimide derivatives with acrylonitrile using dimethyl formamide (DMF) as solvent.

## EXPERIMENTAL

### Materials

Acrylonitrile (BDH) was purified by distillation before polymerization. Azobisisobutyronitrile (AIBN) was purified by repeated crystallization from methanol, and DMF (Prolabo) was used as received. Three basic dyes "Crysoidine RN, Maxillon orange, and Brilliant green B" from Ciba-Geigy were used without further purification.

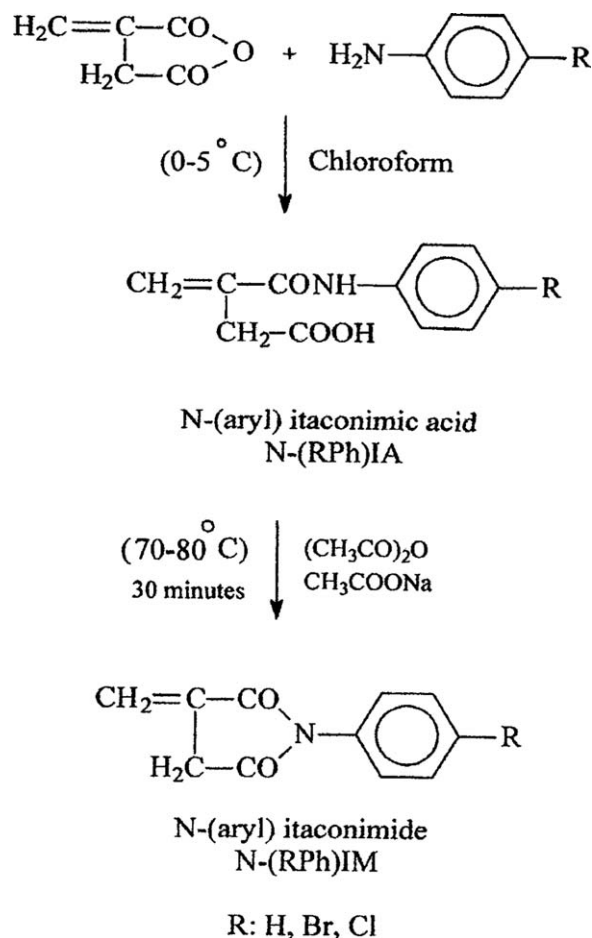
### Preparation of *N*-(substituted phenyl)itaconimide

Four *N*-(substituted phenyl)itaconimide were prepared by the reaction of itaconic anhydride (1 mole), in DMF, with the respective primary amine (1 mole), in DMF, to form the *N*-substituted (phenyl)itaconamic acid (Scheme 1). The later was then dehydrated with acetic anhydride and fused sodium acetate for 30 min at 70°C. The whole solution was precipitated in cold ethanol.<sup>15</sup> These monomers were recrystallized from aqueous ethanol. The purity of the monomers was checked by thin layer chromatography (TLC). Table I gives the melting point data of the *N*-(substituted phenyl)itaconimide.

### Copolymerization procedure

Polymerization ampoules of Pyrex glass were charged with the monomers, the solvent (DMF), and the initiator (AIBN) ( $2 \times 10^{-2}$  mol/L) (Scheme 2). The ampoules were covered with serum caps, cooled, and purged with a slow stream of purified nitrogen. The polymerization was then carried out at

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**Scheme 1** Synthesis of *N*-aryl itaconimide derivatives.

