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Direct Polycondensation of Castor Oil Based Dimer Acid and Aromatic Diamines Using Triphenylphosphite

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ABSTRACT

Aliphatic–aromatic polyamides of castor oil based dimer acid (DA) with various aromatic diamines, viz., 4,4′-diaminodiphenyl sulfone (SD), 4,4′-diamino-diphenyl methane (MD), and *p*-phenylene diamine (PD) were synthesized using triphenylphosphite (TPP) as condensation reagent. Pyridine and *N*,*N*-dimethyl formamide (DMF) were not used in this synthesis. The resulting polyamides were characterized by elemental analysis, infrared spectroscopy, and viscosity and swelling measurements. The solid conductance values for these polyamides were found to be in the range 10^{-10}–$10^{-13}\,\mathrm{S\,cm^{-1}}$, upon heating the conductance values enhanced to 10^{-7}–$10^{-9}\,\mathrm{S\,cm^{-1}}$. These polyamides exhibited heat resistant properties.

Key Words: Dimer acid; Aliphatic–aromatic polyamides; Triphenyl phosphite; Degree of polymerization.

INTRODUCTION

Polyamide formulations derived from castor oil based dimer acid (DA) are commercially useful materials as evident from the appearance of reports in the patent

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literature.[1] Castor oil, a low cost natural vegetable oil, has been utilized for synthesis of polyurethane elastomers with improved application properties.[2]

In the present report, synthesis of aliphatic–aromatic polyamides of DA with various aromatic diamines, viz., 4,4′-diaminodiphenyl sulfone (SD), 4,4′-diamino-diphenyl methane (MD), and *p*-phenylene diamine (PD) has been reported with a view to obtain processable polyamides with high performance properties due to the incorporation of aromatic rings in the main chain.

Wholly aromatic polyamides are sometimes synthesized in the presence of triphenyl phosphite (TPP).[3–5] Pyridine is being employed invariably to activate TPP through a complex formation.[6–9] To the best of our knowledge, no report by this method has appeared so far for the synthesis of polyamides derived from DA. In the present, the preparation of polyamides, using TPP as condensation reagent, pyridine has not been used.

EXPERIMENTAL

Materials

Dimer acid 1010 (DA) (composition: 98% + trimer acid 2%) was supplied by Jayant Oil Mills, Bombay, India. MD, SD, PD diamine, and TPP were supplied by E. Merck, Bombay, India. Pyridine, methanol, benzene, *N*,*N*-dimethyl formamide (DMF) and other solvents were from Qualigens, Glaxo, India.

All chemicals were of analytical grade and were used as received.

Synthesis of Polyamides in Presence of Pyridine

For the preparation of polyamides, the requisite amount of DA, TPP, and pyridine were placed in a three-necked flask fitted with a condenser and an inlet and outlet for nitrogen gas. The mixture was magnetically stirred at 80°C for 30 min. Then the temperature was raised to 110°C ± 5°C, the respective diamines were added and the stirring of the reaction mixture was continued for 5 hr at the same temperature. The amino-terminated oligomers viz., poly(4,4′-diphenylmethane dimeramide) (PMD), poly (4,4′-diphenylsulfone dimeramide) (PSD), and poly(1,4-phenylene dimeramide) (PPD) were precipitated by the addition of 1 : 1 mixture of dilute hydrochloric acid and DMF to the respective reaction mixtures. The resulting brown colored resinous solids were washed thoroughly with a 1 N sodium carbonate solution, followed by water. The polyamides were dried under vacuum and weighed to a constant weight.

Synthesis of Polyamides in the Absence of Pyridine

The same procedure as above was followed for polyamidation except that pyridine was not added in the reaction mixture. By pouring it into a large quantity of methanol, PMD and PSD were precipitated from the reaction mixture. The brown colored resinous solids were filtered and washed thoroughly with methanol. Then PPD was initially precipitated in benzene, filtered, and then washed thoroughly with methanol. The polyamides were vacuum dried and weighed to a constant weight.

Measurements

The course of polyamidation reaction was followed at specific time intervals by end group analysis by dissolving 0.2 g aliquot in 10 mL of acetone and titrating it against a standard alkali solution.[10,11] The elemental analyses were carried out on a Heraeus Carlo Erba 1108 elemental analyzer. The IR spectral measurements were carried out using A Shimadzu 8201 PC infrared spectrophotometer with KBr as dispersant in the 4000–500 cm^{-1} range. The viscosities of the polymers were measured in DMF solutions at 27°C with an Ubblehode viscometer. The intrinsic viscosity was determined in DMF by using the Solomon and Ciuta method[12] and inherent viscosity (η_{inh}) values were calculated for TPP solutions using Eq. (1):

$$\eta_{inh} = (2.3 \log t/t_0)/C \tag{1}$$

where t_0 and t represent the viscometer flow periods of TPP and the polymer solution, respectively, and C, the concentration of solution was 2.5 g/100 mL.

