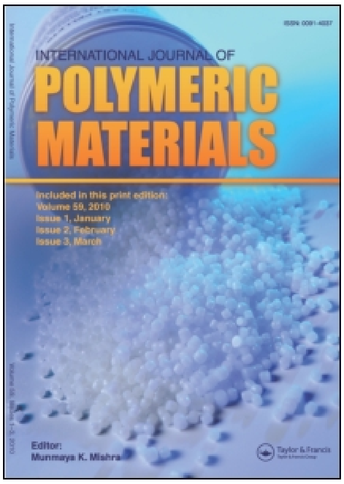

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

NOVEL BIODEGRADABLE POLYAMIDES BASED ON TARTARIC ACID: PREPARATION AND PROPERTIES

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To cite this Article Mathakiya, Ismail A. , Rakshit, Animesh K. , Iyer, Bragadish D. and Shah, Avinash K.(2004) 'NOVEL BIODEGRADABLE POLYAMIDES BASED ON TARTARIC ACID: PREPARATION AND PROPERTIES', International Journal of Polymeric Materials, 53: 5, 405 — 418

To link to this Article: DOI: 10.1080/00914030490429915

URL: http://dx.doi.org/10.1080/00914030490429915

International Journal of Polymeric Materials, 53:405–418, 2004

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490429915

NOVEL BIODEGRADABLE POLYAMIDES BASED ON TARTARIC ACID: PREPARATION AND PROPERTIES

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Copolymers of tartaric acid with various diamines were synthesized by a condensation polymerization technique. The synthesized polymers were characterized by elemental analysis, FTIR, ^{1}H-NMR, paper chromatography, TGA analysis, viscosity measurements and biodegradation studies. Elemental analysis, paper chromatography and spectroscopic studies confirmed polyamide formation. The activation energy values for various stages of decomposition were calculated from TGA analysis using Broido's method. The intrinsic viscosity ($[\eta]$), voluminosity (V_E) and shape factor (ν) were also computed using viscosity data. Microbiological observations of polymer-dependant growth studies using a soil bacterial isolate, suggested that one of these polymers was used as growth substrate and was therefore biodegradable.

Keywords: Tartaric acid, diamines, condensation polymerization, polyamides, characterization, biodegradation studies

Received 13 August 2001; in final form 6 September 2001.

One of the authors (I. A. Mathakiya) is thankful to CSIR, New Delhi, for granting a Senior Research Fellowship (Extended). We are also thankful to Dr. P. V. C. Rao, IPCL, Baroda and Prof. C. F. Desai, Physics Department, MS University of Baroda for experimental help in NMR and FTIR studies, respectively.

