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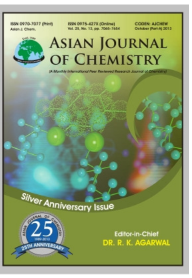

Synthesis, Characterization, Viscosity and Thermo Analytical Studies of Schiff Base Polymers Derived from 6,6-Methylene *bis*(1-napthaldehyde)

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Four new Schiff based polymers were synthesized from 6,6-methylene *bis*(1-napthaldehyde) through polycondensation of 6,6-methylene *bis*(1-napthaldehyde) with diamines 1,3-propylenediamine, 1,2- propylenediamine, ethylenediamine and urea in 1:1molar ratio. The monomer 6,6-methylene *bis*(1-napthaldehyde) was prepared by treating 6,6-methylene *bis*(1-napthaldehyde) with 1,3,5-trioxane in presence of H_2SO_4 and CH_3COOH, respectively. The polymers poly[6,6-methylene*bis*(1-napthaldehyde)1,2-propylenediimine] (PMBNPn), poly[6,6-methylene*bis*(1-napthaldehyde) 1,3-propylenediimine] (PMBNPR), poly[6,6-methylene*bis*(1-napthaldehyde)ethylenediimine] (PMBNen) and poly[6,6-methylene*bis*(1-napthaldehyde)urea (PMBNU), were soluble in few organic solvents. The structure of Schiff bases was confirmed by CHN, FTIR, UV-visible spectroscopy, TGA/DTA and viscosity measurements. The polymers showed shift in band position as compared to monomer, due to conversion of carbonyl to azomethine group and the increased values of reduced and intrinsic viscosities than the corresponding monomer attributed to the formation of polymers.

Key Words: Dialdehydes, Characterization, Viscosity studies, Thermoanalytical studies, Differential thermogravimetric studies.

INTRODUCTION

Synthesis of Schiff base polymers have always attracted the researchers due to their vast applications in different fields, such as medicine as antiamoebic agents and due to highly tensile and impact strength. Some advancement has been made to overcome their solubilities in limited solvents by inserting flexible bonding in aromatic rings[1-3].

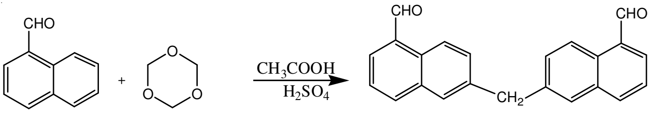
Schiff base polymers (SBPs) and their metal complexes have interesting properties due to their nature of binding toxic and heavy metal ions[4-7] and[8-15]. SBPs have thermal stability similar to polyimides and used in packed columns gas chromatography as solid stationary phase.The monomer 6,6-methylene *bis*(1-napthaldehyde) (MBN) is prepared by reported method of 5,5-methylene *bis*(salicylaldehyde) and 5,5-methylene *bis*(2-hydroxyacetophenone[2,16]. The present study reports the synthesis of four new Schiff base polymers by polycondensation of dialdehyde MBN with four diamines. PMBNPn, PMBNPR, PMBNen and PMBNU.

EXPERIMENTAL

Urea was recrystallized from ethyl alcohol. Glacial acetic acid (E-Merck,Germany), 1,3,5-trioxane, 1,3-propylenediamine,1,2- propylenediamine, ethylenediamine and Urea (Fluka, Switzerland) were used as received.

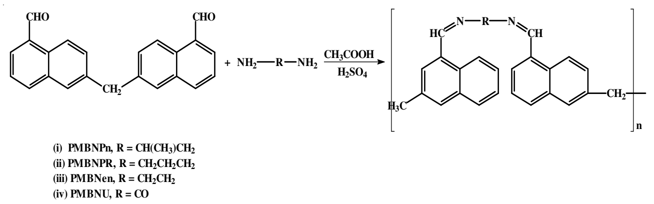
Synthesis of 6,6-methylene *bis*(1-napthaldehyde) (MBN): To a solution of (69 mL) 80 g of α-napthaldehyde and glacial acetic acid (50 mL) at 90-95 ºC was bubbled pure nitrogen gas to maintain inert atmosphere The solution was added dropwise Trioxane (7.0 g) dissolved in mixture containing (0.5 mL) conc. H_2SO_4 and (2.5 mL) glacial acetic acid. The temperature was maintained at 90-95 ºC with constant stirring till the completion of reaction. The mixture was added into 1 L of ice water and kept overnight, after 24 h the compound separated as oily layer. The product was added 10 % solution of sodium carbonate and stirring was continued till neutralized. The contents were left for precipitation. After 24 h the solid was filtered and boiled in acetone for 15-25 min then was filtered and dried in oven for 7-8 h at 60-70 ºC. Melting point observed was above 350 ºC [yield = 5 g, 62.5 %] **Scheme-I**.

