

SYNTHESIS AND PROPERTIES OF POLY-1,3,5-TRIAZINES*

WANG Yulan (王玉兰) and LU Fengcai (卢凤才)

(Institute of Chemistry, Academia Sinica, Beijing)

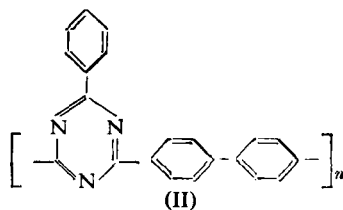
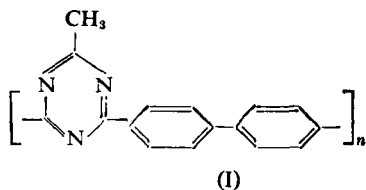
ABSTRACT

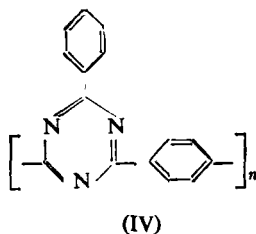
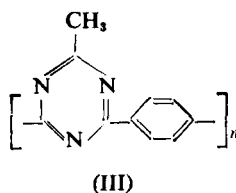
Two new polytriazines: poly[2-methyl-4, 6-(4', 4''-diphenylene)-1, 3, 5-triazine] (I) and poly[2-phenyl-4, 6-(4', 4''-diphenylene)-1, 3, 5-triazine] (II) were synthesized from the solution condensation of biphenyl-4, 4'-diamidine dihydrochloride with acetic anhydride and biphenyl-4, 4'-diamidine with benzaldehyde respectively. These two polymers were characterized by TGA, DTA, elemental analysis and IR spectroscopy. They exhibited good thermal oxidative stability as shown by the fact that the powders of these polymers suffered 5.4%, 2.4% weight loss after isothermal aging in air at 300°C for 200 hours. The decomposition temperature of (II) was 583°C in air and 590°C in N₂. These linear poly-1, 3, 5-triazines were soluble in concentrated sulfuric acid, phosphoric acid and trifluoroacetic acid whereas the crosslinked poly-1, 3, 5-triazines reported in the literature were insoluble and infusible.

It is interesting that these polymers can form complexes with metal halides as determined by X-ray photoelectron spectroscopy (XPS). The polymer metal complex (III) · PdCl₂ possesses catalytic activity for hydrogenation.

Poly-1, 3, 5-triazines are heat-resistant polymers. Many papers on synthesis of the crosslinked poly-1, 3, 5-triazines which are insoluble and infusible have been reported in the literature. In this paper, the synthesis of linear poly-1, 3, 5-triazines from the solution condensation of biphenyl-4, 4'-diamidine dihydrochloride with acetic anhydride and biphenyl-4, 4'-diamidine with benzaldehyde are reported. The new poly-1, 3, 5-triazines (I) and (II) are prepared.