Swelling Measurements

For the determination of the equilibrium swelling, rectangular pieces of polyamide samples each with a weight of 0.1 g were immersed in 25 mL of various organic solvents. The samples were then taken out, surface-dried by pressing gently between filter papers, followed by weighing. The process was repeated until the weights became constant. All the measurements were done at 27°C ± 0.2°C. The swelling coefficient, Q_{sc} was calculated using the Eq. (2):[13]

$$Q_{sc} = (m - m_0)/(m_0 \times d) \tag{2}$$

where m is the weight of swollen polymer, m_0 the weight of polymer taken initially, and d is the density of the solvent used. The characteristic parameters for the solvents were obtained from the literature.[14]

Electrical Conductivity

The measurement of conductivity was carried out under a dust-free and non-humid atmosphere on a Keithley instrument model 610 C electrometer. For measurement of the conductivity, the electrodes were prepared by pressing the hot melt samples between two pieces of aluminum foil, 1 cm in diameter and then cooled under vacuum. The electrodes containing the samples were pressed using a Carver laboratory press, applying 8 ton of pressure for 2 min. Conductivity was obtained by pressing the pellets in silver-coated copper plates and applying a constant disc potential of 450 V across the sample. The temperature was maintained at 35°C ± 2°C. The time of electrification was about

40–50 sec (no change in current was observed when the voltage was applied continuously for 20 min). The conductivity in S cm^{-1} (or $\Omega\,\mathrm{cm}^{-1}$) was calculated using Eq. (3):

$$\sigma = \frac{d\,i}{AV} \tag{3}$$

where σ is the conductivity, d is the thickness of pellet, i the current, A the surface area of pellet, and V is the applied voltage across the sample.

RESULTS AND DISCUSSION

Direct polyamidation of DA with aromatic diamines was carried out by the use of TPP as a condensation reagent. Polyamidation in the presence and absence of pyridine with variation in other parameters, viz., amount of reactants, catalyst, solvent, reaction time, and reaction atmosphere was studied, and the results are presented in Tables 1–3. The reaction progress was followed in some cases, by determination of acid number. The degree of polymerization (DP) for polyamidation reaction was found to be 10 for PMD-7, 7 for PSD-8 and PPD-5 both. Reaction conditions, similar to those reported in the literature[6,7] for phosphorylation reaction, were adopted for polyamidation, for samples PMD-1, PSD-1, and PPD-1. In case of PMD-1, gelation was observed within 2 hr, whereas for PSD-1 and PPD-1, the product could not be precipitated. Kale et al.[15] also reported gelation of the polyamide when monomers were employed in equimolar proportion.

It can be concluded that the appreciable solubility of the polyamides in the solvents employed in the reaction mixture was responsible for this observation. The precipitation of polyamides was even more difficult when salts, such as LiCl or $\mathrm{CaCl_2}$, were added to dissolve the monomers completely in the reaction mixture. The DP was found to decrease when the reaction mixture was allowed to stand at room temperature, thus suggesting that in the homogeneous system, the backward reaction i.e., the hydrolysis of the polyamides was quite prominent. For PSD-2, even 24 hr of reaction yielded a pale yellow slimy product. In all other cases, (PSD-3–PSD-5), where lesser or no pyridine was used, pale yellow resinous products were obtained. Thus, it was inferred that solvent (DMF) and pyridine caused the dilution effect. The highest DP was observed for set, PSD-6, without DMF and pyridine, for 1 : 1 ratio of reactants (DA and diamine).

It was observed that on the addition of an excess of methanol as precipitant, in sets using pyridine but no DMF, no solid product could be obtained. This is due to the solubilizing power of pyridine. Hence, a calculated amount of 1 : 1 mixture of dilute hydrochloric acid and DMF was added to the reaction mixture. The former separated pyridine as hydrochloride and latter kept the lower molecular weight fraction of polyamides in solution. Thus, the high molecular mass fraction gets coagulated. Water present in the aqueous solution of hydrochloric acid acted as the non-solvent because, except for the polar polyamide groups, the major part of the polymer chain is hydrophobic.

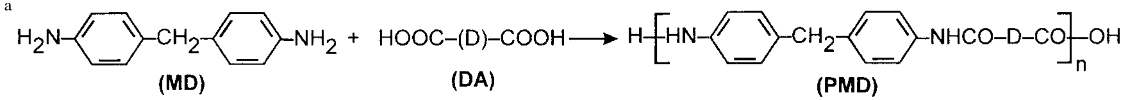
A perusal of Tables 1–3 makes it evident that variation in the reactant ratio, the volume of pyridine, solvent, and atmospheric conditions play an important role in influencing the polyamidation reaction. The tentative reaction schemes for polyamidation of DA carried out in the presence and absence of pyridine are presented in Schs. 1 and 2.

The analytical data for selected samples are presented in Table 4 with the theoretical compositions based on assumed structures, taking DP into consideration. A great

Table 1. Synthesis of polyamides from DA and MD.[a]

Run	DA		MD		TPP		Pyridine	DMF	Yield		Time	
number	g	mM	g	mM	g	mM	(mL)	(mL)	(%)	DP	(hr)	Atmosphere
PMD-1[b]	5.6	10	1.98	10	12.25	39	5	15	95	—	2	AIR
PMD-2[c]	5.6	10	2.38	12	12.25	39	5	—	70	—	2	AIR
PMD-3	5.6	10	2.38	12	12.25	39	5	—	80	2.56	1	N_2
PMD-4	5.6	10	2.38	12	12.25	39	15	—	75	4.83	5	AIR
PMD-5[c]	11.2	20	3.97	20	24.50	78	50	—	95	—	2	AIR
PMD-6	5.6	10	2.38	12	12.25	39	—	—	85	5.57	5	N_2
PMD-7	11.2	20	4.76	24	24.50	78	—	—	80	10.00	5	N_2

[a]



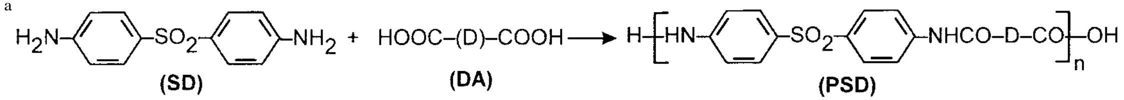
[b] The DP could not be determined due to insoluble nature of the product in acetone.