Synthesis of poly 6,6-methylene *bis*(1-napthaldehyde) 1,2-propylenediimine (PMBNPn): The 6,6-methylene *bis*(1-napthaldehyde) (3.24 g) was added DMF (40-45 mL) and heated till the compound has completely dissolved. The hot solution was filtered and 1,2-propylenediimine (0.85 mL) was added to it. The reaction mixture was refluxed on hot plate for the period of 22-23 h. The mixture was concentrated and (45 mL) ethyl alcohol was added, light brown precipitates were



Scheme-I: Synthesis of monomer

observed, were filtered and finally washed with diethyl ether, acetone and distilled water. The decomposition point was observed as 392 ºC [yield = 3 g, 92.5 %] (**Scheme-II**).



Scheme-II: Synthesis of Schiff base polymers

Synthesis of poly 6,6-methylene *bis*(1-napthaldehyde) 1,3-propylenediimine (PMBNPR): The 6,6-methylene *bis*(1-napthaldehyde) (3.24 g) was added DMF (30-35 mL) and through constant stirring and heating the compound completely dissolved; 1,3-propylenediimine (0.842 mL) was added into the filtered hot solution of *bis*(1-napthaldehyde) and refluxed for (22-23) h. The mixture was concentrated and precipitation occurred due to addition of ethyl alcohol (25-30 mL), brownish precipitate were filtered and washed with di ethyl ether acetone and finally with distilled water. The decomposition point was observed as 389 ºC [yield = 2.5 g, 7.1 %] **Scheme-II**.

Synthesis of poly 6,6-methylene *bis*(1-napthaldehyde) ethylenediimine (PMBNen): The 6,6-methylene *bis*(1-napthaldehyde) (3.24 g) was dissolved in DMF (30-45 mL). Ethylenediimine (0.675 mL) was poured into filtered solution of *bis*(1-napthaldehyde). The reaction product was refluxed for the period of 22 h. The mixture was concentrated and (35-40 mL) ethyl alcohol was added, light brown precipitate recovered was filtered, washed with di ethylether, ethyl alcohol and distilled water. The compound decomposed at 390 ºC [yield = 2.5 g, 77.1 %] **Scheme-II**.

Synthesis of poly 6,6-methylene *bis*(1-napthaldehyde) urea (PMBNU): The 6,6- methylene *bis*(1- napthaldehyde) (3.24 g) was dissolved in DMF (30-45 mL) and heated till dissolved. hot solution was filtered, Urea (0.60 g), dissolved in DMF (4 mL)was added into it. The reaction mixture was refluxed for 22 h, product formed containing solvent was concentrated to its half volume till the appearance of light brownish precipitate, which were recovered after addition of 30 mL ethyl alcohol. Product was filtered,washed with acetone, diethylether and distilled water. The compound decomposed at 385 ºC] **Scheme-II**.

The elemental microanalysis was conducted at HEJ, research institute of chemistry, University of Karachi, Pakistan. The IR spectra were recorded on Nicolet Avatar 330 FT-IR (Thermo Nicolet Electron corporation USA) with Atanulated total reflectance (ATR) accessory smart partner ranging 4000-600 cm^{-1}. UV-visible spectrophotometric analysis was carried out in DMF on a double beam Hitachi 220 spectrophotometer (Hitachi (PVT) Tokyo, Japan, with dual 1 cm silica cuvettes within 185-700 nm. Thermogravimetry and differential thermogravimetric analysis was carried on Pyris DiamondTGA/DTA (Perkin-Elmer, Japan) analyzer from room temperature to 800 ºC with a nitrogen flow rate of 5 mL/min. 2 mg sample was placed each time in platinum crucible, recorded against alumina as reference with heating rate of 20 ºC/min.