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INTRODUCTION

In past decades a great deal of research has been done on the synthesis of polymeric materials for long-term service. In particular, many kinds of thermally and chemically stable polymeric materials have been developed. Today, however, a new field of research has developed, which is concerned with the synthesis of biodegradable polymers and studies of their properties [1]. This field of research is growing rapidly because of the strong demand for such polymers as packaging materials and biocompatible materials for specific medical applications due to the potential for their easy disposal and biodegradation under natural environmental conditions. Hence, current attempts to develop biodegradable polymers have focused on the synthesis of new polymers and on the modification of natural polymers, which show the excellent properties of strength and durability designed into plastics to meet end use requirements and to overcome or solve the problems associated with their disposal. For all these reasons, the interest in synthesis of polymers containing carbohydrate units in the main chain is steadily increasing because of their potential as biodegradable and biocompatible materials [2]. Moreover, the use of carbohydrate-based monomers opens the access to polycondensates containing several asymmetric centers in the backbone of the repeating unit. The conformational properties of these stereoregular poly(hydroxyamides) are the object of current investigation for their capacity to form helical structures containing large cavities of varying geometry depending on the configuration of parent carbohydrate (i.e. tartaric acid) moieties [3]. Several reviews dealing with these classes of polymers have appeared in the past [4]. Moreover, tartaric acid-based polyamides had also been explored by Rodriguez-Galan et al. [5] to study their stereoregular optically active properties. Ducret et al. [6] reported enzymatic preparation of fatty esters of carbohydrates and studied their surface properties such as surface tension, interfacial tension and their ability to stabilize emulsion at 30°C. Paredes and coworkers [7] reported synthesis of an alternating copolyamide consisting of 1-alanine and 11-aminoundecanoic acid by the active ester method. This copolyamide showed its potential applications as a family of biodegradable and biocompatible polymers. Ennis and others [8] suggested that polyamides such as nylon-66 could be modified by N-acetyl substitution to produce materials that are both bio- and photodegradable. Besides, Arvanitoyannis and colleagues [9] have recently investigated the synthesis and properties of two novel series of biodegradable oligo (ester amide)s based on diacids (i.e. sebacic acid and octadecanedioic acid), 1,6-hexanediamine and ε-caprolactone, which could find applications either in reactive blending with polymers or as comonomer units (in prepolymers) for synthesizing, "*tailor-made*" polymers. We have also developed biodegradable terpolymers from acrylamide, acrylic acid, acrylonitrile and studied their biodegradability in synthetic minimal salt medium [10,11]. In this article, we present the results of our study of the synthesis and properties of copolyamides from DL-tartaric acid with various diamines, viz. ethylene diamine and hexamethylene diamine.

EXPERIMENTAL

Materials

DL-tartaric acid (Suvidhinath Lab., Baroda, India), hexamethylene diamine (Fluka, Switzerland), Nylon-6 (commercial grade obtained from G.S.F.C., Baroda, India) and sulphuric acid (98%, AR, SD's Fine-Chem Ltd., India) were used as received. Ethylene diamine (97%, Fluka, Switzerland) was distilled prior to use and middle fraction was used. All solvents (Qualigens, India) used in this study were freshly distilled before use.

Polymerization Method

The polyamides were synthesized by a two stage process: (a) synthesis of diethyl tartarate from tartaric acid and; (b) synthesis of various polyamides using different diamines and diethyl tartarate.

(a) Synthesis of Diethyl Tartarate

Diethyl tartarate was synthesized by refluxing a mixture of tartaric acid (0.1 mol), absolute ethanol (1.0 mol) and concentrated sulphuric acid (2.0 mL) for 24 hours. Excess alcohol was distilled off under vacuum and the reaction mass was poured in 200 mL diethyl ether. The crude ester layer was separated and a trace of acid was neutralized by addition of sodium bicarbonate until effervescence ceases. The crude ester was passed through anhydrous sodium sulphate bed to remove traces of moisture. Transparent viscous diethyl tartarate was obtained on evaporation of ether in bulb oven at ~50°C. The purity of synthesized diethyl tartarate was checked by gas chromatography and found to be 99.9% pure. The gas chromatography was performed on a Shimadzu GC-14B equipped with flame ionization detector. The diethyl tartarate (5 µl) was analyzed by following temperature program using Chromosorb-W-AW column (10% SE 30 + 1% QF, length 2 m, outer diameter 1/8"). Column, injector and detector temperatures were maintained at 120, 295 and 300°C, respectively.

(b) Synthesis of Polyamides

Diethyl tartarate (0.01 mol), diamine (0.011 mol), N-methyl pyrrolidone (NMP, 25.0 mL) were taken in a 100 mL round-bottom flask attached to a reflux condenser. The mixture was stirred magnetically for 6 hours in a water bath kept at 80 °C. The mixture was then poured into excess of nonsolvent (acetone/water) to precipitate the polyamide.

The polyamide of ethylene diamine was also synthesized using alcohol and benzene as solvent mediums. In this route, as condensation reaction proceeds, the polyamide gets precipitated. Various synthesized products are represented as follows:

NL 1: reaction product of ethylene diamine with tartaric acid in alcohol
NL 2: reaction product of ethylene diamine with tartaric acid in benzene.
NL 3: reaction product of hexamethylene diamine with tartaric acid in NMP.