[c] Reaction mixture when kept for 24 hr, converted into a gel.[b]

Table 2. Synthesis of polyamides from DA and SD.[a]

Run number	DA		SD		TPP		Pyridine (mL)	DMF (mL)	Yield (%)	DP	Time (hr)	Atmosphere
	g	mM	g	mM	g	mM						
PSD-1[b]	5.6	10	2.48	10	12.25	39	30	150	—	—	2	AIR
PSD-2	11.2	20	4.97	20	24.50	78	50	—	75	1.02	24	AIR
PSD-3	5.6	10	2.98	12	12.25	39	15	—	80	2.3	5	N_2
PSD-4	5.6	10	2.98	12	12.25	39	5	—	85	3.6	5	N_2
PSD-5	5.6	10	2.48	10	12.25	39	5	—	70	1.49	5	N_2
PSD-6[c]	5.6	10	2.48	10	12.25	39	—	—	75	8.54	5	N_2
PSD-7	5.6	10	2.98	12	12.25	39	—	—	72	6.06	4	N_2
PSD-8	11.2	20	5.96	24	24.5	78	—	—	85	7.14	5	N_2

[a]



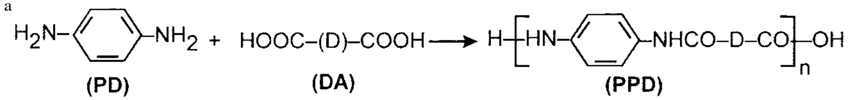
[b] To the reaction mixture 4.5 g LiCl and 1.5 g $CaCl_2$ were also added. No solid product was obtained on addition of methanol.

[c] After 2.5 hr there was no change in DP.

Table 3. Synthesis of polyamides from DA and PD.[a]

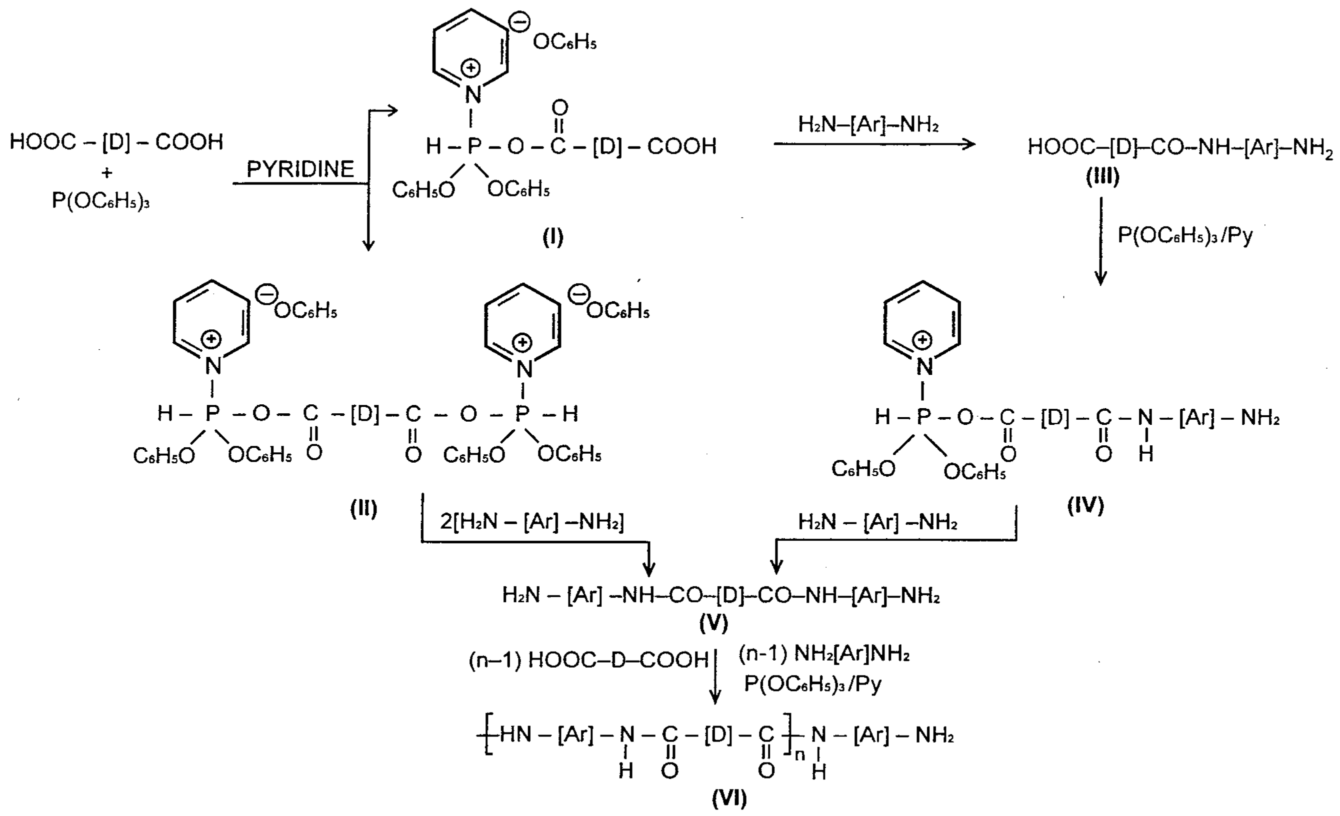
Run number	DA g	DA mM	PD g	PD mM	TPP g	TPP mM	Pyridine (mL)	DMF (mL)	Yield (%)	DP	Time (hr)	Atmosphere
PPD-1[b]	5.6	10	1.08	10	12.25	39	5	15	60	1.62	2.5	AIR
PPD-2	5.6	10	1.08	10	12.25	39	5	—	82	2.32	2.5	AIR
PPD-3[c]	5.6	10	1.30	12	12.25	39	—	—	80	5.61	3.5	N_2
PPD-4	5.6	10	1.30	12	6.12	20	—	—	70	2.42	3.5	N_2
PPD-5	11.2	20	2.60	24	24.50	78	—	—	8	7.84	5.0	N_2