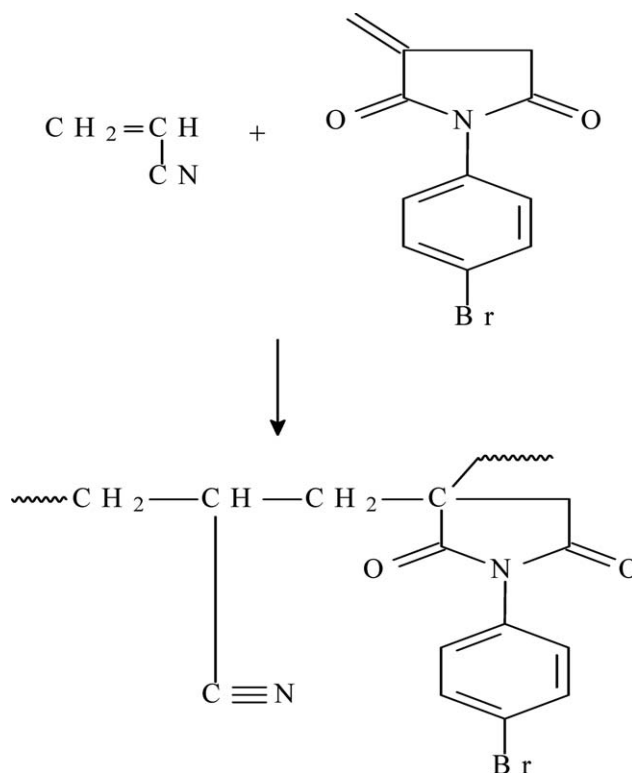
70°C. The reaction was terminated by opening the ampoules and pouring the contents into a large amount of ethanol. The copolymers were dried to constant weight at 60°C. The copolymer compositions were calculated on the basis of their halogen and/or nitrogen contents.

### Spectroscopic measurements

Infrared spectra were obtained using Perkin-Elmer spectrophotometer (FTIR 1650). The spectrum resolution was 4 cm<sup>-1</sup>, and the scanning range was from 700–4000 cm<sup>-1</sup>. UV/visible spectra were obtained using Perkin-Elmer lambda 4 UV/vis spectrophotometer.

**TABLE I**  
**Melting Point of Various *N*-Phenyl Itaconimide Derivatives**

<i>N</i> -phenyl itaconimide	Code name	Melting point (°C)
<i>N</i> -phenyl itaconimide	NPhIM	90°C
<i>N</i> -2-chloro phenyl itaconimide	<i>N</i> -2ClPhIM	122–124°C
<i>N</i> -4-chloro phenyl itaconimide	<i>N</i> -4ClPhIM	125°C
<i>N</i> -4-bromo phenyl itaconimide	<i>N</i> -4BrPhIM	127°C



**Scheme 2** Copolymerization of acrylonitrile with 4-bromophenyl itaconimide.

**TABLE II**  
**Copolymerization Data for the System Acrylonitrile (*M*<sub>1</sub>) and 4-Cl PhIM (*M*<sub>2</sub>) in DMF at 70°C**

$X = \frac{[M_1]}{[M_2]}$	% of conversion	Amount of Cl (wt. %)	$Y = \frac{[m_1]}{[m_2]}$
19.00	5.00	2.7	20.92
9.00	7.80	5.5	8.26
4.00	7.00	9.0	3.52
2.33	9.50	11.2	2.06
1.50	9.00	12.7	1.35
1.00	7.50	13.7	0.97
0.66	10.80	14.6	0.66
0.43	7.50	15.5	0.40
0.25	9.40	16.2	0.22
0.11	9.30	16.6	0.11

**TABLE III**  
**Copolymerization Data for the System Acrylonitrile (*M*<sub>1</sub>) and 2-Cl PhIM (*M*<sub>2</sub>) in DMF at 70°C**

$X = \frac{[M_1]}{[M_2]}$	% of conversion	Amount of Cl (wt. %)	$Y = \frac{[m_1]}{[m_2]}$
19.00	11.00	2.95	18.80
9.00	11.50	5.20	8.97
4.00	9.50	8.0	4.45
2.33	7.00	10.00	2.78
1.50	8.00	12.50	1.44
1.00	5.50	13.50	1.04
0.66	6.00	14.4	0.73
0.43	7.00	15.25	0.47
0.25	8.50	15.85	0.31
0.11	6.00	16.40	0.17

