



## Microwave-accelerated Preparation of Aromatic Polyamides Containing Phthalimide and *S*-Valine Pendant Groups in Ionic Liquids

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### ABSTRACT

Ionic liquids (IL)s represent an attractive and potentially very valuable group of new solvents, which have the benefit of low vapour pressure and therefore easier handling than many conventional solvents. These liquids, because of their unique properties, are attracting a lot of attention to replace volatile organic solvents, eco-friendly and green media. This work describes microwave-assisted polyamidation reaction of 5-(2-phthalimidyl-3-methylbutanoylamino)isophthalic acid as a diacid monomer with various aromatic diamines such as 4,4'-diaminodiphenyl sulphone, 4,4'-diaminodiphenylether, 4,4'-diaminodiphenyl methane, benzidine, *p*-phenylenediamine, *m*-phenylenediamine, 2,5-diaminotoluene and 1,5-naphthalene diamine in the presence of different imidazolium salts and triphenyl phosphite without adding extra compounds. This technique of polymerization is a very fast and green process for polymer synthesis. This polymerization method benefits the advantages of elimination of volatile and toxic solvents such as NMP, very short reaction time and direct polymerization, so there is no need of preparation of diacid chloride and therefore, saves time and energy in this procedure. This method gave polyamides (PAs) with inherent viscosities ranging from 0.32-0.66 dLg<sup>-1</sup>. The resulting wholly aromatic PAs with bulky pendent groups, each has polyisophthalamide backbone substituted with phthalimide and *S*-valine groups in ring position 5 of the diacid, and different aromatic diamines. These polymers have chiral centre in the pendant groups and show optical activity. They were characterized by FTIR, <sup>1</sup>H NMR, elemental analysis and specific rotation techniques. Introduction of bulky and flexible clusters in these polymers pendant group; make them soluble in most polar aprotic solvents. Thermogravimetric analysis showed that these PAs exhibit high thermal stability.

### Key Words:

ionic liquids;  
green chemistry;  
microwave heating;  
optically active polymers;  
direct polycondensation.

### INTRODUCTION

Many chemical processes involve volatile organic solvents that evaporate into the atmosphere with detrimental effects on the human health and environment. Obviously, replacement of these sol-

vents in a process with non-volatile solvents would reduce losses through evaporation. Ionic liquids (IL)s are the chemicals that can be applied as solvents and catalysts in green chemistry processes.

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Non-volatility of ILs as well as their high solvation power for many organic, inorganic and metalloorganic compounds, make ILs as a new and remarkable class of media for various asymmetric synthesis, homogeneous, heterogeneous catalysts and biocatalysts [1-3]. They are being used as green solvents because they are non-volatile, recyclable, non-explosive, easy handling, thermally robust, and in addition they are compatible with various organic and organometallic compounds. ILs, in particular those based on the 1,3-dialkylimidazolium cations, are amongst the most popular and investigated type of alternative media to water and organic solvents for various physico-chemical process [4]. This is in part due to their very low vapour pressure, non-inflammability and high thermal stability and large electrochemical window.

On the other hand, the synthesis of polymers in ILs media is also of significant scientific interest [5]. Direct polyamidation reaction in ILs is a recently developed method of polymerization [6-8]. The polyamidations in ILs proceed as one pot path-way reactions and have the advantages of direct polycondensation.

Microwave irradiation is a well-known technique for heating and drying materials and is employed in many private households and industrial applications for these purposes. In general, most organic reactions are usually heated using traditional heat transfer equipment such as oil baths, sand baths and heating jackets. These heating techniques are, however, rather slow and a temperature gradient can develop within the sample. Additionally local overheating and a hot vessel surface can lead to product, substrate and reagent decomposition and undesirable side reactions. In contrast, in microwave heating, the microwave energy is introduced into the chemical reactor remotely and direct access by the energy source to the reaction vessel is obtained. In addition, microwave energy heats the entire sample at once, eliminating "hot spots" and reducing reaction times, all of which result in larger, and purer yields [9,10]. The advantages offered by microwave assisted organic synthesis are suited to the increased demands in industry. Reactions that would take days with conventional methods can be completed in few minutes in the microwave oven. There has been growing interest in applying

microwave energy to synthetic organic chemistry as well as synthetic polymer chemistry [11,12]. It has been shown that microwave activation for polymer synthesis allows enhancements in the reactivity and selectivity [13-16]. Recently we have used microwave irradiation for the synthesis of polymeric materials via different methods [7, 8, 17-19].