The schematic representation of polyamide synthesis is given in Figure 1.

Characterization

The FTIR spectra of the copolymers were recorded on a Bomem-MB140, Canada, FTIR spectrometer. For FTIR spectra, the solid polymers and KBr (spectroscopic grade) were thoroughly mixed and this mixture was pressed to form a pellet, whereas liquid sample was spread over the NaCl cells and the spectra were recorded. ^{1}H-NMR spectra of copolymers solutions were recorded under standard conditions at room temperature in D_2O on a JEOL JNM FX-100, FT-NMR spectrometer operating at 100 MHz. TMS was used as an internal reference and D_2O as an internal lock.

The polyamides were further characterized by ascending paper chromatography. Nylon-6 (as reference), NL 1, NL 2 and NL 3 (as samples) were used for the above studies. 25 µl of 1% solution of polyamides in 85% formic acid were spotted on a Whatman No. 3 paper and the chromatogram was developed in the ascending mode using both 85% and 60% formic acid. After drying the chromatogram, spots were detected by (i) UV-fluorescence, (ii) a color reaction based on the conversion of carbonamides to chloramines by chlorine [12]. The procedure followed for the latter method is briefly as follows: the dried chromatograms were exposed to chlorine gas and subsequently

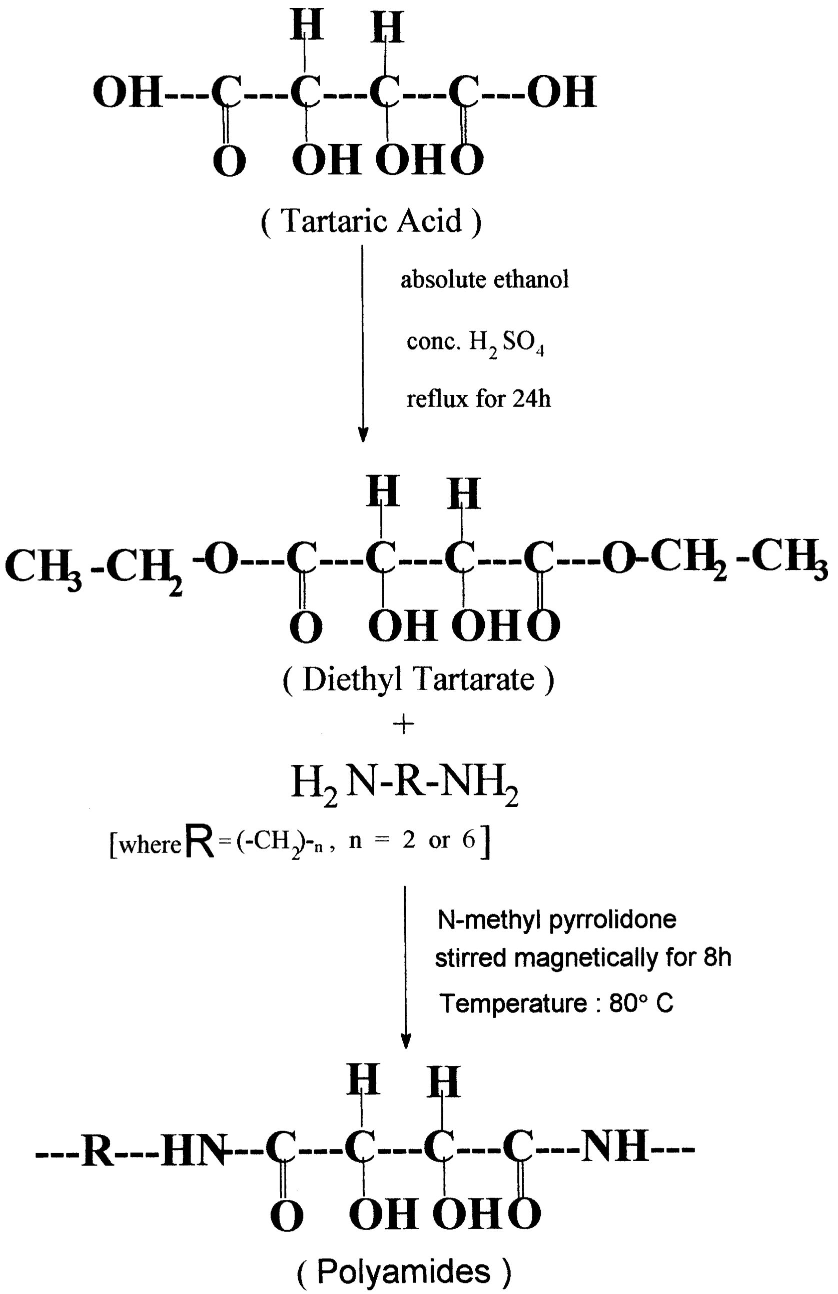

FIGURE 1 Schematic representation of polyamides synthesis.

exposed to NH_3 until the background was white (2–3 sec). The chromatograms were then dipped into a mixture of equal quantities of water saturated solution of *o*-toluidine: 0.50% KI (pH 5.5), and subsequently washed with water.

The elemental analysis was carried out with Perkin Elmer-2400 C, H, N, S analyzer. The TGA was recorded on a Shimadzu thermal analyzer DT-30B. The TGA analysis was done in the presence of air at heating rate of 10 $\mathrm{K\,min^{-1}}$. Viscosity studies of different solutions were carried out with the help of an Ubbelohde viscometer, placed vertically in a thermostated bath at all required temperatures ($\pm 0.05\,^{\circ}C$).

