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### Synthesis and Characterization of Heat-Resistant Polyamides from Thiadiazacycloheptatriene Dicarboxylic Acid

K. Audishesha Reddy<sup>a</sup>; M. Srinivasan<sup>a</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology, Madras, India

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## **SYNTHESIS AND CHARACTERIZATION OF HEAT-RESISTANT POLYAMIDES FROM THIADIAZACYCLOHEPTATRIENE DICARBOXYLIC ACID**

K. AUDISESHA REDDY and M. SRINIVASAN

Department of Chemistry  
Indian Institute of Technology  
Madras 600036, India

### **ABSTRACT**

Novel polyamides containing 2,3,6,7-dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene-4',4''-dicarboxy-1,1-dioxide (VII) are reported. The acid VII was prepared in several steps from *p*-chlorobenzoic acid and characterized by spectral data and elemental analysis. Prior to polymer synthesis, a model diamide (MDA) was prepared from VII and *p*-toluidine. The model diamide and several polyamides were obtained in an overall yield of (75–90%) by direct polycondensation of acid VII with certain diamines through a phosphorylation reaction at 100–110°C employing a solvent mixture of NMP–pyridine. The resulting polyamides and MDA were characterized by spectral, analytical, and thermal methods. The solubility, density, viscosity, and morphology (X-ray) were also studied for the polyamides. These polymers were moderately soluble in conventional polymer solvents, and the inherent viscosities were measured in concentrated sulfuric acid. Integral procedural decomposition temperatures (ipdt) were calculated from their primary thermogram in the temperature range 100–650°C in order to have quantitative data regarding their relative thermal stabilities. The polymers exhibit a 10% weight loss at 500°C in static air.

## INTRODUCTION

Totally aromatic high molecular weight polyamides have excellent thermal stability due to the rigidity of the polymer backbone and the hydrogen bonding through the amide groups. These polymers have only limited solubility in available aprotic solvents. Extensive work is in progress the world over to prepare polyamides with good solubility without the loss of thermal stability [1-6].

The introduction of heterocycles between arylene units yielded polyamides with improved thermal properties. Preston et al. [7, 8] prepared similar polymers by the low temperature solution method by condensing arylene diamines containing preformed heterocyclic units with an aryl dicarboxylic acid or its derivatives. Imai et al. [9] found that phenoxathin containing polyamides had similar solubility characteristics but better thermal stability than the corresponding polymers with open-chain diphenyl ether linkages. Sato et al. [10] observed that phenoxaphosphine-containing polymers exhibited thermal properties similar or superior to aromatic polypyromellitimides. Srinivasan et al. made similar observations for polyamides containing dibenzothiophene [11, 12], thianthrene [13], and thioxanthone [14]. Because of these interesting thermal properties, attempts have been made to prepare polyamides with double-strand heterocyclic units. In an effort to find thermally stable polymers for use in the development of heat-resistant materials, novel polyamides containing a double-strand seven membered heterocyclic unit are now reported. The basic structure, 1-thia-4,5-diazacyclohepta-2,4,6-triene, has been shown [15] to be thermally stable without showing any tendency to lose nitrogen even at 250°C. This prompted an investigation of such units for the preparation of new heat-resistant polymers.

An elegant and direct synthesis of polyamides was undertaken to obtain high molecular weight polymers by conventional polycondensation methods [16]. Recently various methods have been developed to prepare polyamides directly from dicarboxylic acids and diamines under mild conditions by phosphorylation reactions [17-23]. Yamazaki et al. [24] reported the direct synthesis of poly-*p*-benzamide from *p*-amino benzoic acid and polyamides from terephthalic acid with aromatic diamines by the use of phosphites in the mixed solvent NMP-pyridine containing LiCl. The conventional methods have several limitations, including multiple steps such as the preparation of acid chlorides, their incomplete reaction due to hydrolysis, formation of soluble oligomers, etc. Any

method that would lead to high molecular weight polyamides directly from free carboxylic acids under mild conditions would be useful. Thus the phosphorylation method for polyamide preparation would be an elegant substitute for the conventional methods. These reaction conditions were extended to the synthesis of eight polymers from acid VII (see the Monomer Preparation section below) and their characterization was documented.

## EXPERIMENTAL

### Measurements

IR spectra were obtained on a Perkin-Elmer 781 infrared spectrophotometer, and  $^1\text{H-NMR}$  spectra were recorded on a Varian EM-390 instrument by using TMS as the internal standard. X-ray diffractograms were obtained on a Phillips PW instrument by using nickel-filtered  $\text{CuK}_\alpha$  radiation. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Stanton Red Croft thermobalance at a heating rate of  $10^\circ\text{C}/\text{min}$ . Densities were determined with a small pycnometer in hexane as the nonsolvent at  $30^\circ\text{C}$ . Inherent viscosities were determined at a concentration of  $0.1\text{ g/dL}$  in concentrated  $\text{H}_2\text{SO}_4$  at  $30^\circ\text{C}$ . The UV-visible spectra were recorded by using a Shimadzu UV-visible recording spectrophotometer UV-240. Elemental analysis was done on a Perkin-Elmer 240.

The melting points are uncorrected and were determined directly on a heating block.

### Solvents and Materials

Pyridine was freshly distilled over KOH pellets. *N*-Methylpyrrolidone (NMP) was purified by vacuum distillation over  $\text{P}_2\text{O}_5$  to give a clear, colorless liquid which was kept dried over Molecular Sieves until it was used. Triphenyl phosphite was distilled under reduced pressure prior to use. *p*-Chlorobenzoic acid was recrystallized. Raney nickel was freshly prepared as per the procedure in Ref. 27. Commercially available diamines like *p*-phenylene diamine, benzidine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl sulfone, and 1,5-naphthalene diamine were recrystallized. All solvents used for solubility were distilled.

## MONOMER PREPARATION

### 3-Nitro-4-chlorobenzoic Acid (I)

Nitration of *p*-chlorobenzoic acid with fuming nitric acid gave Compound I in 95% yield; mp 179–180°C (literature 180°C) [26].

### Ethyl-4-chloro-3-nitrobenzoate (II)

Esterification of Compound II with absolute ethanol in the presence of concentrated H<sub>2</sub>SO<sub>4</sub> gave II, mp 60–61°C (literature 59°C). This ethyl ester II was prepared following the literature procedure [27] for ethyl benzoate.