Since ionic liquids are comprised entirely of ions, they can be heated rapidly at high rates under microwave irradiation by ionic conduction mechanism. A small amount of ionic liquid has been proved to have a remarkable effect on the heating characteristics of solvents under microwave irradiation [13, 20, 21]. The use of ILs in combination with microwave heating, benefits from both microwave technique and ILs. Several polymerization reactions have been performed in ILs under microwave irradiation [13,17]. This combination leads to advantages such as: very short reaction times, very high heating rate and many benefits of the eco-friendly approach, named green chemistry.

Aromatic polyamides (PA)s are characterized by their excellent balance of thermal and mechanical properties and by an outstanding chemical resistance, which make them useful as high-performance materials. But, the applications of PAs are sometimes restricted because of difficulty in their fabrication. For example, wholly aromatic PAs, particularly those with *para* substituted rings, are quite intractable materials that do not melt and only dissolve in strong mineral acids such as concentrated sulphuric acid or in very polar aprotic solvents containing salts. Therefore, much effort has been made to modify the structure of PAs in order to have better properties in terms of both solubility and processability with protection of their high thermal stability [22,23]. Approaches investigated in attempting to improve the solubility of polyamides include the addition of pendant groups to the polymeric backbone [24,25], preparation of copolymers such as poly (amide-imide)s [26-28], poly (amide-ester-imide)s [29], introduction of different heterocyclic rings into the macromolecular chains of polyamides [30,31], and incorporation of bulky substituents [32] or flexible units [33] within the parent chain.

Synthesis of optically active polymers is an important field in polymer science as they find wide variety

of potential uses based on the chiral structure. An important application of these macromolecules is chiral recognition. This ability of chiral polymers has been utilized in various forms of catalytic and separation chemistry [34,35]. Optically active polyamides are promising materials where chiro-optical effects can be combined with good mechanical and thermal properties [36]. On the other hand, incorporation of  $\alpha$ -amino acid moieties along the polyamide chain could be an effective strategy for enhancing the biodegradability [37].

In connection with our interest in preparing thermally stable optically active polymers, this work deals with the successful application of ILs in combination with microwave heating for green and rapid synthesis of wholly aromatic optically active PAs containing *S*-valine and phthalimide groups in the side chain.

## EXPERIMENTAL

### Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. 4,4'-Diaminodiphenylsulphone (DA1) was used as obtained without further purification. Benzidine (DA4) and 4,4'-diaminodiphenyl methane (DA3) was purified by recrystallization from ethanol and water, respectively. 4,4'-Diaminodiphenylether (DA2), *p*-phenylenediamine (DA5), *m*-phenylenediamine (DA6) and 2,5-diaminotoluene (DA7) were purified by sublimation. ILs were prepared according to the literature procedure [5].

### Apparatus

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR, 500 MHz) spectra were recorded in dimethyl sulphoxide- $d_6$  (DMSO- $d_6$ ) solution using a Bruker (Germany) Avance 500 instrument at Sharif University of Technology, Tehran, Iran. FTIR spectra were recorded on (Jasco-680, Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers ( $\text{cm}^{-1}$ ). Inherent viscosities were measured by using a Cannon-Fenske routine viscometer

(Germany) at concentration of 0.5 g/dL at 25°C. Specific rotations were measured by a Jasco Polarimeter (Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on Perkin Elmer in nitrogen atmosphere at a rate of 10°C/min. Elemental analyses were performed by the Iran Polymer and Petrochemical Research Institute, Tehran, Iran. The microwave apparatus used for the polycondensation was a Samsung (South Korea) microwave oven (2450 MHz, 900 W). All of the polymerization reactions were carried out in a hood with strong ventilation.