The viscosity measurements of monomer and respective Schiff base polymers in DMF with 0.024-0.064g/dl with a temperature range from 283-323 K with a 10 K interval, using a suspended level viscometer (TechnoASTM 445).

RESULTS AND DISCUSSION

The dialdehyde 6,6-methylene *bis*(1-napthaldehyde) (MBN) was prepared by using the reported method for the preparation of 5,5-methylene *bis*(salicylaldehyde) and 5,5-methylene *bis*(2-hydroxyacetophenone)[2,16,17]. The structure of monomer was confirmed by elemental analysis. The results of elemental analysis correlated to the expected values (Table-1) and supports the formation of polymers. The monomer MBN was further condensed with four different diamines, namely 1,2-propylenediimine (PMBNPn), 1,3-propylenediimine (PMBNPR), (PMBNen) and (PMBNU), respectively. The results of elemental analysis of polymers PMBNPn, PMBNPR, PMBNen and PMBNU derived from MBN are in good aggrement with the expected values. Recrystallization of the Schiff base polymers was not accomplished due to their poor solubility in common organic solvents (Table-2). The FTIR of MBN indicate a strong characterstic peak of carbonyl stretch ν(C=O) vibrations at 1700 cm^{-1}. The peak in the respective polymers appeared as a weak band of low intensity due to end on group. The polymers PMBNPn, PMBNPR, PMBNen and PMBNU indicated a strong characteristic band with in 1660-1620 cm^{-1} due to ν(C=N) vibrations and support its formation. A band at 1720 cm^{-1} is observed for polymer PMBNU due to ν(C=O) group contributed from urea. The monomer and respective polymers indicated bands within 1440-1580 cm^{-1} due to ν(C=C) vibrations. A weak to medium intensity bands of CH vibration and ring breathing was observed between 1060-810 cm^{-1}, respectively (Fig. 1). The results of spectroscopic

TABLE-1
CHN ELEMENTAL MICROANALYSIS

Compounds	Calcd. (%)			Experimental (%)		
	C	H	N	C	H	N
6,6-Methylene *bis*(1-napthaldehyde) MBN	85.16	4.90	–	86.80	5.21	–
Poly6,6-methylene *bis*(1-napthaldehyde)1,2propylenediimine (PMBNPn)	86.20	5.60	7.80	86.16	5.25	6.99
Poly6,6-methylene *bis*(1-napthaldehyde)1,3propylenediimine (PMBNPR)	86.21	5.60	7.81	85.90	5.65	7.00
Poly6,6-methylene *bis*(1-napthaldehyde)ethylenediimine (PMBNen)	86.01	5.59	6.95	85.92	5.67	6.99
Poly6,6-methylene *bis*(1-napthaldehyde) UREA (PMBNU)	84.02	4.44	7.34	83.89	4.35	6.90

TABLE-2
Solubility (a, b) OF MBN AND SCHIFF BASE POLYMERS IN VARIOUS SOLVENTS

Compounds	H_2O	CH_3OH	C_2H_5OH	$CHCl_3$	Acetone	*n*-hexane	Ether	DMF
MBN	–	–	–	–	±	–	–	±
PMBNPn	–	–	–	±	±	–	–	±
PMBNPR	–	–	–	±	±	–	–	±
PMBNen	–	–	–	±	±	–	–	±
PMBNU	–	–	–	±	±	–	–	–

a: 0.05 g compounds in 10 mL solvent at 30 ºC, b: (+) soluble, (±) partially soluble, (–) insoluble.

studies in UV-visible region in DMF as a solvent are shown in (Table-3). The monomer MBN indicates three bands within 251-353 nm due to π-π^* transitions in benzenoid or napthyl ring systems and carbonyl π electrons with molar absorptivities 19011, 11890 and 7320 L mol^{-1} cm^{-1}. The polymers PMBNPn, PMBNPR, PMBNen and PMBNU in (Fig. 2) indicates four bands, a shift in band position and an origin of a new band as compared to monomer MBN, may be due to chromophores of conjugated azomethine, due to polycondensation.