### Bis-(2-nitro-4-carboethoxyphenyl) Sulfide (III)

The ethyl ester II was treated with anhydrous sodium sulfide flakes in alcoholic medium to give Compound III in 80% yield; mp 125–127°C. This sulfide III was prepared according to a literature procedure [28] for substituted diphenyl sulfides.

IR (KBr pellet): 1715 (ester carbonyl), 1520, 1330 (–NO<sub>2</sub>), 670 (C–S) cm<sup>-1</sup>.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ1.3–1.5 (t, 6H, CH<sub>3</sub>), δ4.2–4.4 (q, 4H, –COOCH<sub>2</sub>), δ7.5–8.7 (m, 6H, ArH).

Analysis. Calculated for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>S (420.39): C, 51.41; H, 3.84; N, 6.66%. Found: C, 51.82; H, 3.60; N, 6.5%.

### Bis-(2-nitro-4-carboethoxyphenyl) Sulfone (IV)

The sulfide III (30 g) was dissolved in acetic acid (200 mL), and chromium trioxide (10 g) was added over a period of 15 min to the hot solution. The mixture was refluxed for 8 h and poured into ice. The crude product was collected by filtration and recrystallized from acetic acid (90%), mp 218–220°C.

IR (KBr Pellet): 1715 (ester carbonyl), 1530, 1340 (–NO<sub>2</sub>), 1120 (SO<sub>2</sub>) cm<sup>-1</sup>.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ1.3–1.5 (t, 6H, CH<sub>3</sub>), δ4.2–4.4 (q, 4H, –COOCH<sub>2</sub>–), δ7.7–8.5 (m, 6H, ArH).

Analysis. Calculated for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>10</sub>S (452.39): C, 47.79; H, 3.56; N, 6.19%. Found: C, 47.10; H, 3.25; N, 6.82%.

**Bis-(2-nitro-4-carbohydroxyphenyl) Sulfone (V)**

Compound IV (9 g) in acetic acid (100 mL) and sulfuric acid (5 mL) (1 *N*) was refluxed for 6 h. The solution was then diluted with water, and the solid was collected and recrystallized from acetic acid. Yield 98%, mp 312–314°C.

IR (KBr pellet): 3400 (OH), 1680 (acid carbonyl), 1530, 1340 (–NO<sub>2</sub>) cm<sup>-1</sup>.

<sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>): δ7.0–8.5 (m, aromatic).

Analysis. Calculated for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O<sub>10</sub>S (396.28): C, 42.43; H, 2.03; N, 7.07%. Found: C, 43.10; H, 2.01; N, 6.95%.

**2,3,6,7-Dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene-4',4''-dicarboxy-1,1-dioxide (VII)**

Compound V (0.01 mol) in isopropyl alcohol (400 mL) was treated with molecular hydrogen in the presence of freshly prepared Raney nickel (6 g) at atmospheric pressure until 525 cm<sup>3</sup> of hydrogen was absorbed. Nickel was filtered out and the alcoholic solution was then gradually concentrated in vacuum. Air was passed (12–15 h) through the solution in the presence of a few drops of sodium hydroxide solution. The orange solution was neutralized with dilute hydrochloric acid and filtered to give a mixture of Compounds VIA and VIB.

This mixture was refluxed with dry methanol and Mg turnings to give Compound VII. The acid was further purified by dissolution in bicarbonate followed by reprecipitation twice and final recrystallization from methanol. Yield 60%, mp 409°C dec. (by DTA).

IR (KBr pellet): 3400 (OH, broad), 1675 (acid carbonyl) cm<sup>-1</sup>.

UV (MeOH): 430 (weak, n-π\*), 320 (intense, π-π\*), 255 (intense, aromatic ring) nm.

<sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>): δ7.0–8.4 (m, ArH).

Analysis. Calculated for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>S (332.28): C, 50.60; H, 2.43; N, 8.43%. Found: C, 50.48; H, 2.45; N, 8.28%.

**Diamines**

4,4'-Thiodianiline [31], 4,4'-diaminoazobenzene [32], and 4,4'-diaminodiphenyl ether [33] were prepared according to literature methods.

### Model Diamide (MDA)

A mixture of acid VII (0.01 mol), *p*-toluidine (0.02 mol), and triphenylphosphite (0.025 mol) was heated at 100–110°C for 6 h in a mixed solvent of NMP (40 mL) and pyridine (10 mL) containing LiCl (2 g) with stirring under a nitrogen atmosphere. After cooling, the reaction mixture was poured into methanol (20 mL), and the precipitated solid was filtered, washed well with methanol, and dried at 50°C under vacuum (90% yield, mp > 360°C).

IR (KBr pellet): 3300 (NH band I), 1690 (amide carbonyl), 1600 (NH band II), 1340 (sulfone)  $\text{cm}^{-1}$ .

$^1\text{H-NMR}$  (DMSO- $d_6$ ):  $\delta$ 2.2 (s, 6H,  $\text{CH}_3$ ),  $\delta$ 6.9–8.5 (m, 14H, ArH),  $\delta$ 10.2 (s, 2H, NH).

UV (DMF solution): 420, 315, 250 nm.

Analysis. Calculated for  $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$  (510.56): C, 65.87; H, 4.34; N, 10.97%. Found: C, 66.00; H, 4.18; N, 10.78%.

### General Polymerization Reaction

To a mixture of acid VII (0.01 mol) and one of the diamines listed (0.01 mol) in NMP (40 mL) and pyridine (10 mL) containing LiCl (2 g), triphenylphosphite (0.025 mol) was added under nitrogen atmosphere. The reaction mixture was heated at 100–110°C with stirring for 6 h. The polymer was obtained by pouring the reaction mixture into methanol, followed by filtration and drying at 50°C under vacuum. Yield 75–90% (PAP 1-8, PAP representing the code for Polyamide by *Phosphorylation*).