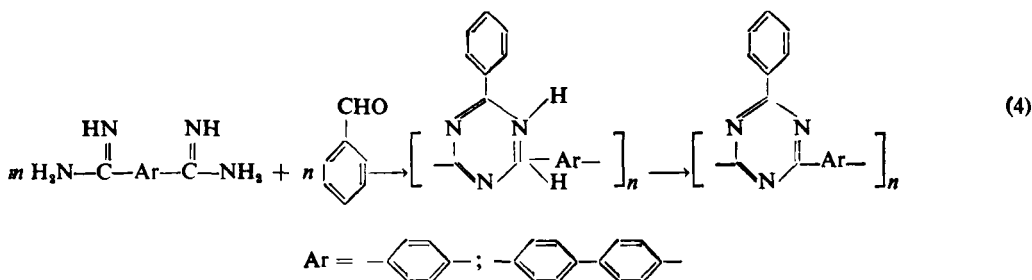
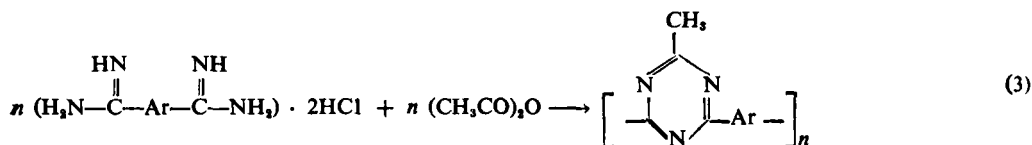
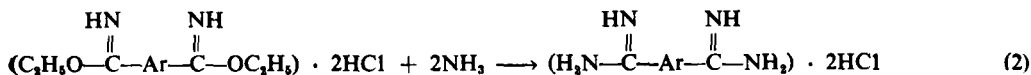
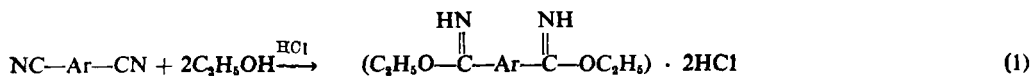
Although synthesis of polymer (III) and (IV) have been reported in literature^[1, 2], but the characterizations were not given, and the elemental analysis reported deviated more than





5% from that of theoretical value. The synthesis of these two polymers together with their characterizations are also reported.

The synthetic routes of (I)—(IV) are shown in the following reactions (1)—(4):

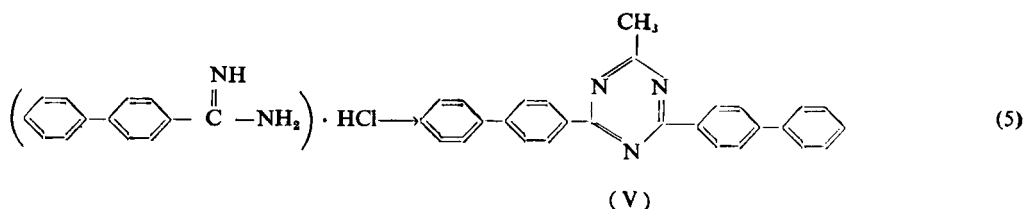


These four polymers were characterized by thermogravimetric analysis, differential thermal analysis and infra-red spectroscopy. The elemental analysis agreed well with the theoretical value. The inherent viscosities determined were between 0.20 and 0.56 dl/g (1% in conc. H_2SO_4 at 25°C). Their T_g were in the range of $285\text{—}342^\circ\text{C}$ and the polymer decomposition temperature of (II) and (IV) in air were 583° and 573°C respectively. They exhibited 2.4 and 2.6% weight loss after isothermal aging in air at 300°C for 200 hours and good hydrolytic stability. A new polymer metal complex was formed by reacting polymer (III) with PdCl_2 which possessed high catalytic activity for hydrogenation.

RESULTS AND DISCUSSION

Model compound

2-Methyl-4, 6-diphenylene-1, 3, 5-triazine was prepared from the reaction of biphenyl-4-amidine hydrochloride with acetic anhydride according to the reaction (5):



The IR spectra showed absorptions of 1, 3, 5-triazine at 1520, 1450, 1370 and 820 cm^{-1} ^[1] as shown in Fig. 1. Its molecular peak, M^+ was equal to 399 by means of mass spectrography.

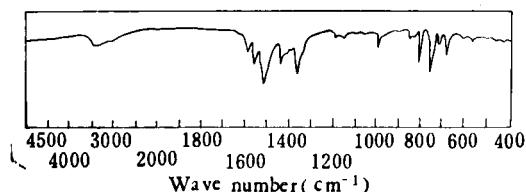


Fig. 1 IR spectrum of model compound (V)