In the biodegradation studies, minimal salt medium (1 L, pH 7.0) which contained [$\mathrm{g\,L^{-1}}$] 4.3 K_2HPO_4, 3.4 KH_2PO_4, 0.3 $MgCl_2 \cdot H_2O$, and 0.5 mL of trace element solution having [$\mathrm{mg\ L^{-1}}$] 1.0 $MnCl_2 \cdot 4H_2O$, 0.6 $FeSO_4 \cdot 7H_2O$, 2.6 $CaCl_2 \cdot H_2O$, 6.0 $NaMoO_4$ was used for growth studies [13]. Ammonium sulphate [$1.0\,\mathrm{L^{-1}}$] was supplied as a nitrogen source. Polyamide [NL 1] containing DL-tartaric acid and ethylene diamine as monormers was added to the above medium as the sole source of carbon and energy and the medium was sterilized by autoclaving at 10 psi for 20 min. Minimal medium without the polymer was also inoculated and served as a control.

Following the conventional enrichment culture technique [14] and using 1% (w/v) polymer [NL 1] in minimal medium as a sole carbon and energy source, a bacterial culture (designated here as TED-1) capable of growth on the polyamide was isolated after three enrichments in the minimal medium by streaking onto Luria agar.

For growth studies, cultures were cultivated in 5.0 mL of the minimal medium in 50 mL culture tubes at 30°C on a rotary shaker at 180 rpm. The growth was followed (i) turbidimetrically at 600 nm and (ii) by estimating the whole-cell protein. For whole-cell protein determination, cellular proteins were solubilized by treating the cells (approx. 100 μg dry weight in 0.5 mL) with 0.5 mL of 1.0 N NaOH at 100°C for 5 min and were subsequently estimated by the method of Lowry et al. discussed by Herbert et al. [15].

RESULTS AND DISCUSSION

Elemental Analysis

The experimentel and theoretical values for percentage of nitrogen, carbon and hydrogen present in polyamides are shown in Table 1. The values are in reasonably good agreement with each other, indicating the polyamide formation.