[a]

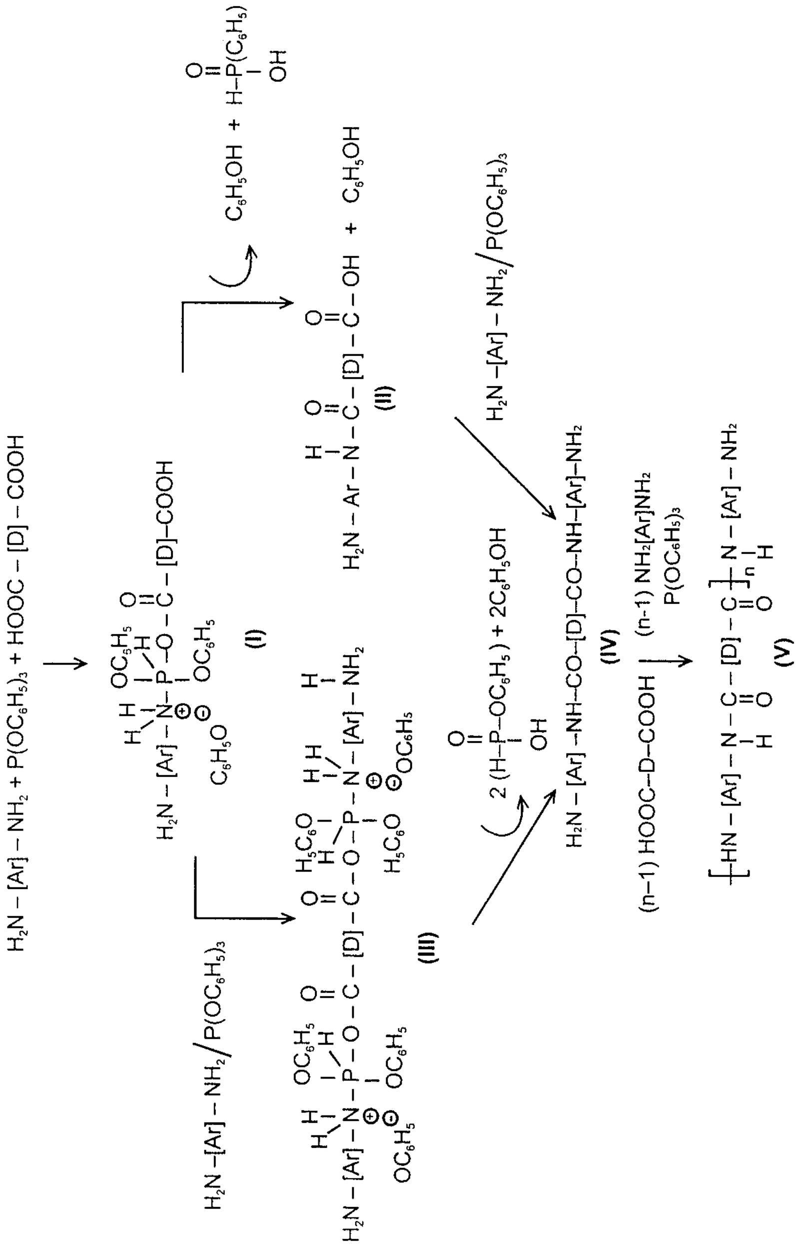


[b] Product partially soluble in methanol.

[c] Gelation within 3.5 hr.



Scheme 1. Tentative scheme for synthesis of polyamides in presence of pyridine.



Scheme 2. Tentative scheme for synthesis of polyamide in absence of pyridine.

Table 4. Analytical and physical data of some selected samples of polyamides

Compounds	Elemental analysis[a]			Yield %	M_n	Softening range/ viscous flow (°C)	$[\eta]$	η_{inh}	EC[b] ($S\,cm^{-1}$)	EC[c] ($S\,cm^{-1}$)
	%C	%H	%N							
PMD-7	67.16	8.09	2.74	78	7222	45–50, 55	0.52	6.31	3.32×10^{-10}	4.0×10^{-7}
$C_{503} \cdot H_{764} \cdot O_{20} \cdot N_{22} \cdot 87H_2O$	67.11	10.42	3.42	—	—	—	—	—	—	—
PSD-8	67.89	8.85	2.54	90	5624	40–45, 50	0.33	5.03	2.6×10^{-13}	2.72×10^{-10}
$C_{348} \cdot H_{523} \cdot O_{30} \cdot N_{16} \cdot S_8 \cdot 27H_2O$	67.95	9.38	3.64	—	—	—	—	—	—	—
PPD-5	67.63	9.75	2.74	86	4985	65–70, 90	1.10	9.01	7.78×10^{-12}	7.0×10^{-9}
$C_{300} \cdot H_{491} \cdot O_{15} \cdot N_{16} \cdot 43H_2O$	67.55	10.82	4.20	—	—	—	—	—	—	—

[a] In each case, values in upper row represent experimentally determined values and the lower row values represent theoretical analysis.

[b] Electrical conductance of original samples.

