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Synthesis, Characterization and Optical Properties of Poly(4,4'-dioctyloxy-3,3'-biphenylene vinylene) Copolymers

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A B S T R A C T

Iternating block copolymers of poly(4,4'-dioctyloxy-3,3'-biphenylene vinylene)alt-(1,4-naphthalene vinylene) (P1), poly(4,4'-dioctyloxy-3,3'-biphenylene vinylene)-alt-(1,5-naphthalene vinylene) (P2), poly(4,4'-dioctyloxy-3,3'-biphenylene vinylene)-alt-(2,6-naphthalene vinylene) (P3), poly(4,4'-dioctyloxy-3,3'-biphenylene vinylene)-alt-(9,9'-dioctyl-2,7-fluorenylene vinylene) (P4), and poly[(4,4'-dioctyloxy-3,3'-biphenylene vinylene)-alt-(1,2-bis(2-thienylethylene)-5,5'-vinylene)] (P5) were synthesized through Wittig polycondensation of aryl bis(methyl triphenylphosphonium) dibromide with aryl dialdehyde. The effect of positional isomers was studied using three naphthalene isomers, viz., 1,4, 1,5 and 2,6 linking positions, respectively. All the alternating copolymers showed good solubility in organic solvents. The synthesized polymers were characterized by GPC, ¹H NMR, FTIR and TGA. Thermal analysis of the polymers showed that they have thermal stability up to 250°C and their glass transition temperatures are around 50-70°C. The optical properties of the polymers both in solution and films were investigated. Optical studies of the polymers revealed that all the polymers except P5 had absorption maxima between 347 nm and 360 nm and emission maxima in the range 430-460 nm in solution whereas polymer P5 had absorption maxima at 452 nm and emission maxima at 515 nm. 4,4'-Dioctyloxy-3,3'biphenylene in the polymer backbone caused blue shift in optical properties compared with polymers having either of phenylene or 4,4'-biphenylene backbones. Optical properties of the polymers showed they are promising materials for opto-electronic devices, as well.

Key Words:

4,4'-dioctyloxy-3,3'-biphenylene; photoluminescence; naphthalene isomer; bisthiophene.

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INTRODUCTION

Over the past two decades, much research works have been focused on the synthesis of conjugated polymers due to their diverse applications in photo-voltaic devices [1], polymer light-emitting diodes (PLEDs) [2-4] and rechargeable batteries [5]. Their application in PLEDs, in particular, continues to receive considerable interest because of their easy processing, good mechanical property, flexible geometry and high efficiency. A variety of polymers with different backbone structures such as poly(phenylene vinylene) (PPV), poly(*p*-phenylene) (PPP), poly (naphthalene) (PN), poly(fluorene) (PF), poly(thiophene) (PT), and copolymers of poly(arylene) and poly(arylene vinylene) were synthesized through Wittig polycondensation and Gilch, Heck, Suzuki and Yamamoto coupling reactions [4, 6-13]. The shortcomings in the use of conjugated polymers for applications as PLEDs are the low color purity, short life time and low quantum efficiency in the solid state. Many efforts have been made to improve these characteristics.

The low quantum efficiency and red shifted emission wavelength in the solid state are due to the presence of interchain π - π interactions of polymers arising mainly from aggregation, excimer formation and poloron formation [14-16]. One approach to minimize interactions is to introduce bulky substituents to limit close vicinities between aromatic chromophores [17]. Another approach is to enhance structural asymmetry by introducing meta-linkages in the main chains of the conjugated polymers [18].

Polymers containing biphenyl moieties limit or preclude effective π stacking by twisting as compared to linear conjugated polymers [19-20]. Poly(4,4'biphenylene vinylene) system has structure that is intermediate between PPV and PPP. It is, therefore, expected that the poly(4,4'-biphenylene vinylene) would show optical properties intermediate between those of PPV and PPP.

Although polymers with 4,4'-biphenylene groups are reported [21-23], their low solubility has been an impediment to be used in optoelectronic devices [24-25]. Therefore, biphenylene polymers with substituted alkyl chain were synthesized and investigated by Karaz et al. [26].

Polynaphthalene vinylenes are another class of conjugated polymers with photoluminescent properties whose applicability is limited by low solubility [27,28]. The problem of low solubility was addressed by use of alkyl, alkoxy side chain-substituted polynaphthalenes or naphthalene copolymers with aromatic substituents, e.g., 1,4-dioctyloxy benzene [29].

In this work, we describe the synthesis and characterization of (1) 4,4'-dioctyloxy biphenyl-3,3'dicarboxaldehyde and (2) new alternating block copolymers having 4,4'-dioctyloxy biphenylene vinylene with aromatic moieties such as fluorene, bisthiophene and naphthalene as building blocks. The linking position of 3,3'-biphenylene vinylene makes the polymer exhibit lower emission maxima compared to 4,4'-biphenylene vinylene system. The alternating copolymers were synthesized by Wittig polycondensation and their physical and optical properties were studied. The changes in their quantum efficiency and emission maxima were studied as a function of the position of naphthalene linkage, namely: 1,4, 1,5 and 2,6 positional isomers of naphthalene.