### Monomer Synthesis

5-(2-Phthalimidyl-3-methylbutanoylamino)isophthalic acid (1) as a diacid monomer was prepared according to our pervious published paper [38].

### Polymer Synthesis

PAs were prepared by the following procedure. Taking PA1 as an example, into a porcelain dish, 0.100 g ( $2.44 \times 10^{-4}$  mol) of dicarboxylic acid 1 and 0.061 g ( $2.44 \times 10^{-4}$  mol) of DA1 were dissolved in 0.15 g of IL (1,3-dipropylimidazolium bromide) under heating, then 0.13 mL ( $4.88 \times 10^{-4}$  mol) of triphenyl phosphite (TPP) was added. The dish was covered with a watch glass and subjected to microwave irradiation at 50% of power level for a period of 50+20s. The resulting polymer was precipitated by adding 20 mL of methanol follow by trituration. The polymer was filtered and dried at 80°C under vacuum to give 0.140 g (87% yield) of PA1.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$ = 1.07 (d, 3H), 1.19 (d, 3H), 2.79 (m, 1H), 4.61 (d, 1H), 7.16 (m, 4 aromatic H), 7.30 (m, 4 aromatic H), 7.98 (m, 4 aromatic H), 8.20 (m, 1 aromatic H), 8.33 (m, 2 aromatic H), 10.37 (s, NH), 10.85 (s, NH) ppm.

## RESULTS AND DISCUSSION

### Synthesis of Polyamides

In order to choose the best IL for the preparation of PAs, first the reaction of monomer 1 with DA1 was carried out in different synthetic ILs bearing different alkyl groups and in the absence of any IL under microwave irradiation (Table 1). The best inherent

**Table 1.** The effects of type of ILs on yield and inherent viscosity of the PA1<sup>a</sup>.

Polymer code	IL	Irradiation time (s)	Non-solvent	Yield (%)	$\eta_{inh}$ (dL/g)
PA1a	No IL	50+20	MeOH	-	No polymer
PA1b		50+20	MeOH	87	0.60
PA1c		50+20	MeOH	85	0.58
PA1d		45	MeOH	74	0.41
PA1e		45	MeOH	65	0.33
PA1f		40	MeOH	70	0.40
PA1g		50+20	MeOH	55	0.18
PA1h		50+20	MeOH	63	0.31

<sup>(a)</sup> All reactions were carried out in the presence of TPP at 50% of power level.

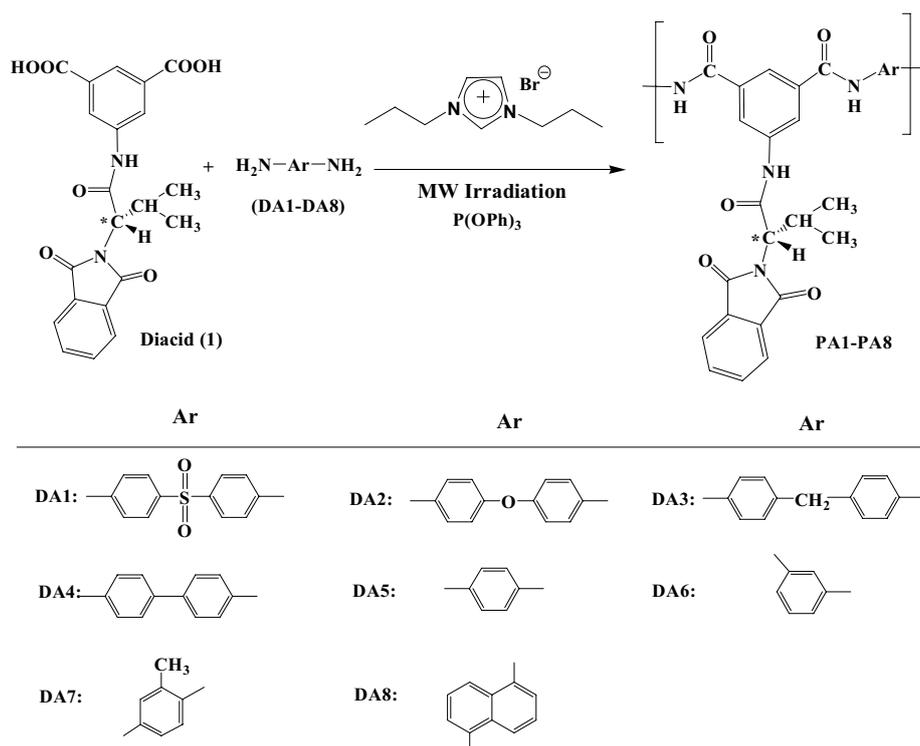
viscosity and yield was obtained when 1,3-dipropylimidazolium bromide used as IL for direct polycondensation (Table 1, PA1b). Therefore, 1,3-dipropylimidazolium bromide was selected for other polymerization. It is interesting to mention that, the polymers were not obtained in the absence of either ILs or TPP, so the presence of both components are necessary for polyamidation reactions, and consequently ILs play as a catalyst as well as solvent for these reactions. The amounts of ILs were used for each reaction is very low, so we did not recycle them. Otherwise, these ILs could be easily separate from resulting polymers and reused.