TABLE 1 Elemental Analysis Results for Various Polyamides

Polymer samples	Nitrogen (wt. %)	Carbon (wt. %)	Hydrogen (wt. %)
NL 1	15.58 (16.09)	38.83 (41.38)	6.27 (5.75)
NL 2	15.55 (16.09)	40.98 (41.38)	6.49 (5.75)
NL 3	11.15 (12.13)	50.20 (52.17)	7.83 (7.83)

Data in the parenthesis indicates theoretical values.

FTIR Analysis

Conformation and environmental changes of polymers at the molecular level were obtained by FTIR spectrum. Ester of tartaric acid (i.e. diethyl tartarate) shows very sharp ester stretching vibration at 1745 cm^{-1}, whereas hydroxyl (-OH) stretching was observed as a broad peak in the region 3250-3450 cm^{-1}. Besides this, other prominent peaks at their respective positions confirm diethyl ester formation. In the case of polyamide the carbonyl stretching frequency was observed at 1640 cm^{-1}, whereas secondary -NH- stretching and bending vibrations were observed at 3285 and 1548 cm^{-1}. These give clear evidences for amide formation. Other functional groups also showed characteristic IR absorption bands, which agreed well with those reported in the literature [10,16]. IR and NMR spectra were submitted to the Editor but are not reproduced herein.

^{1}H-NMR Spectroscopic Studies

Further evidence for the formation of polyamide was supported by nuclear magnetic resonance (NMR) spectroscopy. The peaks corresponding to structure given above were obtained. In ^{1}H-NMR spectrum the signals that occur around $\delta = 3.09$ ppm are associated with the methylene protons (a), whereas very sharp intensive peak (c) appears in a region of $\delta = 3.46 - 3.54$ ppm results from HOD (due to exchange of protons with D_2O). The signals at $\delta = 4.38 - 4.52$ ppm corresponding to secondary amide (d) and $\delta = 4.57 - 4.61$ ppm represent the absorption of methine protons (b). All these signals agreed well with those reported in the literature [16, 17].

Chromatographic Studies

A paper chromatographic technique was also used to confirm the synthesized polyamides by taking NL 1, NL 2 and NL 3 as compared to nylon-6, which was taken as a reference compound. Paper chromatographic studies of all the polyamides have been visualized under UV-radiation and also detected as blue-brown spots using color reaction. A similar color reaction has been used earlier for the characterization of nylon-6 [12]. All the polyamides including nylon-6 showed good mobility in 85% formic acid whereas 60% formic acid failed to make nylon-6 and NL 3 move from the starting line. Such behavior of polyamides is attributed to the differences in solubility of these polyamides in the two solvent systems containing different proportion of water [18]. The high proportion of water in the 60% formic acid has adversely affected the mobility of these polyamides. The intensity of the spots varied depending upon the composition of the polyamides used. These observations indicated that paper chromatography could be useful for the characterization and separation of a mixture of polyamides.

Solubility Test

When the solubility of the above synthesized polyamides in various solvents were studied, they were found to be insoluble in methanol, acetone and benzene. However, they were found to be soluble in solvents like formic acid, N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), and 1,4-dioxane. NL 1 and NL 2 were soluble in cold water, whereas NL 3 was sparingly soluble even in hot water. It is known that nylon 6 is a water insoluble polyamide and is soluble in formic acid. NL 3 was found to be completely soluble in 85% formic acid while it was only sparingly soluble in 60% formic acid (3 mg ml). This decrease in the solubility of NL 3 as compared to NL 1 and NL 2 could be due to the increase in the chain length of methylenic back-bone conferred by the presence of hexamethylene diamine monomer.