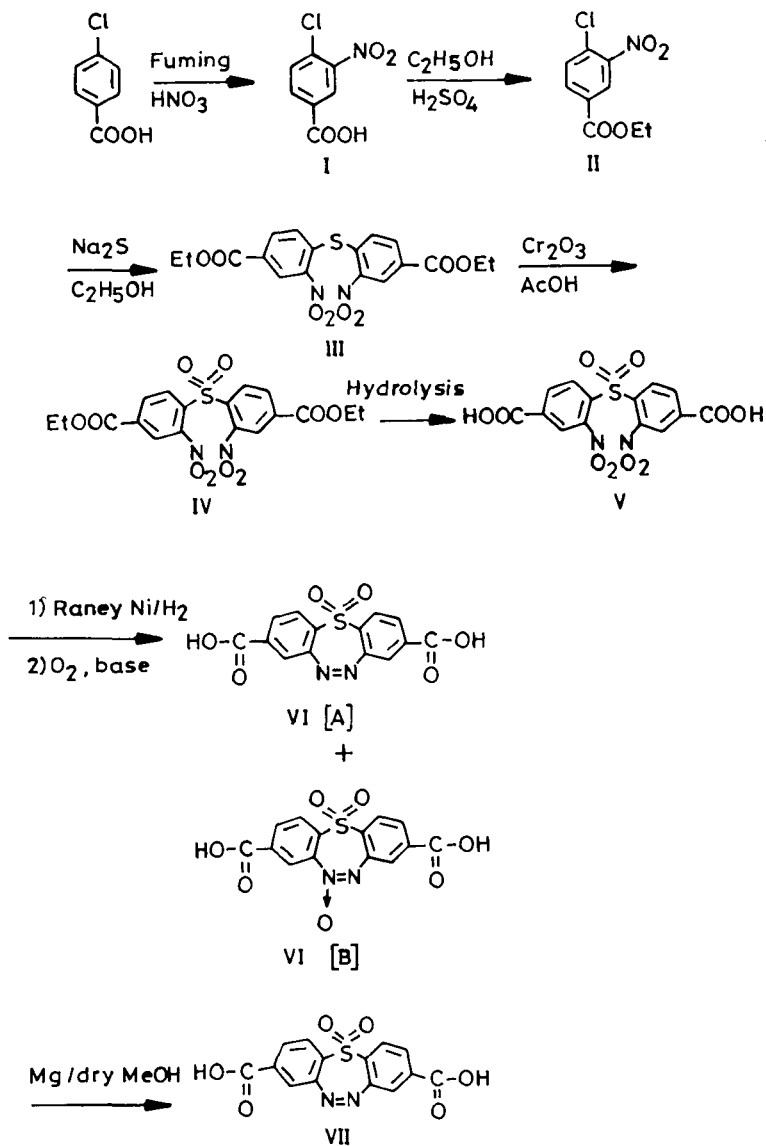
IR (KBr pellet): (PAP-1 to PAP-8)  $3300 \pm 50$  (NH, Band I),  $1670 \pm 20$  (amide carbonyl),  $1610 \pm 20$  (NH, Band II),  $1330 \pm 10$  (sulfone)  $\text{cm}^{-1}$ .

UV (DMF) (PAP-1 to PAP-8): 410–430, 305–330, 245–255 nm.

Analysis. Calculated for PAP-IV ( $\text{C}_{26}\text{H}_{16}\text{N}_4\text{O}_5\text{S}$ ) (496.49): C, 62.90; H, 3.25; N, 11.28%. Found: C, 63.35; H, 3.13; N, 11.21%.

## RESULTS AND DISCUSSION

2,3,6,7-Dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene-4',4''-dicarboxy-1,1-dioxide (VII) was prepared [25] from *p*-chlorobenzoic acid (Scheme 1). Nitration of *p*-chlorobenzoic acid by fuming nitric acid [26] gave Compound I which on esterification [27] gave Compound II in good yield. The replacement of the chlorine atom by the  $\text{Na}_2\text{S}$  method in the



SCHEME 1.



presence of the acidic group is difficult and hence esterification was found essential. The sulfide III was obtained in 80% yield on treatment of the chloro compound with alcoholic sodium sulfide. The substitution of chlorine atom on ethyl ester II was facile due to the two powerful electron withdrawing groups  $-\text{NO}_2$  and  $-\text{COOR}$  in the phenyl ring; a clean product (III) was obtained in high yield.

The IR spectrum of III showed strong absorption characteristics of ester carbonyl ( $1715\text{ cm}^{-1}$ ) and absorptions of nitro groups ( $1520, 1330\text{ cm}^{-1}$ ). The low absorption at  $670\text{ cm}^{-1}$  could be due to C—S absorption. As the C—S absorption is variable and weak, it is of little value in structural elucidation.

The  $^1\text{H-NMR}$  spectrum of III in  $\text{CDCl}_3$  showed a multiplet at  $\delta 7.5\text{--}8.7$  (ArH), a quartet at  $\delta 4.2\text{--}4.4$  ( $-\text{COOCH}_2$ ), and a triplet at  $\delta 1.3\text{--}1.5$  ( $\text{CH}_3$ ).

The sulfide III on chromium oxide oxidation [15] in acetic acid medium gave the corresponding sulfone IV which showed the characteristic absorption of ester carbonyl and nitro groups at  $1715, 1530, \text{ and } 1340\text{ cm}^{-1}$ , respectively. The absorption peak at  $1340\text{ cm}^{-1}$  could be due to both nitro and sulfone groups because it is fairly broad and intense. The signal at  $1120\text{ cm}^{-1}$  is due to the sulfone group. The  $^1\text{H-NMR}$  spectrum of IV showed a multiplet at  $\delta 7.7\text{--}8.5$ , a quartet at  $\delta 4.2\text{--}4.4$  ( $-\text{COOCH}_2$ ), and a triplet at  $\delta 1.3\text{--}1.5$  ( $-\text{CH}_3$ ).

Basic hydrolysis of Compound IV failed to yield any clean product due to its sensitivity to this reaction condition, but acidic hydrolysis of IV gave Compound V in high yield. The IR spectrum of V showed absorption at  $3400$  and  $1680\text{ cm}^{-1}$  due to OH and acid carbonyl, respectively. The  $^1\text{H-NMR}$  spectrum of Compound V showed only a multiplet at  $\delta 7.0\text{--}8.5$  due to aromatic protons.

Although several methods are available [34–37] for the reduction and simultaneous ring closure of compounds of type V, only the method of Szamant et al. [29] yielded Compound VII from V. The acid V in isopropyl alcohol was treated with molecular hydrogen in the presence of Raney nickel under ambient pressure to give cyclic hydrazo compound. Subsequent oxidation by  $\text{O}_2$  gas in alkaline medium gave a mixture of cyclic azo VIA and azoxy VIB compounds. The mixture of VIA and VIB was refluxed [30] with dry methanol and Mg turnings to give the corresponding azo acid VII.