Polymers

Polymers (I) and (III) were synthesized from the reaction of aromatic diamidine dihydrochlorides with acetic anhydride while (II) and (IV) from that of aromatic amidine with benzaldehyde forming an intermediate after evolution of water and ammonia, followed by the elimination of hydrogen by using lead tetraacetate and were produced in high yield of (II) and (IV). All the reagents and solvents used in these reactions must be anhydrous. The IR spectra exhibited strong absorptions at the same wave numbers as that of model compound and are shown in Fig. 2. From the result of thermogravimetric analysis, the polymer decomposition temperature of either (I) or (III) containing methyl group was lower than that of (II) or (IV) containing phenyl group as shown in Table 2. In comparison, the polymer decomposition temperatures of (II) and (IV) were about 150°C higher than that of polyphenyl-1, 2, 4-triazines^[3] and with lower weight loss. This means that the carbon-nitrogen bond was more stable than the nitrogen-nitrogen bond in the six-membered ring containing three nitrogen atoms. As to the solubility, the linear poly-1, 3, 5-triazines (I)–(IV) were easily soluble in conc. H_2SO_4 , (I) and (III) were readily soluble in H_3PO_4 and CF_3COOH , but (II) and (IV) were only partially soluble in acids as shown in Table 3.

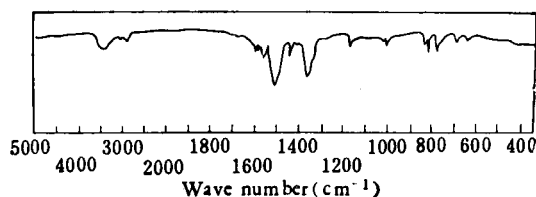


Fig. 2 IR spectrum of polymer (II)

Table 1 Characterization of polymer (I)—(IV)

Polymer	η (dl/g)	T_g (°C)	PDT (°C)	
			Air	N ₂
I	0.56	300	405	590
II	0.46	342	583	
III	0.20	285	480	
IV	0.20	335	573	

1) η_{inh} (1% conc. H₂SO₄, at 25°C).2) T_g was determined by DTA, the rate of heating: 10°C/min.

3) Polymer decomposition temperature (PDT) was determined by TGA, the rate of heating: 10°C/min.

Table 2 Isothermal aging of polymers (I)—(IV) in air

Polymer	300 (°C) wt. loss (%)				371 (°C) wt. loss (%)		
	50	100	150	200 hours	3	50	100 hours
I	1.9	3.4	3.9	5.4	4.1	42.5	55.8
II	1.4	2.3	2.3	2.4	3.2	16.6	21.2
III	7.3	16.3	20.0	28.4	15.6	96.8	
IV	1.6	2.5	2.6	2.6	3.5	28.0	34.7

Polymers (I)—(IV) exhibited good hydrolytic stability and IR spectra did not change any more after being treated in boiling water for 24 h, in water at room temperature for 50 hours, or in boiling 40% NaOH or 5% H₂SO₄ for 1 hour. After immersion in conc. H₂SO₄ for 90 days, η_{inh} of (II) and (IV) remained unchanged.

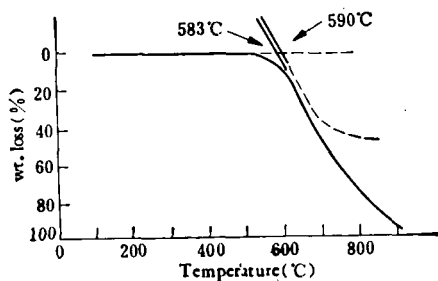


Fig. 3 Thermogravimetric analysis of polymer (II)

The rate of heating: 6°C/min.

—in air; --- under N₂.

Table 3 Solubility of polymers (I)–(IV)

Solvent	I	II	III	IV
Conc. sulfuric acid	++	++	++	++
Phosphoric acid	++	+	++	+
Cresol	+	—	+	—
Trifluoroacetic acid	++	+	++	+
N-Methylpyrrolidone	+	+	+	+
Dimethyl sulfoxide	—	—	—	—
Hexamethylphosphorictriamide	—	—	—	—

++ Easily soluble; + Partially soluble; — Insoluble.