TABLE IV  
Copolymerization Data for the System Acrylonitrile ( $M_1$ )  
and 4-Br PhIM ( $M_2$ ) in DMF at 70°C

$X = \frac{[M_1]}{[M_2]}$	% of conversion	Amount of Br (wt. %)	$Y = \frac{m_1}{m_2}$
19.00	5.00	3.50	38.92
9.00	5.50	7.25	16.26
4.00	9.50	11.30	8.52
2.33	9.00	15.50	4.96
1.50	11.00	18.85	3.35
1.00	10.50	21.00	2.47
0.66	8.50	23.60	1.66
0.43	9.90	25.75	1.10
0.25	10.80	29.00	0.42
0.11	7.00	30.13	0.25

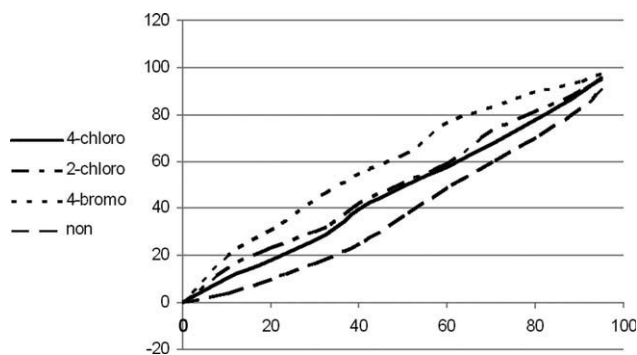


Figure 1 Copolymer composition diagram of AN [ $M_1$ ] and different  $N$ -substituted itaconimide; — 4ClPhIM; - - 2ClPhIM; . . . 4BrPhIM; - . - PhIM.

### Thermal analysis

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were performed from 25 to 500°C, in air, at heating rate of 10°C/min using Shimadzu thermal analyzer DA-30.

### Dyeing method

The fine homogeneous powdered polymer samples were immersed at room temperature in the dye bath using a dye/liquor ratio of 1 : 100. The pH was adjusted at 3–4 using acetic acid/sodium acetate