[c] Electrical conductance of samples heated at 360°C.

discrepancy was observed between the calculated and observed values of C, H, and N beyond experimental error and the best agreement between the two was obtained only after considering the adsorbed water. It is known that aromatic polyamides with moderately high molecular weights exhibit a strong tendency for moisture pick up.[16,17]

Puffer and Sebenda[18] revealed that amide groups, disregarding the negligible content of the end groups in the region accessible to water, are sorption centers. Based on sorption equilibria for several crystalline polyamides, they suggested that in Nylon 6, three molecules of water are sorbed on two neighboring amide groups in an accessible region (capillary condensation is not considered). The first molecule forms a double H-bond between the CO group (firmly bound water) and the other two molecules form H-bonds between the CO and NH groups (loosely bound water). Favored sorption of water into a "monolayer" takes place only in the samples containing no mesomorphous regions, since three water molecules are sorbed on two amide groups at the same time. In the present case, agreement between the theoretical and the experimental values for C, H, and N was obtained by taking 8.7 water molecules for PMD-7, 2.7 water molecules for PSD-8, and 4.3 water molecules for PPD-5 per monomeric unit of ligand. It is suggested that besides the water molecules bound to the amide groups, an appreciable amount of water is present as capillary condensate. The IR spectra of polyamides PMD-1–PMD-6 are depicted in Fig. 1.

For samples prepared in the presence of pyridine (viz., PMD-1–PMD-5), the coupled vibrations with a main contribution from the carbonyl group were distinctly apparent as two bands near the 1650–1600 cm^{-1} range. For samples PMD-6 and PMD-7, prepared without the use of solvent and pyridine, the IR spectra (Figs. 1 and 2) showed a single band in 1625–1599 cm^{-1} range.

In these two samples, the band at 1352 cm^{-1}, which is normally considered as the amide III band, is also well defined in comparison to the other samples of PMD series. This band arises due to mixed vibrations involving OCN and NH groups. It is suggested that in the presence of pyridine, a lesser number of water molecules are adsorbed on the polyamide samples. In samples PMD-6 and PMD-7, a broad and strong band in the range 3200–3600 cm^{-1} was observed due to ν_{NH} overlapped by ν_{OH} from adsorbed water molecules. The merger of ν_{OH} and ν_{NH} is suggestive of strong H-bonding interactions, which also led to the merger of amide I and amide II band.

Three samples, viz., PMD-7, PSD-8, PPD-5, obtained by polyamidation in the absence of pyridine, were used as the representative samples for further measurements. The IR spectra of PMD-7, PSD-8, and PPD-5, presented in Fig. 2(a), (c), and (e), respectively, exhibited very intense and broad bands due to ν_{NH} of amide groups in 3600–3200 cm^{-1} region with a maxima in the 3300–3420 cm^{-1} range. In solids, a ν_{NH} band is usually observed near 3280 cm^{-1}.[19a] The slightly higher value in the present study may be attributed to the additional absorption from ν_{OH}. It is suggested that amide groups are involved in extensive hydrogen bonding with adsorbed water molecules.[19b] The ν_{CH} (asymmetric and symmetric) at 2927 and 2854 cm^{-1} appear as weak bands in the case of PMD-7. These bands, though stronger in the case of PSD-8 and PPD-5, are slightly merged with the broad band due to ν_{OH} and ν_{NH}.

Amide I band with main contribution from ν_{co} and δ_{NH} was observed in the 1680–1630 cm^{-1}range.[19c] The amide II band for primary and secondary amides lies in 1600–1500 cm^{-1} region that arises from the NH deformation mode.[19d] In the case of PMD-7 and PSD-8, this band appeared at 1599–1595 cm^{-1} and near 1600 cm^{-1} in the case of PPD-5.