Thermal Analysis

The thermogravimetric data provide information regarding the thermal stability of the polymers. The thermogram of the polyamides NL 1, NL 2 and NL 3 are shown in Figure 2. All the polyamides showed two stage decomposition due to the rapid decomposition to water, carbon dioxide, ammonia, hexamethyleneimine and other volatile products [19]. The activation energy associated with each stage of decomposition was evaluated by the well-known Broido method [20]. The equation used for the calculation of the activation energy (E_a) was

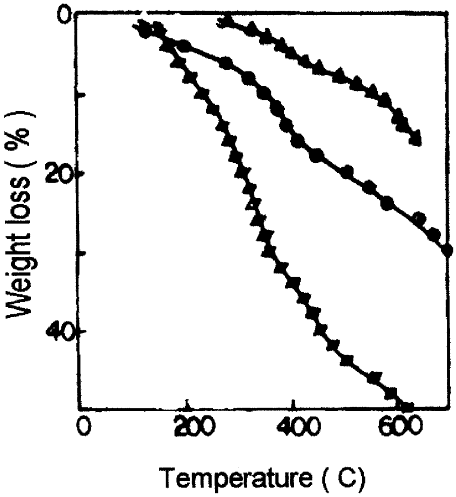

FIGURE 2 TGA plots for polyamides: (●) NL 1, (■) NL 2 and (▲) NL 3 at heating rate of 10° K min^{-1}.

$$\ln|\ln(1/Y)| = (-E_a/R)(1/T) + \text{Constant} \qquad (1)$$

where $Y = (W_t - W_\infty)/(W_0 - W_\infty)$ is the fraction of the number of initial molecules not yet decomposed; W_t is the weight at any time t; W_∞ is the weight at infinite time (Zero) and W_0 is the initial weight.

On plotting $\ln|\ln(1/Y)|$ versus $1/T$ (Figure 3) a straight line is observed. The slope yielded activation energy. The calculated values for the activation energy of decomposition are listed in Table 2. It is observed that for all the polymers the activation energy associated with second stage of decomposition is lower than that of the first stage. NL 3, having a long flexible chain, showed lower weight loss and higher activation energy of decomposition, indicating a higher thermal stability.

Viscosity Studies

The intrinsic viscosity $[\eta]$, which is one of the most important source, of information on the size and shape of polymer molecules [21], can be obtained by the use of Huggins and Kraemer equations

$$(\eta_r - 1)/C = [\eta] + k'[\eta]^2 C \qquad (2)$$

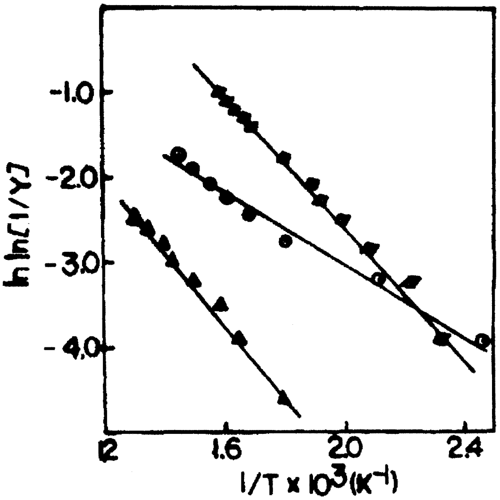

FIGURE 3 Activation energy plots for the polyamides: (●) NL 1, (■) NL 2, and (▲) NL 3 (from the experimental data of Figure 7).

$$\ln \eta_r/C = [\eta] - k''[\eta]^2 C \tag{3}$$

where k′ and k″ are usually referred to as the Huggins and Kraemer constants. The accuracy of the data was checked by calculating k′ and k″ and their difference, which was 0.5 as expected. The intrinsic viscosity [η] values of polymers NL 1, NL 2 and NL 3 were determined in N, N-dimethylacetamide (DMAC) at 3 different temperatures and are presented in Table 3.

It can be seen that [η] decreases as the temperature increases. This indicates that the swelling of the polymer chains is limited in this system and the critical solution temperature is lower for this polymer solution. This is due to the decreased thermodynamic affinity with increased temperature [21].