The IR spectrum (Fig. 1) of VII showed characteristic absorptions at  $3400, 1675, \text{ and } 1340\text{ cm}^{-1}$  due to hydroxy, acid carbonyl, and sulfone,

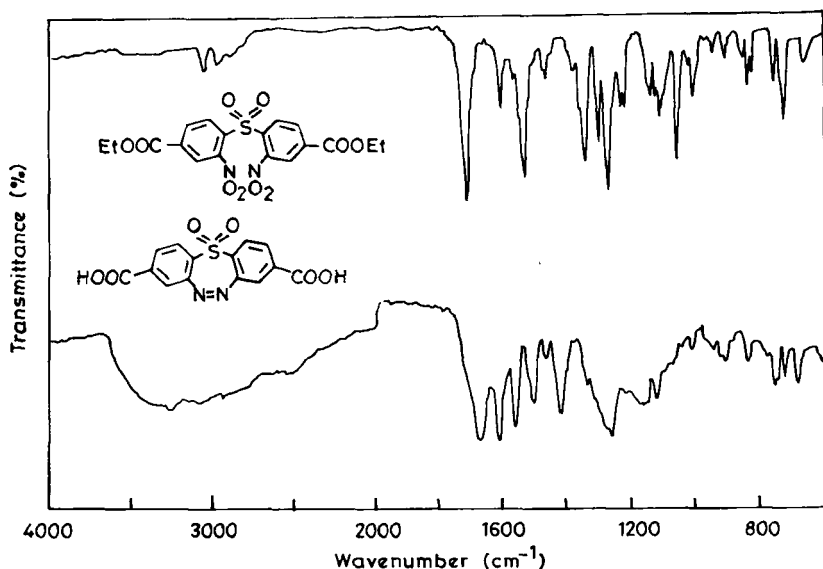


FIG. 1. IR spectra of IV and VII.

respectively. The disappearance of strong absorption of the nitro group at  $1530\text{ cm}^{-1}$  was observed. The sulfone group also absorbs around  $1350\text{--}1300\text{ cm}^{-1}$ , so a peak at  $1340\text{ cm}^{-1}$  of the nitro group did not disappear completely. The  $^1\text{H-NMR}$  spectrum (Fig. 2) of VII gave a multiplet at  $\delta 7.0\text{--}8.4$  due to aromatic protons. The UV-visible spectrum (Fig. 3) of Compound VII in methanol showed absorption at  $\lambda_{\text{max}} = 430\text{ nm}$  due to  $n \rightarrow \pi^*$  transition,  $\lambda_{\text{max}} = 320\text{ nm}$  due to transition of the azo group, and  $\lambda_{\text{max}} = 255\text{ nm}$  due to the aromatic ring. Elemental analysis of all these compounds (III, IV, V, and VII) were in fairly good agreement with calculated values.

### MODEL REACTION

Before attempting a polymerization, a model reaction (Scheme 2) was carried out in order to examine the reactivity of the acid VII and as an aid for structural identification and characterization of the polymers. Two

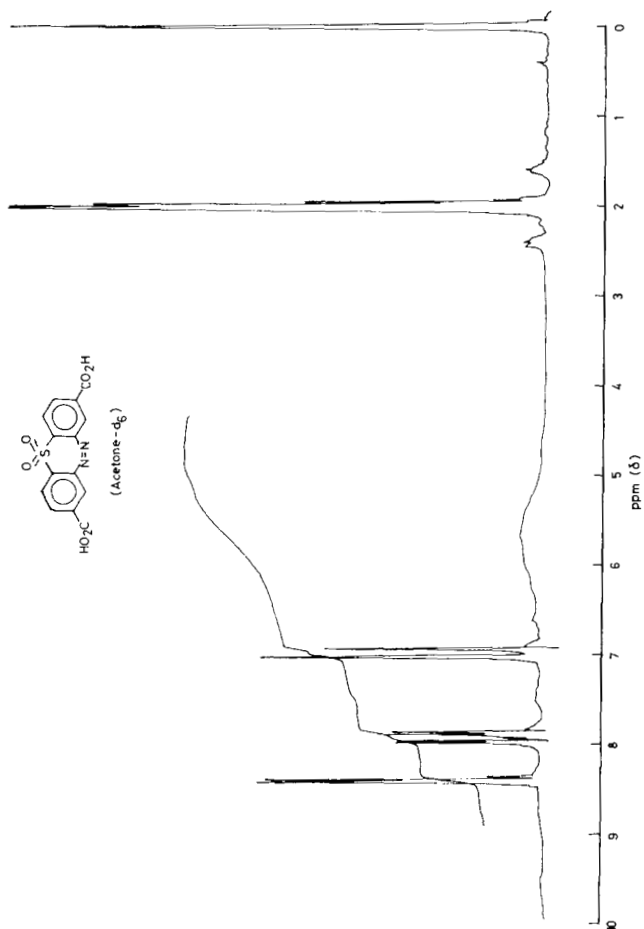


FIG. 2. NMR spectra of VII.