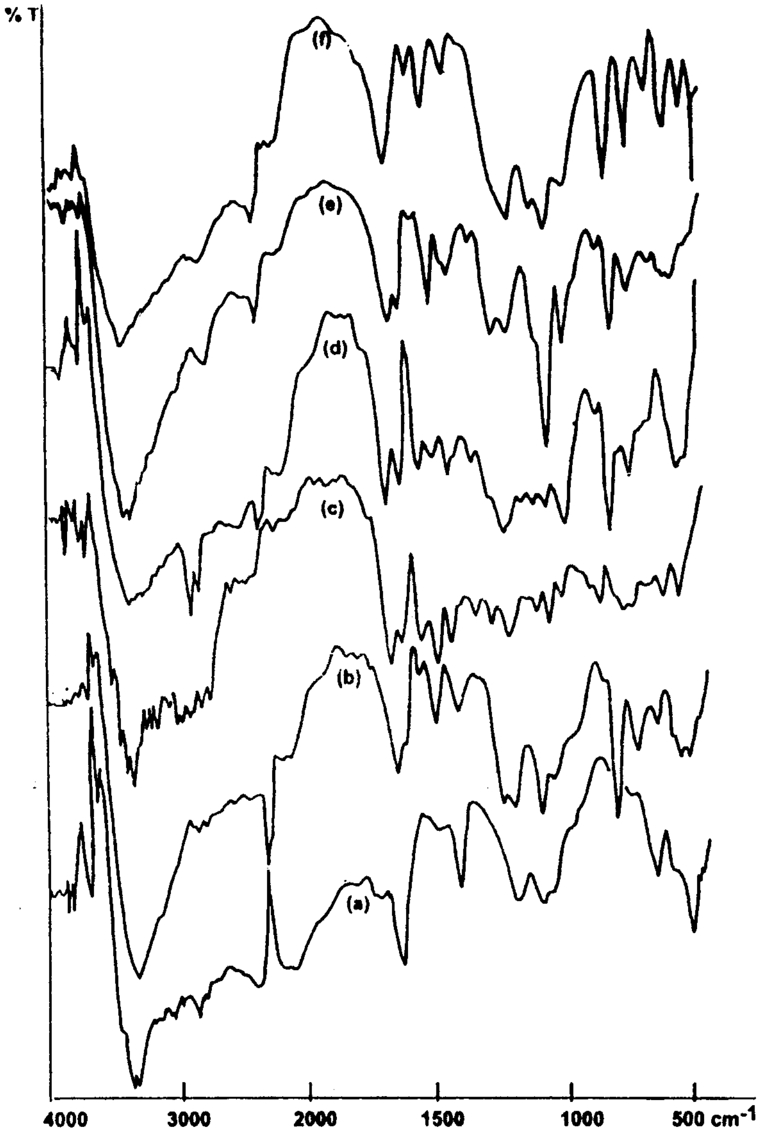


Figure 1. The IR spectra of polyamides (a) PMD-6, (b) PMD-3, (c) PMD-2, (d) PMD-4, (e) PMD-5, and (f) PMD-l.

The amide III band characteristic of secondary amide involving vibrations due to OCN and N–H modes appeared at 1352 cm^{-1} for PMD-7 and PPD-5 as strong and medium bands, respectively. In the case of PSD-8, two pairs of bands appeared in the range 1383–1351 and 1148–1105 cm^{-1}, due to the presence of a SO_2 group. Low frequency absorptions, termed as the amide IV and amide VI bands, appeared as a broad band in the lower range, 550–570 cm^{-1}, along with the amide V band. A band at 721 cm^{-1}, depicted the absorptions due to polymethylene groups of DA. Out of the three polyamides under consideration,

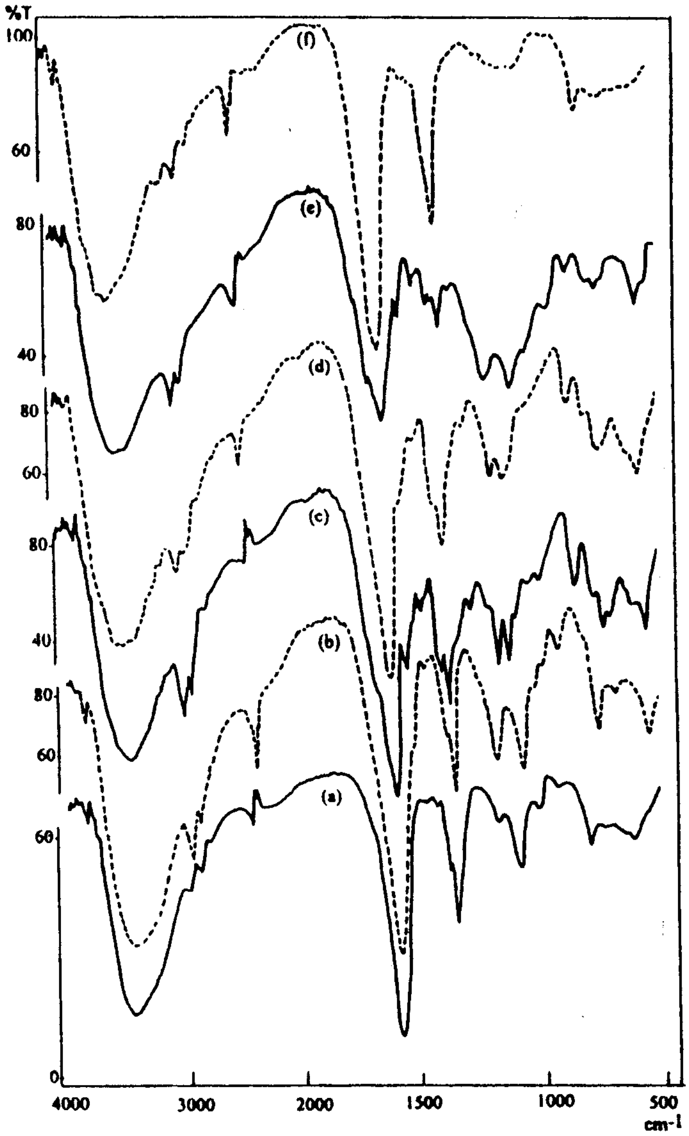


Figure 2. The IR spectra of different polyamide samples (a) and (b) PMD-7, (c) and (d) PSD-8, and (e) and (f) PPD-5 (—, untreated and ---, heated at 180°C).

PMD-7 had the highest DP, which is also reflected from its IR spectrum, as the peaks are broader and less resolved as compared to those of PPD-5 and PSD-8.

The presence of water molecules in the polyamides is apparent from the analytical data and shifting of IR absorption bands involving –CONH– groups towards a lower side. A weighed amount of polymer samples PMD-7, PSD-8, and PPD-5 were heated up to 180°C and their IR spectra were recorded [Figs. 2(b), (d), and (f)]. The same samples were then isothermally heated at 360°C for 4 hr and IR spectra were again recorded (Fig. 3).