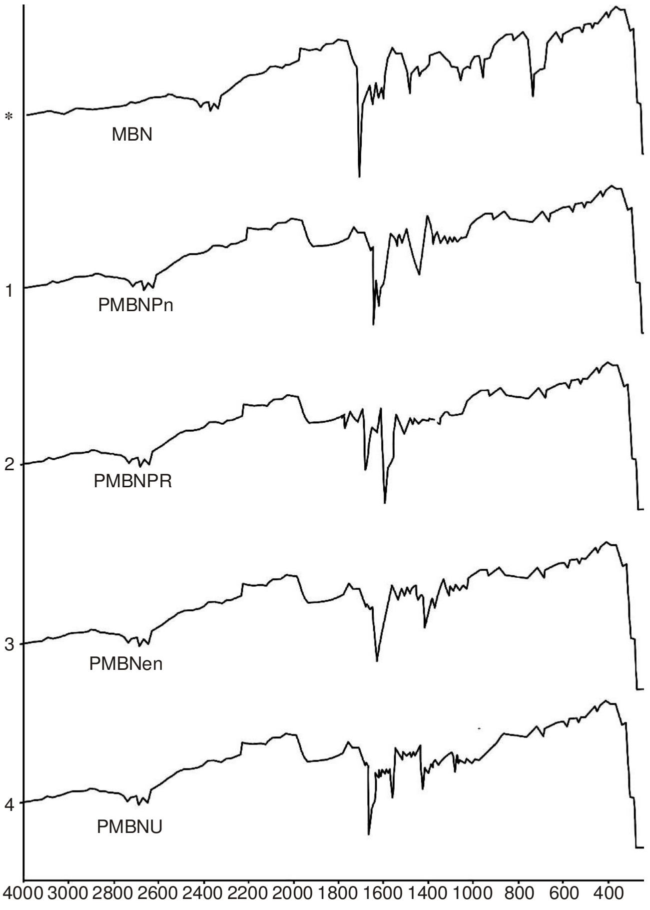


Fig. 1. FTIR analysis of MBN, PMBNen, PMBNPn, PMBNPR, PMBNU* MBN, 1 PMBNPn, 2 PMBNPR, 3 PMBNen, 4 PMBNU

For viscometric measurements, 15 mL solution was taken for all the runs and average flow time of three readings were noted, along with the flow time of solvent. To maintain and control the temperature Gallen kemp viscometer water bath was used. The reduced viscosity (η_{red}) was calculated by dividing specific viscosity (η_{sp}) by concentration in (g/dl). The intrinsic viscosity (η) was calculated from equation η_{red} = [η] + kH[η] 2C, the reduced viscosity was plotted against concentration and extrapolating to zero concentration. The polymers indicated higher values of intrinsic viscosity than the corresponding monomer MBN and are added point in its formation. All thermodynamic parameters of monomer as well as the polymers were calculated. Gibbs free energy (ΔG) was calculated by using eq. ΔG = 2.303RT log (η_{abs}/10-3), R is a gas constant and T is temperature. A plot between log ηabs and 1/T was linear. The heat of activation of viscous flow (ΔHv) were calculated from slope (slope × R). The entropy of activation of viscous flow (ΔSv), was calculated from equation (ΔGv) = ΔHv-TΔSv (Table-4).

TABLE-3
RESULTS OF SPECTROSCOPIC STUDIES IN DMF AS SOLVENT

Compound	λ_{max} nm (ε)
1. MBN	251 19011 L mol^{-1} cm^{-1} 315 11890 L mol^{-1} cm^{-1} 353 7320 L mol^{-1} cm^{-1}
	λ nm ε 1 %
2. PMBNU	257(289.2), 305(121), 395(121.75), 400(106.5)
3. PMBNPR	252(322.8), 309(213.3), 380 (111.4), 405(106.5)
4. PMBNen	261(299), 304(112.2), 370(77), 400(120.5)
5. PMBNPn	251(324.7), 314 (111.2), 370 (78), 410 (121.3)