These polymers can be used not only as heat resistant materials but also can served as ligands for metal halides to form polymer metal complexes which shows high catalytic activities. In this paper, (III) was adsorbed on SiO_2 , and then reacted with PdCl_2 to form polymer metal complex which was identified by X-ray photoelectron spectroscopy as shown in Table 4. The N_{1s} binding energy of $(\text{III}) \cdot \text{PdCl}_2$ was 0.5 eV higher than that of (III). This means that nitrogen in $(\text{III}) \cdot \text{PdCl}_2$ was more positive than the nitrogen in (III). Similarly the Pd_{3d} binding energy of $(\text{III}) \cdot \text{PdCl}_2$ was 1.1 eV lower than that of PdCl_2 . It is obvious, that a pair of free electron of nitrogen in (III) was transferred to Pd^{2+} of PdCl_2 , so that a polymer complex was formed. The IR spectrum of $(\text{III}) \cdot \text{PdCl}_2$ showed that there was strong absorption bands at 405 and 335 cm^{-1} which also indicated the existence of N-Pd^{2+} and $\text{Pd}^{2+}\text{-Cl}$ bonds, and this complex exhibited catalytic activity for hydrogenation as shown in Table 5. In comparison, the PdCl_2 was adsorbed on SiO_2 without polymer under the same conditions as mentioned above. Its initial rate of catalytic hydrogenation of

Table 4 Identification of $(\text{III}) \cdot \text{PdCl}_2$ by means of XPS (eV)

	$(\text{III}) \cdot \text{PdCl}_2$	(III)	PdCl_2	Pd
$\text{Pd}_{3d_{5/2}}$	337.2		338.3	395.5
N_{1s}	399.0	398.5		
$\text{Cl}_{2p_{3/2}}$	199.2		199.2	

cyclohexene 1.18 ml/min and that of $(\text{III}) \cdot \text{PdCl}_2$, 14.5 ml/min. This proved again the existence of polymer metal complex.

EXPERIMENTAL

Model compound

Biphenyl-4-amidine hydrochloride. Biphenyl imidate hydrochloride was prepared by following a known procedure^[8] using biphenyl-4-cyanide as starting material. It was

Table 5 The initial rate of hydrogenation of olefins by using (III)·PdCl₂ as catalyst

Olefins	Cyclohexene	Styrene	Decene-1	Vinyl acetate	Benzaldehyde	Acetone
Rate of hydrogenation (ml/min)	14.5	30	11	36	2	0.8

Condition: N/Pd = 8.64, olefin: 0.05 mol, Pd in (III) · PdCl₂: 0.05 m mol, solvent: anhydrous ethyl alcohol, the total volume of reactants: 15 ml, temp.: 30°C, pressure: 1 atm of hydrogen.

reacted with absolute ethyl alcohol-ammonia solution, and gave white needles of biphenyl-4-amidine hydrochloride. The yield was 75.5%. Analysis: C₁₃H₁₃N₂Cl: (Calc.: N, 12.04%; Cl, 14.58%. Found: N, 11.66%; Cl, 15.06%).

2-Methyl-4, 6-diphenylene-1, 3, 5-triazine. It was prepared from 0.93 g (0.004 mole) of biphenyl-4-amidine hydrochloride with 0.72 g (0.009 mole) of dry sodium acetate and 40 ml of acetic anhydride at 100°C for 72 h, and then cooled, filtered and dried. The product was recrystallized from acetic anhydride and 0.399 g (50%) of white needles were obtained, m.p. 191.5–192.5°C. Analysis: C₂₈H₂₁N₃: (Calc.: C, 84.20%; H, 5.20%; N, 10.53%. Found: C, 83.95%; H, 5.20; N, 10.41%).

Monomer

Terephthalamidine dihydrochloride was prepared according to the known procedure^[3, 4]. Analysis: C₈H₁₂N₄Cl₂: (Calc.: C, 40.85%; H, 5.10%; N, 23.83%. Found: C, 40.52%; H, 5.11%; N, 23.53%).