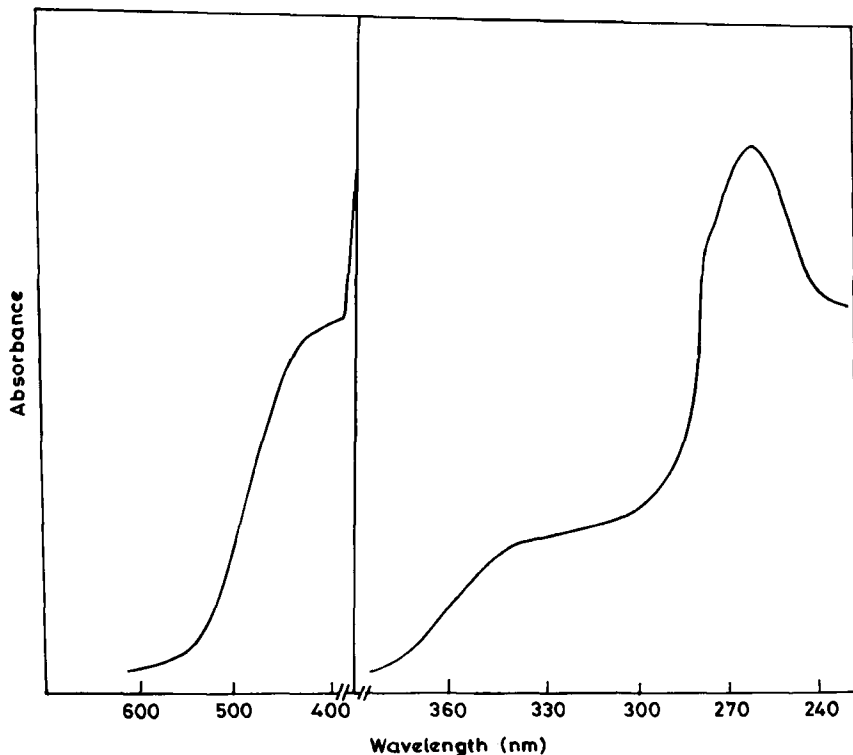
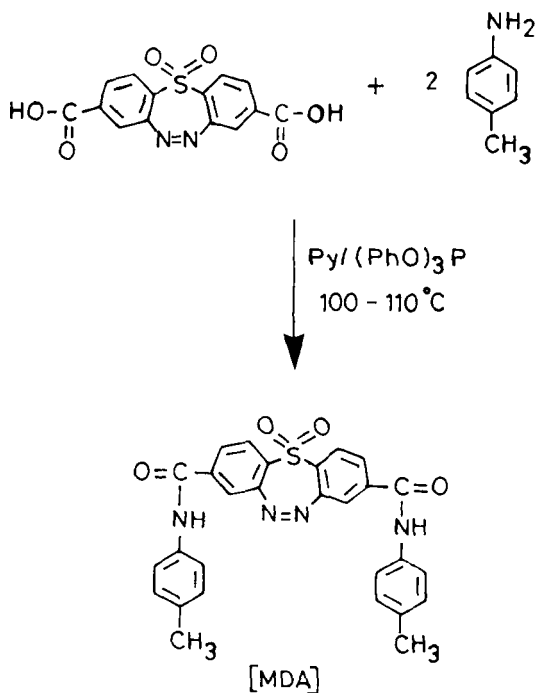


FIG. 3. UV-visible spectra of VII.

moles of *p*-toluidine were condensed [24] with 1 mol acid VII in a mixture of NMP and pyridine containing triphenyl phosphite, and LiCl (4%) at 100–110°C for 6 h under nitrogen to give a model diamide (MDA) in 90% yield, mp > 360°C. Its IR spectrum (Fig. 4) showed characteristic amide absorption bands [3300 (Band I) and 1600 (Band II)] (NH) and 1690 cm<sup>-1</sup> (CO—NH). The <sup>1</sup>H-NMR spectrum (Fig. 5) of MDA in DMSO-*d*<sub>6</sub> showed a singlet at δ2.2 (6H, —CH<sub>3</sub>) and a multiplet at δ6.9–8.5 (14H, ArH) and another singlet for the —NH— protons at δ10.2 which disappeared on D<sub>2</sub>O treatment. The UV-visible spectrum of MDA in DMF showed characteristic absorptions at 420, 315, and 250 nm. Elemental analysis of the MDA agreed well with calculated values.



SCHEME 2.

### POLYMERIZATION

Model reaction conditions were extended to the preparation of several polyamides (PAP-1 to PAP-8) (Scheme 3). The polyamides were prepared by the direct polycondensation method of Yamazaki et al. [24]. An attempt was made to prepare polymers by a phosphorylation reaction [21] in a solvent mixture of pyridine (10 mL) and DMAC (5 mL) containing LiCl (5%), but premature precipitation of the polymers within 0.5 h at 100–110°C was observed. Among the tested aprotic solvents, NMP was shown to be the most effective [24], and a combination of NMP and pyridine yielded high molecular weight polymers. Thus polymers PAP-1 to PAP-8 were obtained in 75–90% yield (Table 1). The IR spectrum (Fig. 6) of the polymers were comparable with that of the MDA and showed absorptions at  $3300 \pm 50$  (Band I NH),  $1670 \pm 20$  (amide carbonyl),  $1610 \pm 10$  (Band II NH), and  $1330 \pm 10$  ( $\text{SO}_2$ )  $\text{cm}^{-1}$ .

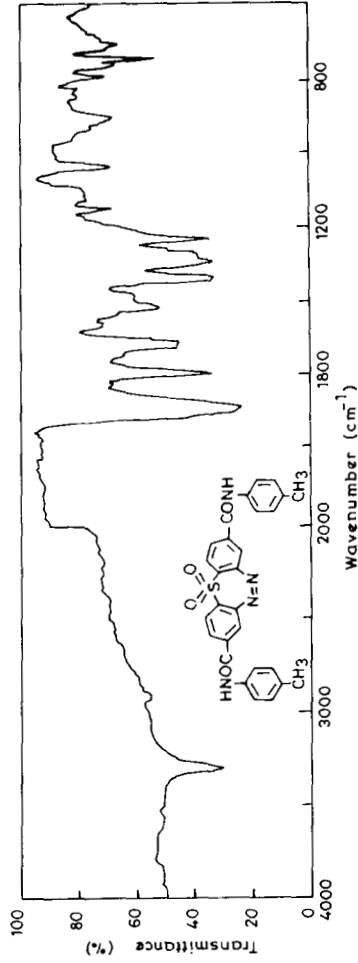


FIG. 4. IR spectra of model diamide (MDA).