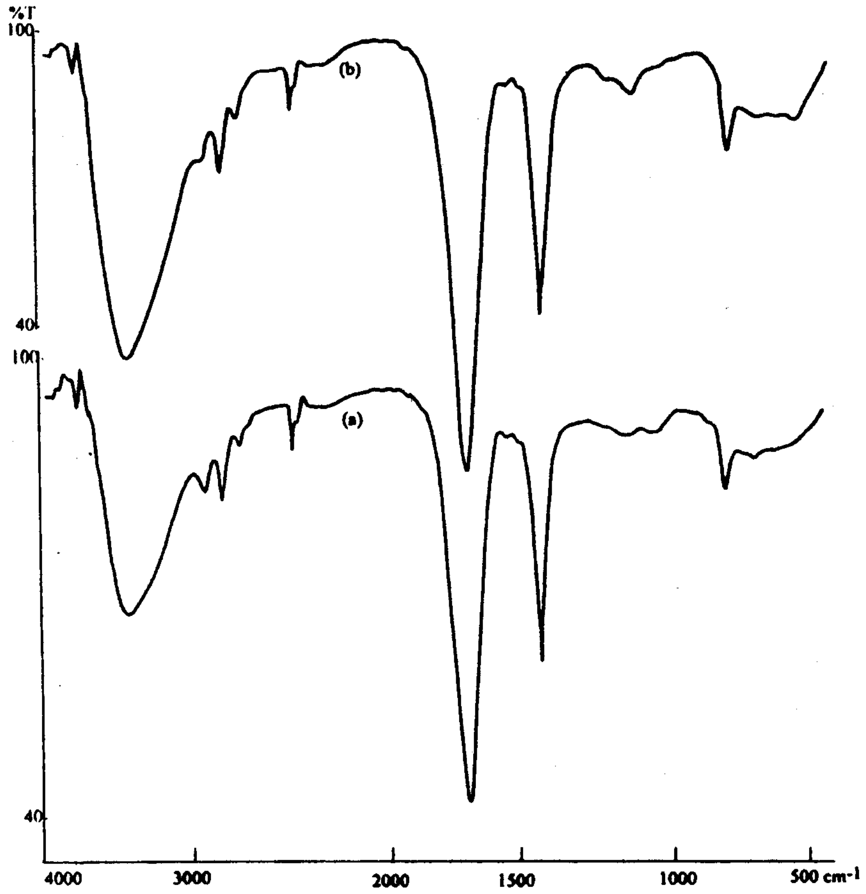


Figure 3. The IR spectra of polyamide samples heated at 360°C (a) PPD-5 and (b) PMD-7.

On heating, the samples did not seem to be decomposed, but became more rigid and the weight loss matched with the calculated weight for the water molecules. A perusal of IR spectra of heat-treated samples further confirmed the loss of water molecules. In PMD-7-180° [Fig. 2(b)], the intensity of ν_{CH2} (asymmetric and symmetric) stretching increased in comparison to that of the broad band from ν_{NH} and ν_{OH}. Furthermore, the peak maxima of the latter shifted to a lower side at 3399 cm^{-1}. Similarly, for PSD-8 and PPD-5, these bands shifted towards a lower range at 3399 and 3405 cm^{-1}, respectively. The amide III band, near 1352 cm^{-1}, observed in all the three cases, intensified and prominent bands appeared in the 2300–2500 cm^{-1} region in heat-treated samples. Similar observation was reported for hydrogen bonded thermotropic liquid crystalline poly(esteramides) from *bis*(hydroxyl alkamido)aranes.[20] This may be attributed to the introduction of considerable double bond character between carbonyl carbon and nitrogen atom of the amide group, as a consequence of lessened hydrogen bonding with adsorbed water molecules, resulting in greater electron polarization within the amide group. The IR spectra, recorded after heating the samples at 360°C (Fig. 3), exhibited great reduction in the intensity of bands in the 3200–3600 cm^{-1}

range, and the increased intensity of bands observed due to amide, I and III substantiated the loss of adsorbed water molecules. Thus, the IR spectra recorded after heating the samples prove that these polyamides possess heat resistance properties, as the heating of the samples resulted in the loss of adsorbed water molecules only.

Swelling Measurement

Equilibrium swelling of polyamide PMD-7 was determined in various solvents viz., water, dimethyl sulfoxide, DMF, acetone chloroform, carbon tetrachloride, benzene, and toluene. Although equilibrium swelling may not be the best absolute measure of the polymer–solvent interaction parameter, it is a very practical method. It relates directly to an important application, namely, the selection of materials for use in the presence of solvents and may give an indirect idea about the possible geometry of the polymer. The solubility parameters (δ) and the square root of the cohesive energy density (CED) can be measured by the indirect method. It is expected that the maximum swelling will take place when δ of the polymer (δ_p) matches with the δ of the solvent (δ_s). A plot of the swelling coefficient Q_{sc}, against δ_s values for various solvents exhibited a maximum value for DMF (12.1 $\mathrm{cal\,cm^{-3}}$) corresponding to δ_p. The value of δ_p reported for Nylon-66 is 13.6.[14b] The lower value for δ_p, in the present case, may be attributed to the greater length of hydrocarbon part in comparison to Nylon-66. However, the value is much higher than that for polyethylene and polypropylene, which are 7.9 and 8, respectively, certainly due to contribution of the polar amide groups of polyamides. The solid conductance of PMD-7, PSD-8, and PPD-5 are reported in Table 4. It is evident that the values are higher than the electrical resistivity values for typical insulators, 10^{-14}–$10^{-22}\,\mathrm{S\,cm^{-1}}$ but lower than the range for semiconductors 10^{2}–$10^{-9}\,\mathrm{S\,cm^{-1}}$.[21] Although the conductivity values are low for these polyamides, they are still significant considering the structure of polyamides, which have no specific features, such as conjugated double bonds necessary for conduction.

The polyamide samples heated for 4 hr at 360°C showed an enhancement in conduction value. This observation further substantiated a high content of sorbed water as capillary condensation in the hydrocarbon part, acting as insulator, however, at a higher temperature due to loss of water molecules, the chains became compact and interchain hopping of electrons was rendered possible.