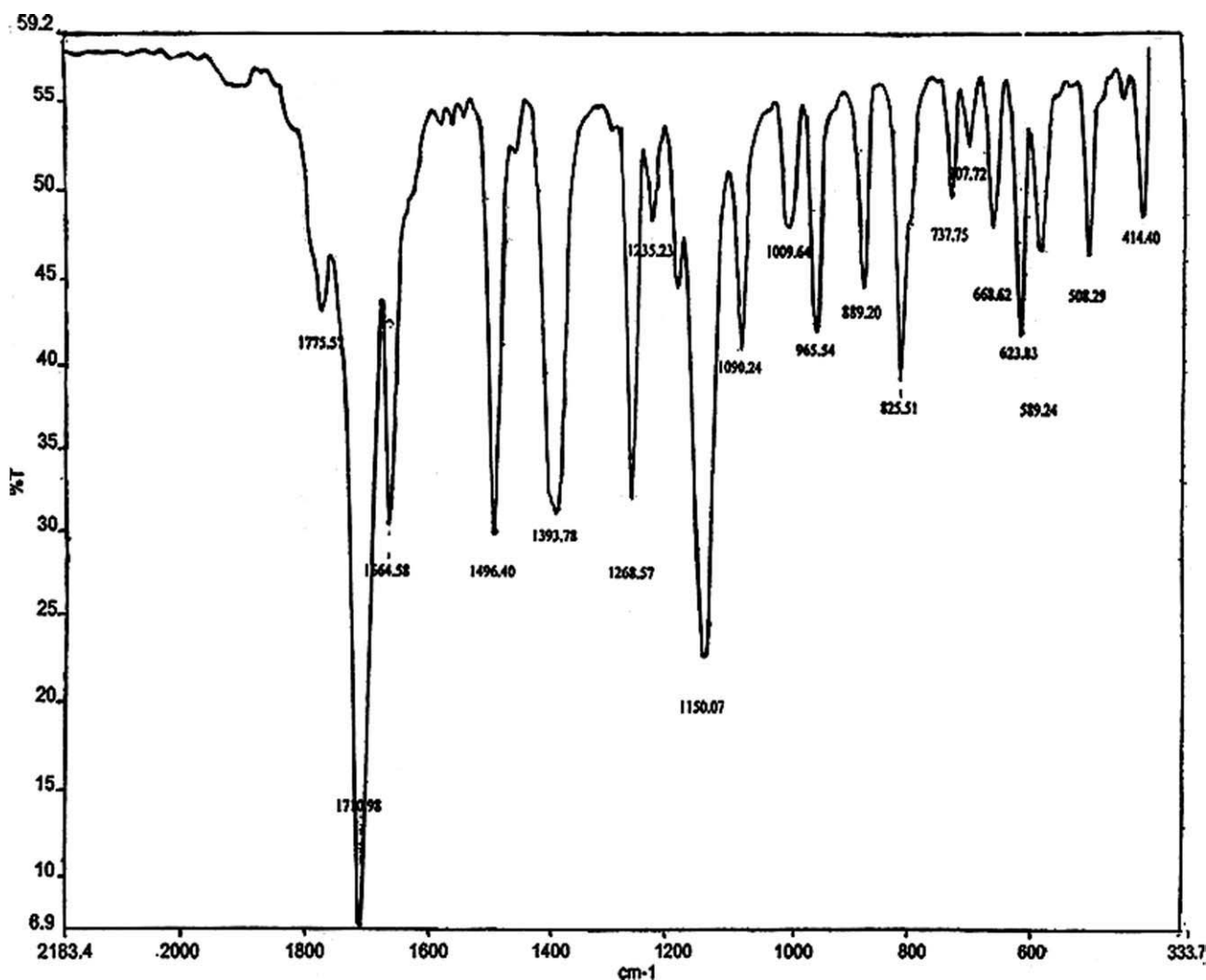


Figure 2 IR spectrum of  $N$ -4-chloro phenyl itaconimide.