Polycondensation was carried out by varying different ILs types, amount of ILs, the duration of irradiation and power level of microwave instrument. The optimum conditions which were applied for polyamidation reaction in ILs are shown in Table 2.

ILs in conjunction with microwave irradiation was used for the direct polycondensation of dicarboxylic acid 1 with various diamines (Scheme I). In this method ILs in the presence of TPP promotes polyamidation reactions, and microwave irradiation was applied as a source of heating for rapid synthesis of PAs. The resulting PAs were obtained in good yields and had inherent viscosity values ranging

**Table 2.** Reaction conditions for polymerization in ILs.

Ionic liquid	
TPP/monomer (mmol/mmol)	2
Irradiation time (S)	50+20
Amount of ILs (g)	0.15
Power level	50% of power level
Non-solvent	MeOH



**Scheme I.** Direct polyamidation reactions of monomer 1 with aromatic diamines with ILs and TPP as activating media and microwave heating.

between 0.32-0.66 dLg<sup>-1</sup> (Table 3). The structure of PAs was confirmed by elemental analysis and FTIR and <sup>1</sup>H NMR spectroscopies.

The main advantages of this method of polymerization is that in this procedure, the volatile and toxic solvents such as *N*-methyl-2-pyrrolidone (NMP) and pyridine are not required to be used and the reaction

is eco-friendly and green. In addition, in this method, contrary to other classical polymerization techniques there was time saving as the polymers were obtained only in a few minutes. The other benefit of this method arises from the fact that; very short reaction time may minimize the polymer decomposition.

The incorporation of chiral unit into polymer back-

**Table 3.** Synthesis and some physical properties of PA1-PA8<sup>a</sup>.

Diamine	Polymer				
	Polymer	Yield (%)	$\eta_{inh}$ (dL/g) <sup>b</sup>	$[\alpha]_{Na,589}^{25,b}$	Colour
DA1	PA1b	87	0.60	-51.22	Yellow
DA2	PA2	78	0.41	-46.36	yellow
DA3	PA3	74	0.38	-24.40	Yellow
DA4	PA4	86	0.66	-36.12	Yellow
DA5	PA5	78	0.40	-18.78	Pale brown
DA6	PA6	83	0.38	-12.66	Yellow
DA7	PA7	76	0.32	-32.58	Pale brown
DA8	PA8	80	0.41	- <sup>c</sup>	brown

(<sup>a</sup>) All reactions were carried out under the conditions shown in Table 2; (<sup>b</sup>) Measured at a concentration of 0.5 g/dL in DMF at 25°C; (<sup>c</sup>) Not observed.

**Table 4.** Elemental analysis of PA1 and PA2.

Polymer code	Formula		Elemental analysis (%)			Moisture intake (%) <sup>a</sup>
			C	H	N	
PA1	C <sub>33</sub> H <sub>26</sub> N <sub>4</sub> O <sub>7</sub> S (622.15) <sub>n</sub>	Calcd	63.66	4.21	9.00	3.4
		Found	61.25	4.44	8.33	
		Corr <sup>b</sup>	63.34	4.28	8.61	
PA2	C <sub>33</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> (574.18) <sub>n</sub>	Calcd	68.98	4.56	9.75	2.3
		Found	67.18	4.69	9.30	
		Corr <sup>b</sup>	68.72	4.58	9.52	

(a) Moisture intake(%) =  $(W-W_0)/W_0 \times 100$ , W = weight of polymer sample after standing at room and  $W_0$  = weight of polymer sample after dried in vacuum at 100°C for 10 h.