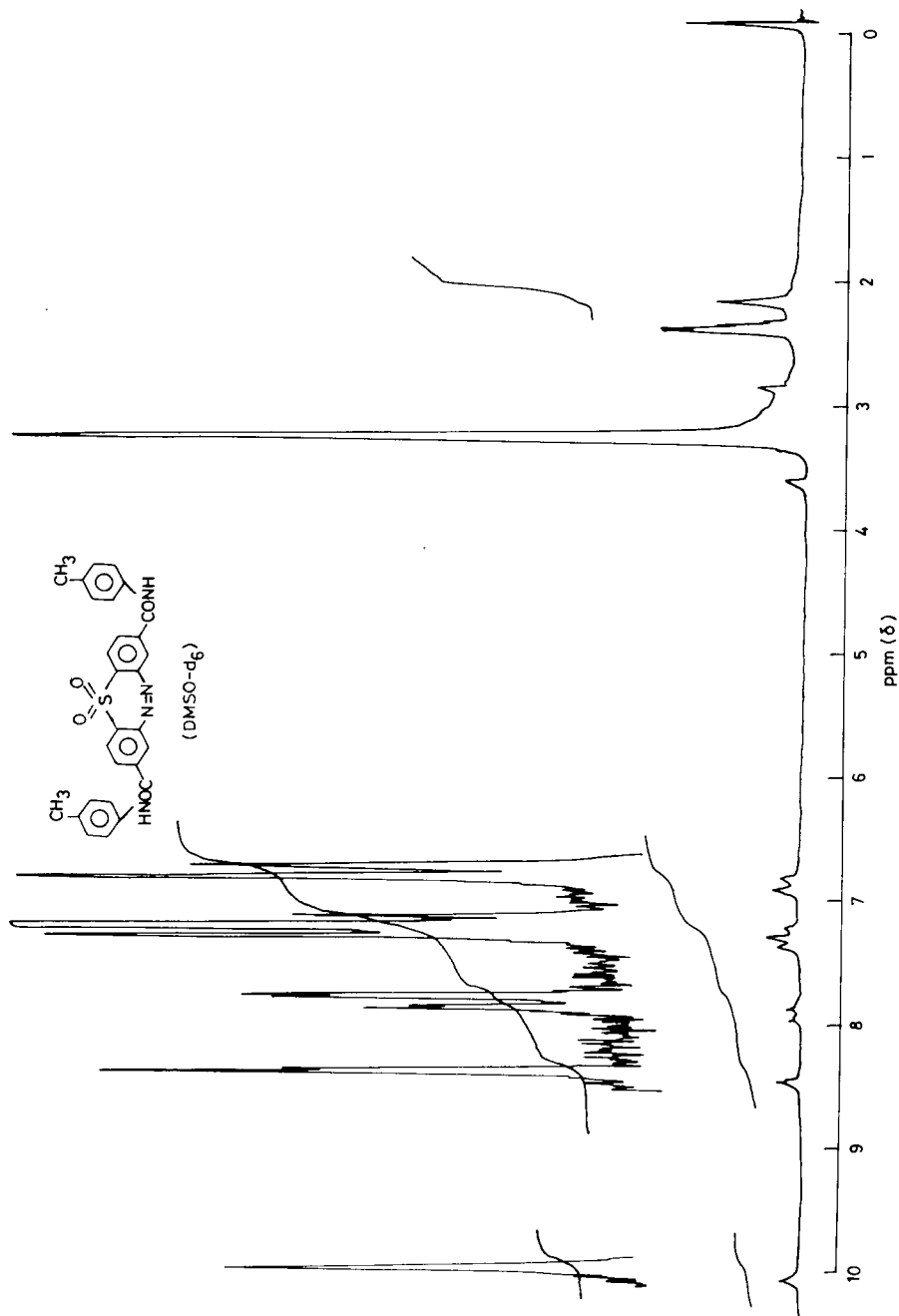
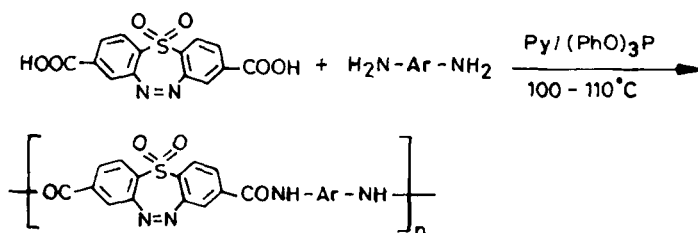

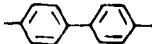
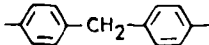
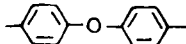
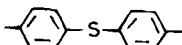
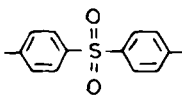
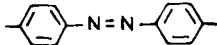



FIG. 5. NMR spectra of model diamide (MDA).



Polymer code	Ar
PAP-1	
PAP-2	
PAP-3	
PAP-4	
PAP-5	
PAP-6	
PAP-7	
PAP-8	

SCHEME 3.



TABLE 1. Preparation and Properties of Polyamides

Polymer code	Yield, %	$\eta_{inh}^a$ , dL/g	Density, <sup>b</sup> g/cm <sup>3</sup>
PAP-1 <sup>c</sup>	82	0.93	0.96
PAP-2	79	0.85	1.15
PAP-3	88	0.98	1.01
PAP-4	90	1.23	0.97
PAP-5	89	1.15	1.02
PAP-6	75	0.88	0.99
PAP-7	78	0.90	0.98
PAP-8	84	1.05	1.14

<sup>a</sup>In concentrated H<sub>2</sub>SO<sub>4</sub> at 30°C,  $c = 0.1$  g/dL.

<sup>b</sup>With hexane solvent at 30°C.

<sup>c</sup>See Scheme 3.

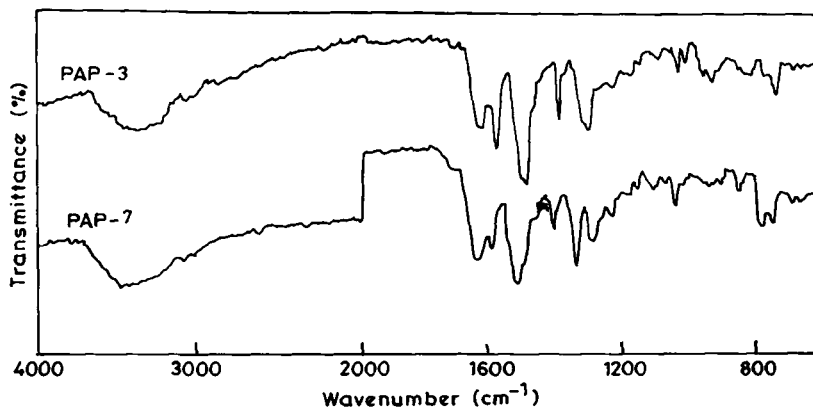


FIG. 6. IR spectra of polyamides PAP-3 and PAP-7.