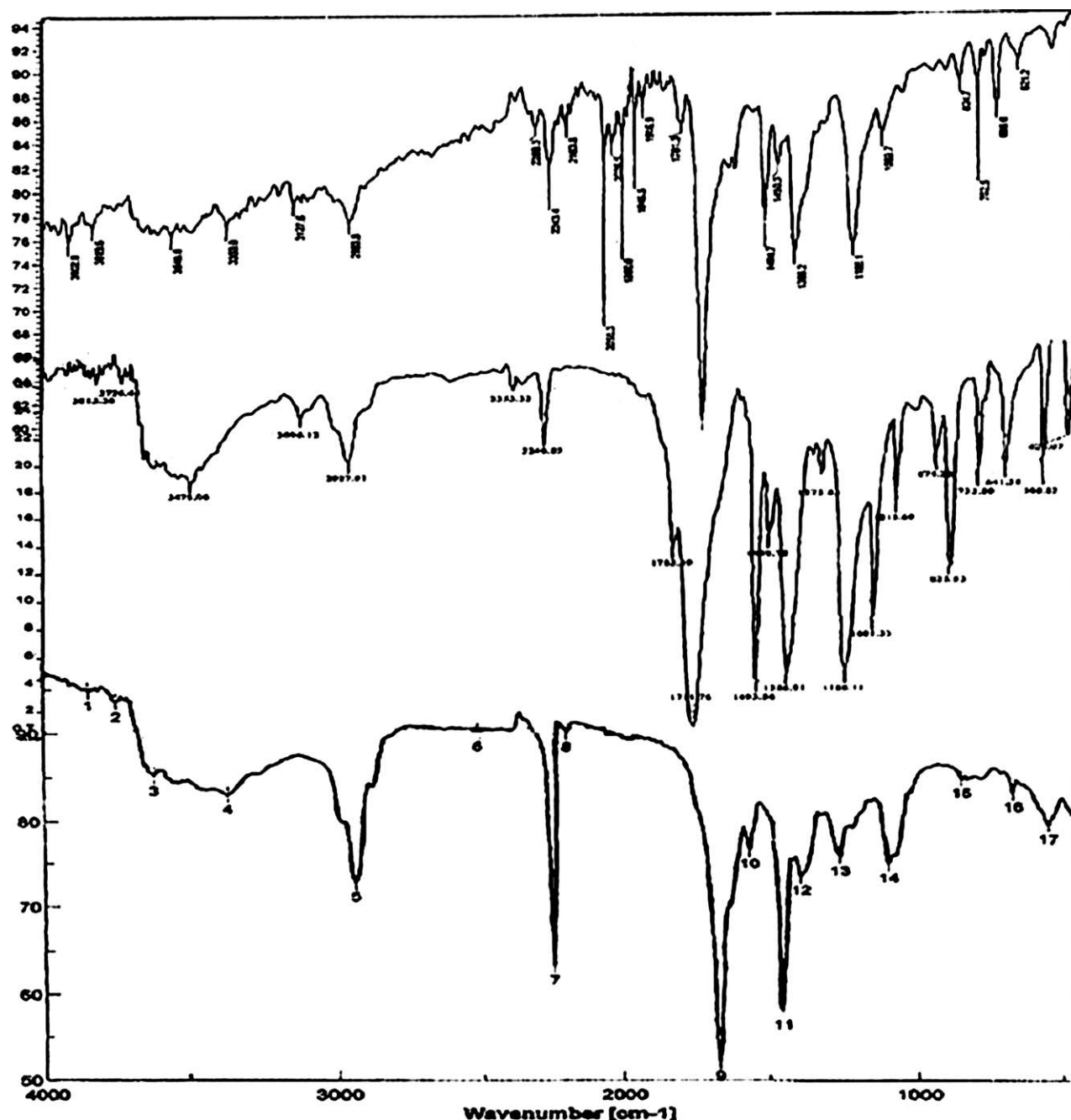


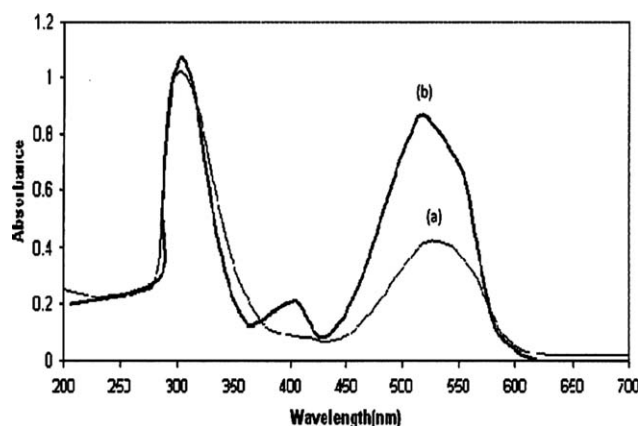
Figure 3 IR spectra of (a) Poly(acrylonitrile); (b) AN/4Cl Ph IM; (c) AN/4BrPhIM.

buffer mixture. The temperature was then gradually increased to 95°C in 30 min and was kept at this temperature for another 50 min. The dye bath was cooled to 60°C, and the sample was centrifuged, rinsed, and dried.<sup>16</sup> The amount of dye absorbed on the sample was measured by the conventional colorimetric method to measure the concentration of dye remaining in the dye bath.