The highest conductance value for PMD-7 may be due to the +I effect from the methylene group, which increases electron density on the ring and the lowest value for PSD-8 may be due to the −I effect as well as repulsion between $-SO_2$-groups because of their size as well as polarity.

Sudha and Pillai[20] inferred from IR and WAXD studies for poly(esteramide)s (PEA) from *bis*(hydroxy alkamido)aranes that rigidity due to H-bonding may be responsible for the liquid-crystallinity for those PEAs. The lateral distances are held close to consistency and that the large fractions of the polymer chains in the samples adhere in the lateral order.

Viscosity Measurements

As the maximum swelling of polyamides was observed in DMF, it was chosen as the solvent for viscosity measurement. One may question whether the same solvent, DMF, can be used as a solvent for swelling purpose and as a solvent to dissolve the polymer. It is well known that in coming in contact with the solvent the polymer swells and then dissolves.[22] When the polyamide was placed in DMF at room temperature, only swelling was observed. However, dissolution in DMF could be achieved only after softening the sample by heating. 0.5 g of the sample softened by heating was dissolved in 100 mL of DMF and then diluted to different concentrations. The plots of reduced viscosity ($\eta sp/C$) vs. concentrations are depicted in Fig. 4(a)–(c) for PMD-7, PSD-8, and PPD-5, respectively.

In the case of PMD-7, the reduced viscosity showed an initial rise and then a fall with the increase in concentration. However, the value of reduced viscosity decreased gradually with an increase in concentration in the case of PSD-8 and steeply in the case of PPD-5. The decrease in viscosity with an increase in concentration of polyamides in DMF solution may be attributed to the fact that DMF, being a polar solvent, may induce the coiling of an aliphatic spacer chain resulting in tight coiling of chains encapped with the polar amide groups.

The solubility and the behavior of solutions are determined by the chemical interaction between solute and solvent molecules. For polymers, many of the theoretical conformations are not possible due to an "excluded volume" effect, i.e., occupation of the same space by different parts of the chain. However, in some conditions a solution in which the tendency for the conformation to be more open due to interaction with solvent

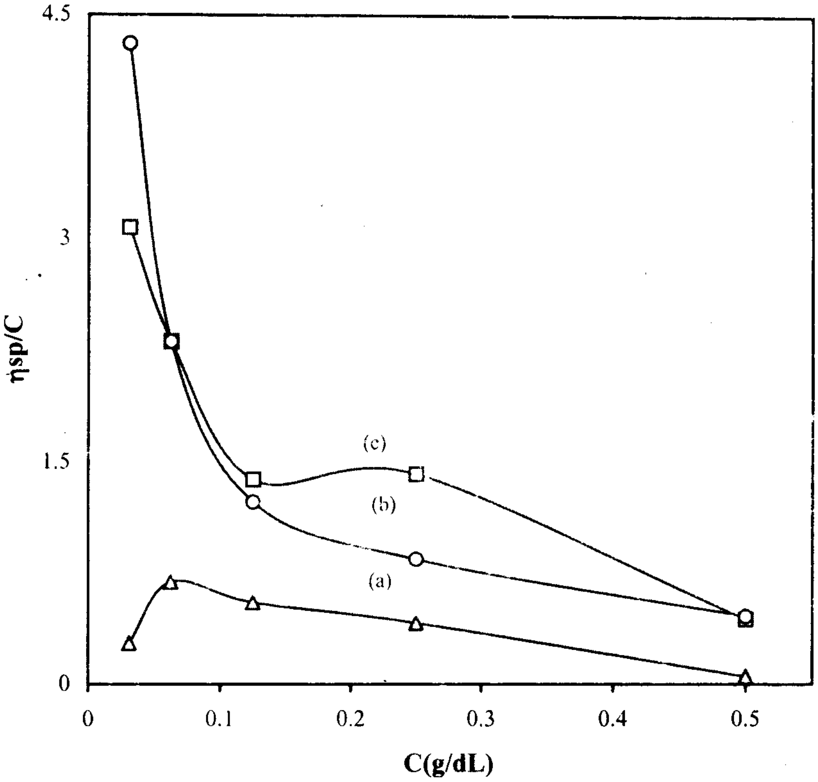


Figure 4. Plots of reduced viscosity vs. concentration for PMD-7 (○), PSD-8 (Δ), and PPD-5 (□).

just counterbalances the excluded volume effect. In a poor solvent the polymer molecule will take up a fairly tight conformation, thus the hydrodynamic volume is reduced. At "theta" temperature the increased energy of vibration alters the effective volume occupied by parts of a chain and the effect of interactions. In a good solvent, the polymer has an open conformation.[23] In polymer solutions, interactions and entanglements between several long chain molecules are very likely to occur. Such interactions lead to an increase in solution viscosity with an increase in concentration.

The values of inherent viscosities ($\ln \eta_r/C$) are comparatively high being 5.03, 6.31, and 9.01 for PSD-8, PMD-7, and PPD-5, respectively, (Table 4). The reported inherent viscosities for rod-like polyamides were at least 3.0 and 1.9 for non-rod like polymers.[4] The high viscosity values in the present case further substantiated the proposed association of the polyamide chains.

CONCLUSION

Polyamides of DA with various aromatic diamines were synthesized using TPP, dispensing with the use of obnoxious pyridine and the solvent DMF. The unusual solid conductance observed for these polyamides, especially upon heating at 360°C for 4 hr is probably because of the packing of polymer chains through hydrogen bonding and conduction may be in a direction perpendicular to the aromatic rings held in parallel position. Such packing is evidenced through the high water content, present as capillary condensation. These polyamides can be further explored for their possible application in heat resistant antistatic surface-coating formulations.

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