The polyamides PAP-6 and PAP-7 were obtained in low yield, probably due to the presence of electron-withdrawing sulfone ( $\text{SO}_2$ ) and azo ( $-\text{N}=\text{N}-$ ) groups between the two phenyl rings in the diamine, thereby causing low basicity. The lower yield of polyamide PAP-2 could be due to lower solubility of the polymer in the reaction medium owing to its rodlike rigid structure. 4,4'-Disubstituted biphenylene systems are known to produce such rodlike structures, thereby causing lower yields and lower molecular weights (lower inherent viscosities). The densities of these polyamides ranged from 0.96 to 1.15  $\text{g}/\text{cm}^3$ . The inherent viscosities of the polyamides were in the range of 0.85 to 1.23  $\text{dL}/\text{g}$ , with PAP-2 at lowest value and PAP-4 at highest value.

The solubility characteristics of the polymers are shown in Table 2. A 10% (w/v) solution was taken as a criterion for solubility. All polymers were insoluble in *m*-cresol and THF but were soluble in formic acid on heating. PAP-1, PAP-6, and PAP-8 were moderately soluble in DMF and DMAc at ambient temperature. It was found that all the polymers were soluble in concentrated  $\text{H}_2\text{SO}_4$  and aprotic solvents like HMPT, NMP, and DMSO at room temperature.

The polyamides prepared from benzidine and 1,5-diaminonaphthalene exhibited partial crystalline pattern (Figs. 7 and 8) whereas the other polyamides were found to be amorphous.

The thermal stabilities of the polyamides were evaluated by thermogravimetric analysis in air at a heating rate of  $10^\circ\text{C}/\text{min}$ . The polymers showed good thermal stabilities (Table 3) and began to decompose around 435–445 $^\circ\text{C}$  in static air with a 10% weight loss occurring around 465–505 $^\circ\text{C}$ . The maximum exothermal peak was observed in the temperature range of 612–710 $^\circ\text{C}$ .

The DTA curves of the polyamides exhibited a broad exotherm in the temperature range of 500–715 $^\circ\text{C}$ . There was no endothermic base line shift to indicate a glass transition temperature, and there was no exothermic peak due to polymer crystallization.

Integral procedure decomposition temperatures (*ipdt*) were calculated [38] from the primary thermograms in the temperature range 100–650 $^\circ\text{C}$  in order to obtain quantitative data regarding the relative thermal stabilities of the polymers. All polymers have *ipdt* values in the temperature range of 504–559 $^\circ\text{C}$ . PAP-8 showed the lowest and PAP-2 the highest thermal stability. Delman et al. [39] observed similar thermal stabilities in Schiff's base polymers. The naphthalene unit has a smaller thermal stability compared to that of benzidine and phenyl units. The greater stabi-

TABLE 2. Solubilities of Polyamides<sup>a</sup>

Polymer code	DMF	DMAc	NMP	HMPT	DMSO	Formic acid	Concentrated H <sub>2</sub> SO <sub>4</sub>	<i>m</i> -Cresol	THF
PAP-1	S	S	SS	SS	SS	S	SS	I	I
PAP-2	S	S	SS	SS	SS	S	SS	I	I
PAP-3	SS	SS	SS	SS	SS	S	SS	I	I
PAP-4	SS	SS	SS	SS	SS	S	SS	I	I
PAP-5	SS	SS	SS	SS	SS	S	SS	I	I
PAP-6	S	S	SS	SS	SS	S	SS	I	I
PAP-7	SS	SS	SS	SS	SS	S	SS	I	I
PAP-8	S	S	SS	SS	SS	S	SS	I	I

<sup>a</sup>SS = Soluble at room temperature. S = Soluble on heating. I = Insoluble.

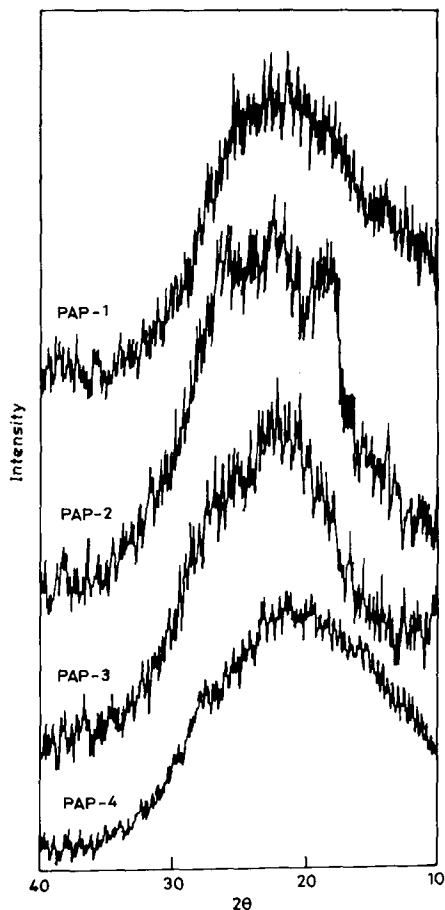


FIG. 7. X-ray diffractograms of polyamides PAP-1 to PAP-4.

ties of these polyamides could be attributed to the presence of double strand heterocyclic units [13, 14] in the polymer structure.

All the polyamides were found to have char yields (15–24%) at 800°C in static air. Decomposition, cyclization, and crosslinking reactions are probably responsible for these char yields [40].

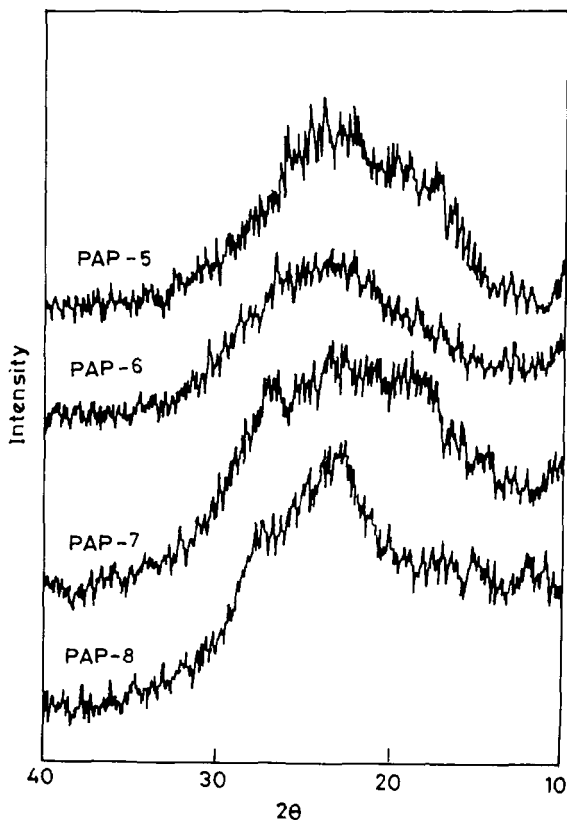


FIG. 8. X-ray diffractograms of polyamides PAP-5 to PAP-8.