## RESULTS AND DISCUSSION

The composition of the initial monomer feed mixtures and that of copolymers for *N*-(substituted

phenyl)itaconimide are compiled in Tables II–IV and Figure 1. The results clearly indicate that the reactivity of *N*-PhIM was found to be slightly less than that of AN, which implies a greater probability for a random copolymerization (Fig. 1). The data in the tables showed that *N*-4-BrPhIM possessed the lowest reactivity, which is a direct consequence of the bulkiness of the bromine atoms. It was also observed that the position of the chlorine atom in the phenyl ring has a slight effect upon the reactivity of the monomer. This can find an explanation in light of the small size of the chlorine atom and the same electronic effect, which



**Figure 4** UV/vis spectra of (a) 4-bromophenyl itaconimide monomer and (b) acrylonitrile/4-bromophenyl itaconimide copolymer.

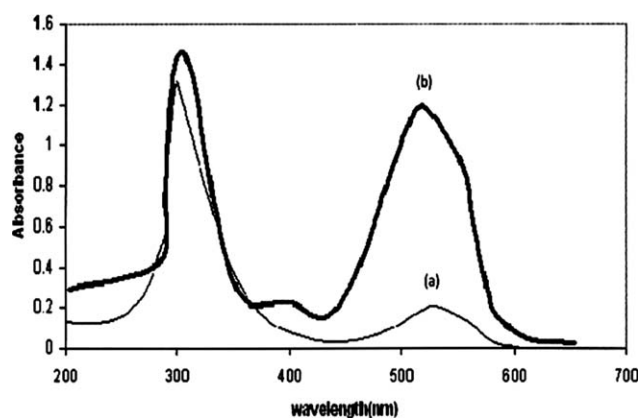
causes either in the ortho or in the para position of the phenyl ring.

### Characterization of the copolymers

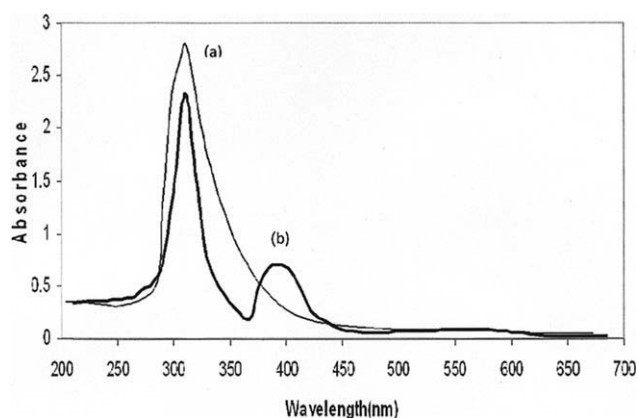
#### Infrared spectroscopic analysis

In the FTIR spectra of the itaconimide monomers, the characteristic absorption bands due to the imide group were observed at  $1709 \pm 3$  and  $1772 \pm 3$   $\text{cm}^{-1}$ . The absorption band due to  $\text{—C=C—}$  stretching was observed at  $1663$   $\text{cm}^{-1}$  (Fig. 2). However, The IR spectra of the acrylonitrile–itaconimide copolymers showed the following peaks when compared with the IR spectrum of PAN (Fig. 3):

1. Presence of the cyano-stretching band at  $2245$   $\text{cm}^{-1}$ .
2. Presence of the imide carbonyl stretching bands at  $1711$  and  $1783$   $\text{cm}^{-1}$ .
3. Absence of the  $\text{—C=C—}$  stretching band at  $1664$   $\text{cm}^{-1}$ .



**Figure 5** UV/vis spectra of (a) 4-chloro phenyl itaconimide monomer and (b) acrylonitrile/4-chloro phenyl itaconimide copolymer.