Terephthalamidine. 4.8 grams (0.02 mole) of terephthalamidine dihydrochloride was completely dissolved in 100 ml of water, and then 25 ml of 25% sodium hydroxide solution was added drop by drop and the reaction vessel was placed in an ice-water bath. The white precipitate was collected, washed with ammonia solution and dried under reduced pressure. The crude product was recrystallized from dimethyl formamide and 1.78 g (53.7%) of white solid was obtained. It decomposed at 160°C (Lit. 160°C). Analysis: C₈H₁₀N₄: (Calc.: C, 59.25%; H, 6.1%. Found: C, 58.89%; H, 5.95%).

Biphenyl-4, 4'-diamidine dihydrochloride and the biphenyl-4, 4'-diamidine were prepared according to the methods mentioned above. Analysis: C₁₄H₁₆N₄Cl₂: (Calc.: C, 54.01%; H, 5.14%; N, 18.00%. Found: C, 53.81%; H, 5.12%; N, 17.29%).

Polymers

Poly[2-methyl-4, 6-(4', 4"-diphenylene)-1, 3, 5-triazine] (I). To a 250 ml flask 1.43 g (0.0046 mole) of biphenyl-4, 4'-diamidine dihydrochloride, 0.82 g (0.01 mole) of dry sodium acetate and 85 ml acetic anhydride were added. The flask was heated at 120°C for 36 hours, and then cooled. The product was filtered and washed with water and ethyl alcohol several times. After drying, 0.7 g (62%) of polymer (I) was obtained. Analysis: C₁₈H₁₁N₃: (Calc.: C, 78.35%; H, 4.52%; N, 17.13%. Found: C, 77.58%; H, 4.38%; N, 16.64%).

Poly[2-phenyl-4, 6-(4', 4"-diphenylene)-1, 3, 5-triazine] (II). This was prepared by heating 0.11 g (0.001 mole) of benzaldehyde, 0.238 g (0.001 mole) of [biphenyl-4, 4'-

diamidine and 10 ml dimethyl sulfoxide at 135°C for 10 hours. The product was washed with hot dimethyl sulfoxide and ethyl alcohol several times, and dried under reduced pressure. 0.3 grams (97%) of yellow polymer was obtained. Then 0.25 g (0.0008 mole) of this polymer was stirred and refluxed with 30 ml of glacial acetic acid and 0.58 g (0.0013 mole) of lead tetraacetate for 6 hours. The precipitate was filtered, and washed thoroughly first with hot glacial acetic acid and then with water and ethyl alcohol several times. The yield of polymer (II) was 0.22 g (88.5%). Analysis: $C_{21}H_{13}N_3$: (Calc.: C, 82.07%; H, 4.26%; N, 13.67%. Found: C, 81.50%; H, 4.12%; N, 13.30%).

Poly[2-methyl-4, 6-(1', 4'-phenylene)-1, 3, 5-triazine] (III). It was prepared by the same procedure as for polymer (I). Analysis: $C_{10}H_7N_3$: (Calc.: C, 70.99%, H, 4.17%; N, 24.84%. Found: C, 70.46%; H, 3.98%; N, 23.22%).

Poly[2-phenyl-4, 6-(1', 4'-phenylene)-1, 3, 5-triazine] (IV). It was prepared by the same procedure as for (II). Analysis: $C_{16}H_9N_3$: (Calc.: C, 77.71%; H, 3.92%; N, 18.17%. Found: C, 75.45%; H, 3.78%; N, 17.56%).

After polymer (III) was dissolved completely in trifluoroacetic acid, a given amount of SiO_2 was added to the mixture which was then stirred thoroughly. The mixture was poured into aqueous ethyl alcohol, filtered and the precipitate was washed with aqueous ethyl alcohol, dried in vacuum and then reacted with $PdCl_2$ to form polymer metal complex.

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