The relative viscosity data were used to calculate the equivalent hydrodynamic volume (voluminosity, V_E), a measure of size of a solvated polymer molecule at infinite dilution. V_E was calculated by plotting ψ against concentration (in g dL^{-1}), where

$$\psi = (\eta_r^{0.5} - 1)\,/\,C\,(1.35\,\eta_r^{0.5} - 0.1) \tag{4}$$

The straight line obtained was then extrapolated to C=O and the intercept yielded V_E. The voluminosity values are a function of temperature. As the temperature increases, the random coil diameter

TABLE 2 Activation Energy of Decomposition for Various Polyamides by Thermogravimetric Analysis

Polymer samples	Decomposition temperature range (°C)	Weight loss (%)	Activation energy[a] E_a (kJ mol^{-1})
NL 1	132–416	16%	17.0
	454–701	30%	13.9
NL 2	155–360	30%	13.9
	380–620	50%	11.7
NL 3	286–495	08%	37.2
	530–615	14%	33.5

[a] Calculated using Broido method at a heating rate of 10 K min^{-1} in air.

decreases, and hence, V_E decreases [21]. The shape factor (ν) was obtained from the equation

$$[\eta] = \nu V_E \tag{5}$$

The shape factor gives an idea about the shape of the polymer molecule in solution [21]. Values of shape factors in different temperatures were found to be 2.5 ± 0.1, suggesting that the macromolecules acquire spherical conformation in water.

Biodegradation Studies

Biodegradation studies of the polyamide [NL 1] of DL-tartaric acid and ethylene diamine were carried out in inorganic minimal salt medium.

TABLE 3 Viscosity of Polyamides at Different Temperatures in DMAc

Polymer	Temperature (°C)	$[\eta]$ (dl/gm)
NL-1	30	0.358
	35	0.327
	40	0.304
NL-2	30	0.320
	35	0.294
	40	0.279
NL-3	30	0.332
	35	0.308
	40	0.295

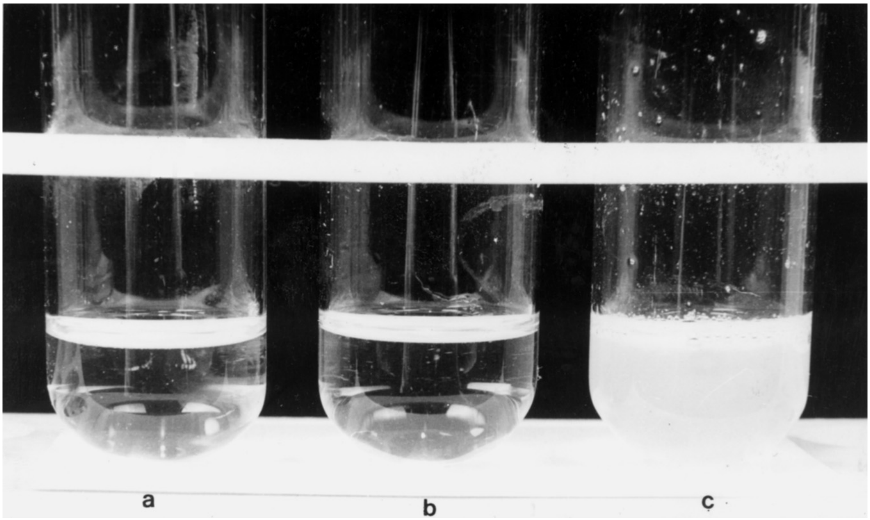

FIGURE 4 Growth* of the organism TED-1 on NL 1 after 72 h. *From left to right: a) minimal medium without polymer inoculated, b) minimal medium with polymer uninoculated, and c) minimal medium with polymer inoculated.