(b) Corrected value for C, N and S = found value  $\times (100 + \text{moisture intake}) / 100$ , and corrected value for H = found value  $\times (100 - \text{moisture intake}) / 100$ .

bone was confirmed by measuring their specific rotation (Table 3). All of the PAs show optical rotation and therefore are optically active.

Elemental analysis data of two typical PAs are listed in the Table 4. The chemical structures of these newly synthesized polymers were confirmed by the good agreement of the elemental analysis values with those of the calculated values.

### Polymer Characterizations

#### FTIR study

The structures of these polymers were confirmed as PAs by means of FTIR spectroscopy. The FTIR spectra of all polymers showed absorptions around 3300  $\text{cm}^{-1}$  (N-H), 1765  $\text{cm}^{-1}$  (C=O asymmetric, imide), 1710  $\text{cm}^{-1}$  (C=O symmetric, imide), 1670  $\text{cm}^{-1}$  (C=O, amide). All these PAs exhibited absorption at 1380-1385  $\text{cm}^{-1}$  (C-N, imide) and 715-725  $\text{cm}^{-1}$  that show the presence of the imide heterocycle in these polymers. The PA1 showed characteristic absorptions at 1250, 1152  $\text{cm}^{-1}$  due to the sulphone moiety (SO<sub>2</sub> stretching).

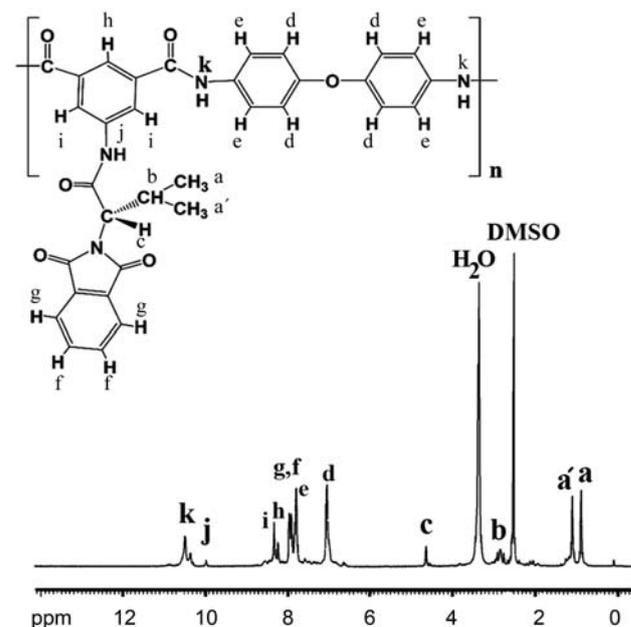
#### <sup>1</sup>H NMR Study

Figure 1 shows the <sup>1</sup>H NMR (500 MHz) spectrum of PA2 as a typical of PAs. In the <sup>1</sup>H NMR spectrum of this polymer, appearance of the two N-H protons of amide groups around 10.00-11.00 ppm indicate two different amide groups in the polymer chain. The absorption of aromatic protons appeared at a range of 7.00-8.50 ppm. The proton of the chiral centre

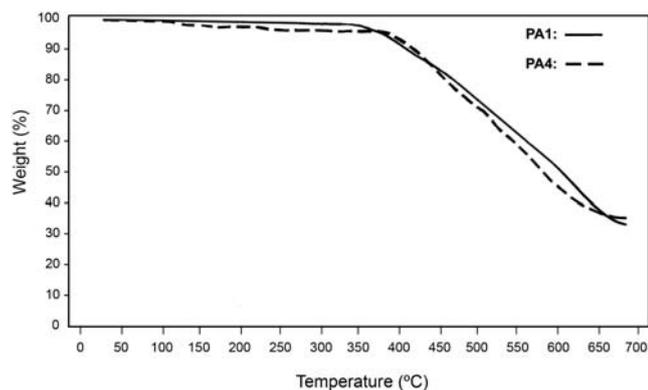
appeared at 4.63 ppm. The peak of C-H isopropyl group of *S*-valine appeared at 2.80 ppm as a multiple peak. The absorption of the two diastrotopic CH<sub>3</sub> protons groups of *S*-valine appeared around 1.00 and 1.15 ppm.