**Figure 6** UV/vis spectra of (a) phenyl itaconimide monomer and (b) acrylonitrile/phenyl itaconimide copolymer.

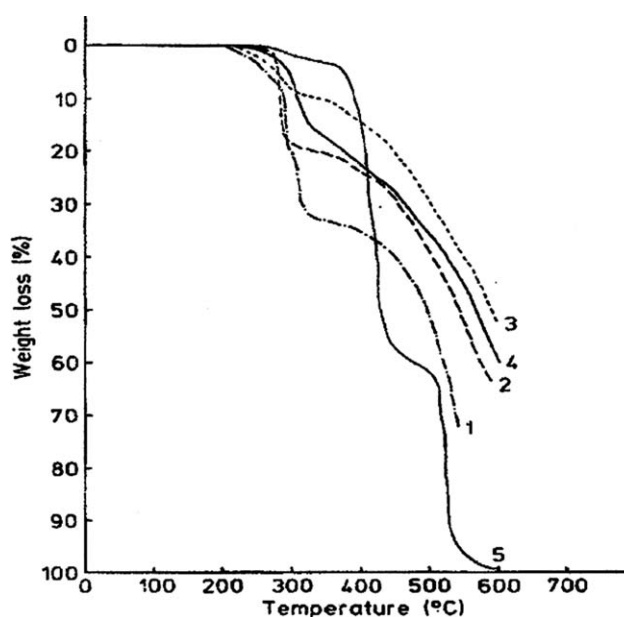
The aforementioned observations confirmed the presence of the itaconimide moieties in the PAN matrix as comonomers.

#### UV/vis spectroscopic analysis

Investigation of the prepared copolymers samples in DMF, AN/4BrPhIM, AN/4ClPhIM, and AN/PhIM (Figs. 4–6), by the UV spectrophotometer showed new peak at  $\lambda = 400$  nm when compared with the itaconimide spectra. This peak also confirmed the copolymers formation.

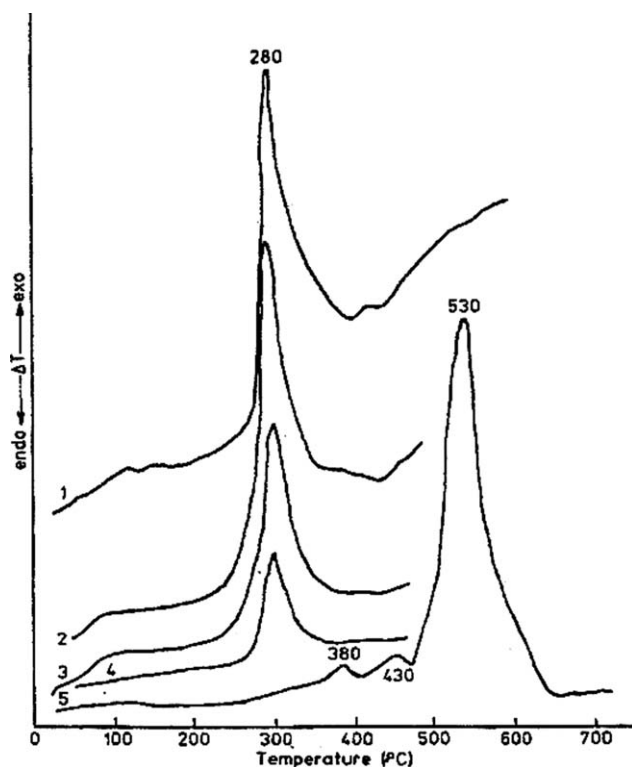
#### Thermal characterization

The TG and DTA curves of PAN, poly(4-chlorophenylitaconimide) (P4ClPhIM) together with some



**Figure 7** TG curves for AN/N-substituted itaconimide polymers and copolymers, heating rate  $10^\circ\text{C}/\text{min}$  in air; (1) PAN; (2) AN/5 mol % 4Cl Ph IM; (3) AN/2.5 mol % 4BrPhIM; (4) AN/10 mol % 4Cl Ph IM; (5) P4ClPhIM.