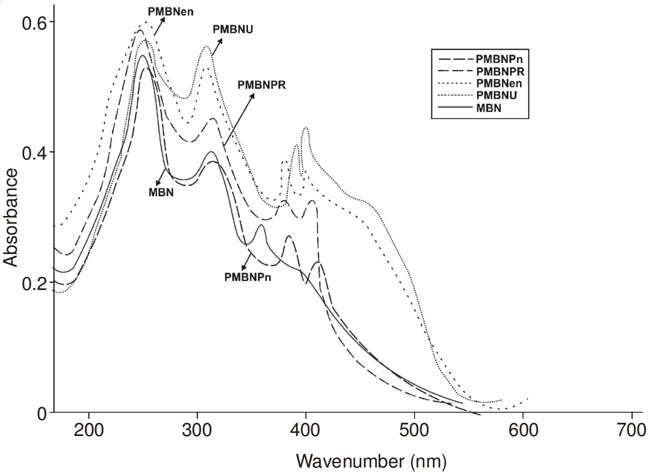


Fig. 2. UV-Visible spectra of PMBNen, PMBNPn, PMBNPR, PMBNU

TABLE-4
INTRINSIC VISCOSITY VALUES OF MONOMER (MBN) AND SCHIFF BASE POLYMERS (dl/g)

Compound	283	293	303	313	323
MBN	0.3000	0.2660	0.2410	0.2110	0.1940
PMBNU	0.4430	0.3810	0.3630	0.3420	0.3260
PMBNPR	0.4321	0.3995	0.3815	0.3720	0.3422
PMBNen	0.4111	0.3720	0.3510	0.3320	0.3200
PMBNPn	0.4554	0.4476	0.4332	0.4369	0.4320