When the individual polymer [NL 1] was supplied as a sole carbon and energy source in a synthetic medium at a concentration of 0.5% (w/v), the isolate TED-1 was found to grow on the polymer as shown in Figure 4. The above isolate was found to be a gram negative, rod shaped bacterium. The isolate did not grow in the absence of the polymer in the synthetic medium. Thus, for the growth of the isolate TED-1, the presence of the polymer in the medium was found to be essential and thereby indicating the biodegradable nature of this ploymer. Using a similar strategy, degradation of copolyesters of citric acid-1,2,6-hexane triol [22], succinic acid-glycerol-poly(ethyleneglycol-200) copolymer [23] and terpolymers of acrylamide, acrylic acid and acrylonitrile [11] has been reported. The isolate grew without a lag period and the maximum growth reached at $\sim$30 h is shown in Figure 5. This observation was further confirmed by estimating the biomass of growth in tems of whole-cell protein, where the increase in biomass followed a similar pattern as above.

CONCLUSION

A series of polyamides were synthesized using a condensation technique. The properties of polyamides vary with respect to their

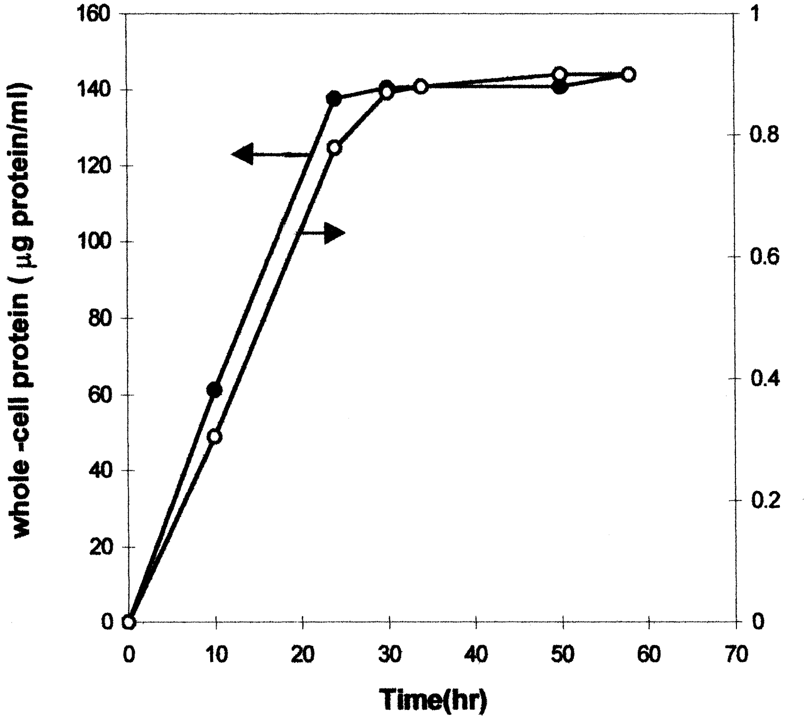

FIGURE 5 Time course of the growth* of isolate TED-1 on NL 1#. *Growth was determined in terms of absorbance at 600 nm (○) and whole-call protein (●). #Polyamide [NL 1] was supplied as a sole carbon and energy source in minimal medium at a concentration of 0.5% (w/v). Control had no polymer and was inoculated.

constitution. Elemental analysis, FTIR, NMR, paper chromatography, solubility tests, thermal analysis, viscosity measurements and biodegradation studies characterized the polymers. The spectroscopic techniques provide information regarding the structure and environmental change of the polymers. Elemental analysis and paper chromatography support the polyamide formation. Solubility of polyamides depends on constitutions of their back-bone structure. The activation energy of decomposition (E_a) associated with second stage of decomposition is lower than that of the first stage. Higher thermal stability was observed for NL 3 in comparison to other polyamides. Preliminary studies carried out in terms of growth supporting ability of the polymer indicated the biodegradable nature of the NL 1 polymer.

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