### CONCLUSION

These results indicate that higher thermal stability and moderate solubility can be obtained by incorporating double strand, seven-membered, azo/sulfone heterocyclic units into aromatic polyamides.

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TABLE 3. Thermal Properties of Polyamides in Static Air<sup>a</sup>

Polymer code	Temperature at various percentage decompositions, °C								Char yield, %	ipdt, °C
	10	20	30	40	60	$T_{\max}$ , °C				
PAP-1	490	547	575	612	639	631		19	531	
PAP-2	499	543	603	657	702	693		24	559	
PAP-3	475	528	566	603	631	612		15	515	
PAP-4	485	529	612	657	745	710		20	540	
PAP-5	480	535	605	640	715	690		18	525	
PAP-6	505	547	612	650	737	702		23	535	
PAP-7	470	524	594	644	710	680		20	508	
PAP-8	465	509	584	621	657	648		23	504	

<sup>a</sup>Heating rate 10°C/min.<sup>b</sup>Temperature at which the maximum exothermal peak was observed in DTA.<sup>c</sup>Percent char yield at 800°C.<sup>d</sup>Integral procedural decomposition temperature.

## REFERENCES

- [1] R. Takatsuka, K. Uno, F. Toda, and Y. Iwakura, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1905 (1977).
- [2] R. Takatsuka, K. Uno, F. Toda, and Y. Iwakura, *Ibid.*, **16**, 361 (1978).
- [3] M. Ballauff, *Macromolecules*, **19**, 1366 (1986).
- [4] (a) H. G. Rogers, R. A. Gaudiana, and C. McGowan, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 2669 (1985). (b) R. A. Gaudiana, R. A. Minns, H. G. Rogers, R. Sinta, L. D. Taylor, P. S. Kalyanaraman, and C. McGowan, *Ibid.*, **25**, 1249 (1987).
- [5] H. Finkelmann, *Angew. Chem., Int. Ed. Engl.*, **26**, 816 (1987).
- [6] M. Ballauff, *Ibid.*, **28**, 253 (1989).
- [7] J. Preston and W. B. Black, *J. Polym. Sci., Part B*, p. 267 (1966).
- [8] J. Preston and W. B. Black, *J. Polym. Sci., Part C*, **23**, 441 (1968).
- [9] Y. Imai, M. Ueda, and T. Aizawa, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2739 (1977).
- [10] M. Sato and M. Yokoyama, *Eur. Polym. J.*, **15**, 733 (1979).
- [11] P. R. Srinivasan, M. Srinivasan, and V. Mahadevan, *Makromol. Chem.*, **182**, 1937 (1981).
- [12] P. R. Srinivasan, M. Srinivasan, and V. Mahadevan, *Polymer*, **22**(9), 1290 (1981).
- [13] S. Prema and M. Srinivasan, *Eur. Polym. J.*, **23**(11), 897 (1987).
- [14] T. A. Reddy and M. Srinivasan, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 1063 (1988).
- [15] H. Szmant, H. Lapinski, and R. L. Lapinski, *J. Am. Chem. Soc.*, **75**, 6338 (1953).
- [16] P. W. Morgan, *Condensation Polymers by Interfacial and Solution Methods*, Interscience, New York, 1965.
- [17] N. Ogata and H. Tanaka, *Polym. J.*, **2**, 672 (1971).
- [18] N. Ogata and H. Tanaka, *Ibid.*, **3**, 365 (1973).
- [19] N. Ogata and H. Tanaka, *Ibid.*, **6**, 461 (1974).
- [20] N. Ogata, K. Sanui, and M. Harada, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2401 (1979).
- [21] N. Yamazaki, F. Higashi, and J. Kawabata, *Ibid.*, **12**, 2149 (1974).
- [22] G. Wu, H. Tanaka, K. Sanui, and N. Ogata, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 343 (1981).
- [23] N. Ogata, K. Sanui, H. Tanaka, and Yasuda, *Polym. J.*, **13**, 989 (1981).

- [24] N. Yamazuki, M. Matsumoto, and F. Higashi, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1373 (1975).
- [25] K. A. Reddy and M. Srinivasan, *Chem. Ind.*, p. 228 (1989).
- [26] H. King and W. O. Murch, *J. Chem. Soc.*, p. 2632 (1926).
- [27] A. I. Vogel, *Text Book of Practical Organic Chemistry*, 3rd ed., ELBS, p. 782.
- [28] H. H. Hodgson and D. P. Dodgson, *J. Chem. Soc.*, p. 1002 (1948).
- [29] H. H. Szamant and R. L. Lapinski, *J. Am. Chem. Soc.*, **78**, 458 (1956).
- [30] B. W. Langley, B. Lythgoe, and L. S. Rayner, *J. Chem. Soc.*, p. 4191 (1952).
- [31] Y. L. Chi and J. Y. Moh, *Tunghai Hsueh Pao*, **2**, 50 (1957); *Chem. Abstr.*, **53**, 188961 (1959).
- [32] P. W. Morgan, *Macromolecules*, **10**, 1381 (1977).
- [33] G. A. Reynolds, *J. Am. Chem. Soc.*, **73**, 4996 (1951).
- [34] M. L. Tomlinson, *J. Chem. Soc.*, p. 756 (1946).
- [35] H. W. Galbraith, E. F. Degering, and E. F. Hitch, *J. Am. Chem. Soc.*, **73**, 1323 (1951).
- [36] W. Tadros, M. S. Ishak, and E. Bassili, *J. Chem. Soc.*, p. 627 (1959).
- [37] B. T. Newbold and R. P. Leblanc, *Ibid.*, p. 1547 (1965).
- [38] C. D. Doyle, *Anal. Chem.*, **33**, 77 (1961).
- [39] A. D. Delman, A. A. Stein, and B. B. Simms, *J. Macromol. Sci., Part A1*, **1**, 147 (1967).
- [40] Y. P. Khanna and E. M. Pearce, *J. Appl. Polym. Sci.*, **27**(6), 2053 (1982).

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