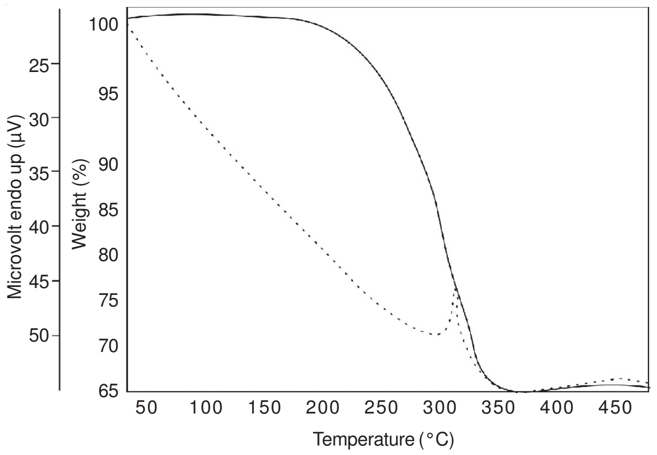


Fig. 3. TGA and DTA of MBN

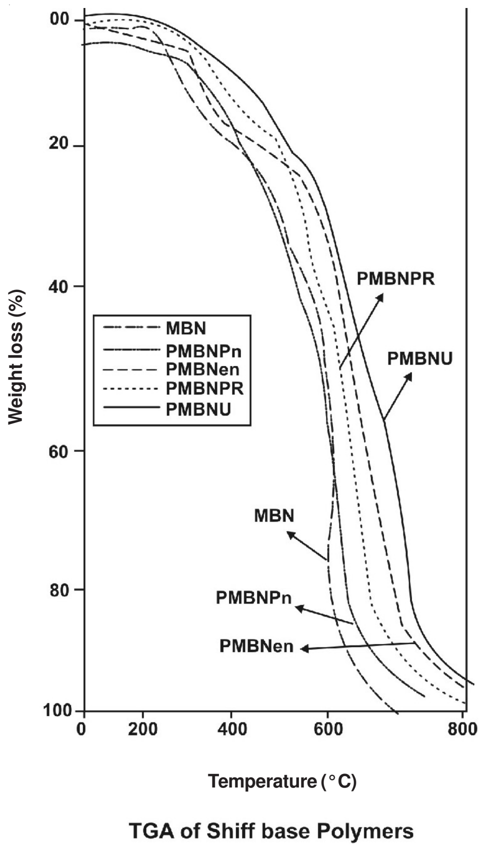


Fig. 4. TGA of PMBNen, PMBNPn, PMBNPR, PMBNU

The results of thermogravimetric (TG) analysis recorded, (Fig. 3) showed that for the monomer MBN, weight loss started at 200 ºC and 100 % loss was observed at 740 ºC and primary weight loss of 36 % was observed at 200-489 ºC, secondary weight loss of 27 % occurred within 489-595 ºC, tertiary weight loss of 33 % at 590-800 ºC, followed by maximum and rapid weight loss at 600 ºC (Table-5). The DTA of MBN indicated a strong well defined endotherm at 310 ºC and may be attributed to melting of the monomer. The TGA of polymer PMBNPR (Fig. 4) showed weight loss in three stages initial loss of 9 % within 240-255 ºC, secondary loss of 16 % within temperature range of 410-590 ºC, this is followed by rapid and total weight loss of 97 % upto temperature 800 ºC, with a maximum rate of loss by 679 ºC. The DTA 0f PMBNPR showed three endotherms first one at 189 ºC due to less quantity of solvent left in the sample and at 659 ºC and at 739 ºC which could be attributed to the decomposition of compound. The TGA of polymer PMBNU showed initial weight loss of 10 % between 235-288 ºC, secondary loss of 18 % within 478-548 ºC, followed by tertiary and total loss 100 % at 678 ºC with a maximum of rate of loss at 598 ºC. The DTA showed (Fig. 5) three endotherms at 178 ºC, due to loss of solvent second one at 259 ºC due to vaporisation, or voltalization and last at 659 ºC owing to its decomposition (Table-6). The TGA of polymer PMBNPn showed weight loss in three stages, initial weight loss of 11.5 % between 159-274 ºC secondary loss of 16.5 % between 378-399 ºC, followed by tertiary and total weight loss 97 % at 719 ºC with maximum rate of weight loss at 548 ºC. The DTA showed two endotherms, a weak endotherm at 149 ºC is due to less quantity of solvent left in sample and a sharp endothermal 594 ºC due to decomposition of polymer. The TGA of polymer

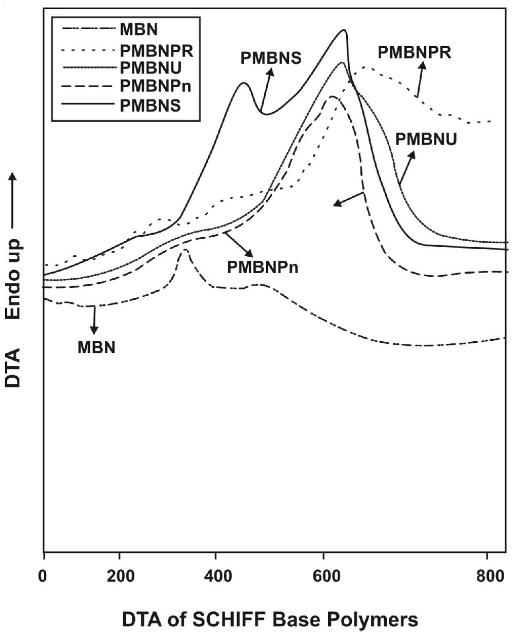


Fig. 5. DTA of PMBNen, PMBNPn, PMBNPR, PMBNU

TABLE-5
TGA ENDOTHERM

Characterization	MBN	PMBNU	PMBNPR	PMBNen	PMBNPn
1. Primary wt loss (%)	36	10	9	3.8	11.5
Temperature (ºC)	200-489	235-268	240-255	189-337	159-274
2. Sec wt loss (%)	27	18	16	_	16.5
Temperature (ºC)	489-595	479-548	410-590	–	378-399
3. Tertiary wt loss (%)	33	100	97	95	97
Temperature (ºC)	590-800	678	800	689	719
4.Max and rapid loss (ºC)	600	598	679	589	548

PMBNen showed weight loss in two stages primary loss of 3.8 % within temperature 189-337 ºC, followed by total loss of 95 % at 689 ºC with rapid loss at 589 ºC. The DTA of compound showed two endotherms first one at 359 ºC and a strong endotherm at 599 ºC was may be due to decomposition of polymer.

TABLE-6
DTA ENDOTHERM (ºC)

Characterization	MBN	PMBNU	PMBNPR	PMBNen	PMBNPn
	310	178	189	359	149
	–	259	659	599	594
	–	659	739	–	–

Conclusion

Four Schiff based polymers were synthesized by condensing these with monomer MBN, all were characterized through elemental microanalysis, FTIR, UV-visible, viscosity and thermodynamic parameters. The polymers showed less solubility in majority of organic solvents and that could be regarded as their major drawback. The polymers showed good thermal stability, which could be analyzed by observing their melting points.

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