**Figure 8** DTA curves for AN/*N*-substituted itaconimide polymers and copolymers, heating rate 10°C/min in air; (1) PAN; (2) AN/5 mol % 4Cl Ph IM; (3) AN/2.5 mol % 4BrPhIM; (4) AN/10 mol % 4Cl Ph IM; (5) P4ClPhIM.

representative copolymers are given in Figures 7 and 8, respectively. The thermal analysis of PAN shows the usual thermogram with an initial decomposition temperature at 250°C and an exotherm with a maximum at 280°C, which results from the oligomerization of the nitrile groups and formation of some aromatic structure.<sup>17</sup>

On the other hand, the thermogram of P4ClPhIM shows a different behavior. Its TG curve contains two steps with initial decomposition temperatures at 360 and 480°C, where the corresponding DTA curve has only two small exotherms with maxima at 380 and 430°C followed by a greater one at 530°C. In spite of the fact the copolymers have degradation curves similar to those of PAN, the exotherm maximum at 280°C is reduced significantly due to the presence of 2–5 mol % bromophenyl itaconimide or chlorophenyl itaconimide as comonomers and is fur-

**TABLE V**  
Dye Absorption Data of Acrylonitrile/*N*-Phenyl Itaconimide Copolymers

Polymer	$T_o$ (°C)	Weight % at 500°C
1. PAN	250	59
2. AN/5 mol % 4ClPhIM	280	45
3. AN/2.5 mol % 4BrPhIM	300	32
4. AN/10 mol % 4ClPhIM	260	39
5. P4ClPhIM	360	62

**TABLE VI**  
UV Fastness of Dyed Samples Exposed to Low-Pressure Mercury Lamp

Polymer Mol %	CrysoidineRN $\lambda = 450$ nm	Brilliant greenB $\lambda = 620$ nm	Maxillon orange $\lambda = 498$ nm
PAN	35 P	56 P	35 M
AN/10% PhIM	93 G	77 M	97 G
AN/10% 4BrPhIM	82 G	68 M	94 G
AN/10% 4ClPhIM	66. M	61 M	97 G
P4ClPhIM	97 VG	96 G	94 G

VG: very good, G: good. M: moderate, P: poor.

ther reduced by increasing their molecular amounts in the copolymer. This could be explained by the fact that the itaconimide monomer affects the nitrile oligomerization process. Moreover, the initial decomposition temperature,  $T_o$ , temperature at which the decomposition of the polymer starts, increased with increasing the mol % of the itaconimide monomer (Fig. 7 and Table VI). The AN/BrPhIM copolymer possesses the highest  $T_o$  value. Thus, the introduction of limited ratios of the itaconimide monomers into the PAN matrix leads to the improvement of its thermal stability.

### Dyeing and fastness properties of the copolymers

The homopolymers and their copolymers were dyed with three basic dyes. A comparison between the amounts of absorbed dye by different samples is given in Table V. The data clearly reveal the higher affinity of the copolymers toward the absorption of the dyes compared with PAN. This affinity bears very small relation to the nature of the *N*-substituted group in the itaconimide moiety.

The color fastness of the dye toward light is known to depend much on the substrate fibers. As the color fastness toward UV light is considered to be an accelerated light fastness test, it is of interest to investigate if the presence of the itaconimide derivatives as comonomers with AN affects the light fastness property of the latter. Table VI illustrates the grades of the UV fastness of different dyed samples when exposed to a low-pressure mercury lamp up to 100 min. These grades were obtained by matching the exposed samples with the originals. The surrounding temperature was 85°C while the distance was kept constant at 10 cm. The results show an appreciable improvement of the color fastness as a result of copolymerization with itaconimide.

### CONCLUSIONS

The introduction of some units in the PAN main chain improves the thermal property as well as the

dyeability of the latter with regard to basic dyes. It also increases the UV fastness of the dyed copolymers. The acrylonitrile/bromophenyl itaconimide copolymer possessed the best thermal property when compared with AN/chloro phenyl itaconimide and AN/phenyl itaconimide copolymers.

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