#### Solubility of the PAs

One of the objectives of this study was to produce modified PAs with enhanced solubility. The incorporation of bulky side groups into the monomer, reduces molecular packing, and restricts the formation of



**Figure 1.** <sup>1</sup>H NMR (500MHz) Spectrum of PA2 in DMSO-d<sub>6</sub> at room temperature.



**Figure 2.** TGA Thermograms of PA1 and PA4 under  $N_2$  atmosphere and a heating rate of  $10^\circ\text{C}/\text{min}$ .

interchain hydrogen bonds, which are responsible of the PAs intractability. Because of flexible bulky groups in polymer's pendant, these polymers are expected to have higher solubility. The solubility of PAs was tested at a concentration of 0.5 g/dL and at ambient temperature in various solvents. Almost all the PAs are soluble in organic polar aprotic solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide, dimethyl sulphoxide, NMP and polar protic solvent such as  $H_2SO_4$  at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

### Thermal Properties

Thermal gravimetric analysis (TGA) was used in order to study the thermal properties of PAs. The thermal stability of the polymers were assessed based on initial decomposition temperatures ( $T_i$ ), temperature of 5% ( $T_5$ ) and 10% ( $T_{10}$ ) weight loss together with

**Table 5.** Thermal properties of typical PAs.

Polymer code	$T_i^a$ (°C)	$T_5^b$ (°C)	$T_{10}^c$ (°C)	Char yield (%) <sup>d</sup>
PA1	344	380	414	53
PA4	363	383	421	44

(a) Initial decomposition temperature; (b) temperature at which 5% weight loss was recorded by TGA at heating rate of  $10^\circ\text{C}/\text{min}$  under  $N_2$  atmosphere; (c) temperature at which 10% weight loss was recorded by TGA at heating rate of  $10^\circ\text{C}/\text{min}$  under  $N_2$  atmosphere; (d) weight percent of the material left undecomposed after TGA at maximum temperature  $600^\circ\text{C}$  in a  $N_2$  atmosphere.

weight residue at  $600^\circ\text{C}$ . Figure 2 shows the TGA thermograms of PA1 and PA4, which indicate single step thermal degradation. Thermal behavior data of these polymers are listed in Table 5. The TGA measurement of the polymers show that these polymers exhibited good thermal stability.

The introduction of heat resistant phthalimide groups as well as the presence of imide and amide group may counter-balance any loss of thermal stability that may cause by the existence of flexible aliphatic group.

### CONCLUSION

In this work, the use of ILs in the presence of TPP in conjunction with microwave heating for direct polyamidation reaction of 5-(2-phthalimidyl-3-methylbutanoylamino)isophthalic acid (1) with various diamines are reported. The main advantages of this method of polycondensation reaction can be listed as follows: (1) no need of using volatile and toxic solvents such as NMP in this procedure, make it as an environmentally friendly and green method, (2) polymerization reactions take place in a few minutes and consequently may minimize polymer degradation and (3) this method is a one-pot reaction and we do not need to prepare diacid chloride and therefore, saves time and energy. Thermogravimetric analyses demonstrate that these PAs show high thermal stability. The resulting PAs have bulky pendent groups along the polymer backbone results in a less ordered polymer matrix, therefore disturbs the macromolecular rigidity, and consequently increasing the solubility characteristics. In addition, because of the existence of amino acid in the polymer pendant group these polymers are expected to be biodegradable and therefore are classified under environmentally friendly polymers. The resulting polymers are optically active and can be used as a chiral stationary phase in chromatography technique for the separation of chiral mixtures.

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