EXPERIMENTAL

Materials and Methods

4,4'-Dihydroxy biphenyl, dimethyl naphthalene isomers, 1-bromo octane, fluorene and thiophene 2carbaldehyde were purchased from Sigma-Aldrich, India Pvt Ltd., India. All solvents (Sisco Research, India) and hydrogen peroxide (Merck, India) were used as they were purchased. Procedures reported in the literature were adopted for the synthesis of compounds M1-M3 [29], M4 and M5 [30].

Synthesis of 4,4'-Dioctyloxy-1,1'-biphenyl (DOBP)

A 250 mL round bottom flask was charged with 4,4'dihydroxy biphenyl (9.3 g, 50 mmol) in 150 mL butanol. Sodium hydroxide (4.4 g, 110 mmol) was added to this mixture and stirred well for 30 min. Then, 1-bromooctane (19.14 mL, 110 mmol) was added and the mixture was refluxed under stirring for 24 h. The content was cooled and filtered to obtain the required product which was subsequently crystallized from methanol as white flakes (85% yield).

¹H NMR (CDCl₃) δ (ppm): 7.46-7.50 (d, J = 8.4 Hz, 4H), 6.94-6.97 (d, J = 8.4 Hz, 4H), 4.0 (t, J = 6.4 Hz, 4H), 1.8 (m, 4H), 1.4-1.5 (m, 4H), 1.3 (m, 16H), and 0.9 (t, J = 6.4, 6H).

¹³C NMR (CDCl₃) δ (ppm): 156.31, 127.36, 126.72, 114.44, 67.81, 31.56, 29.10, 29.02, 28.96, 25.79, 22.40, and 13.81.

Synthesis of 3,3'-Bis(bromomethyl)-4,4'-dioctyloxy-1,1'-biphenyl (BBDOBP)

A sample of 4,4'-dioctyloxy-1,1'-biphenyl (DOBP, 8.21 g, 20 mmol) was dissolved in 100 mL of acetic acid in a 250 mL RB flask. Paraformaldehyde (6 g, 200 mmol) was added to the solution and stirred well.

It was then followed by dropwise addition of hydrobromic acid (8 mL, 47%) in 100 mL acetic acid. The mixture was refluxed for 24 h and then cooled. It was poured into cold water and filtered to obtain a whitish yellow powder. The product was further purified by repeated washing with a sodium bicarbonate solution and crystallized in acetone to produce pure 3,3'-bis(bromomethyl)-4,4'-bis(octyloxy) biphenyl (70% yield).

¹H NMR (CDCl₃) δ (ppm): 7.51 (d, J = 2.4 Hz, 2H), 7.45 (dd, J = 2.4 Hz, J = 8.4, 2H), 6.90-6.92 (d, J = 8.4, 2H), 4.63 (s, 4H), 4.05-4.08 (t, J = 6.4 Hz, 4H), 1.83-1.90 (m, 4H), 1.50-1.57 (m, 4H), 1.31-1.37 (m, 16H), and 0.90-0.92 (t, 6.4 Hz, 6H).

¹³C NMR (CDCl₃) δ (ppm): 155.91, 132.45, 128.81, 127.94, 126.20, 111.77, 68.13, 31.58, 29.05, 28.99, 28.92, 25.82, 22.40, and 13.87.

Synthesis of 4,4'-Dioctyloxy-1,1'-biphenyl-3,3'bis(methyl triphenyl phosphonium) Salt (DOBPBMTP)

A sample of BBDOBP (5.97 g, 10 mmol) was dissolved in 100 mL DMF. Triphenyl phosphine (5.77 g, 22 mmol) was added to the mixture and refluxed overnight. DMF was evaporated and the residue was washed with diethyl ether to obtain a white powder as the product (yield 85%).

¹H NMR (CDCl₃) δ (ppm): 7.62-7.80 (m, 32H), 7.25-7.27 (d, J = 8.4 Hz, 2H), 6.63-6.64 (d, J = 8.4 Hz, 2H), 5.1 (d, J = 13.6 Hz, 2H), 3.3-3.4(t, J = 6.4 Hz, 4H), 2.1 (m, 4H), 1.2-1.35 (m, 20H), and 0.9-0.93 (t, J = 6.4 Hz, 6H).

Synthesis of 4,4'-Dioctyloxy-1,1'-biphenyl-3,3'dialdehyde (DOBPDA)

A sample of BBDOBP (5.97 g, 10 mmol) was dissolved in 100 mL of ethanol in a 200 mL RB flask, and hydrogen peroxide (20 mL, 30%) was added as an oxidizing agent and the solution was refluxed for 24 h. Ethanol was evaporated and the product was crystallized in acetone to give a white powder with 45% yield.

¹H NMR (CDCl₃) δ (ppm): 10.55 (s, 2H), 8.04 (s, 2H), 7.76-7.79 (dd, J = 2.4 Hz, J = 8.4 Hz, 2H), 7.01-7.07 (d, J = 8.4, 2H), 4.11-4.15 (t, J = 6.4 Hz, 4H), 1.84-1.91 (m, 4H), 1.47-1.55 (m, 4H), 1.30-1.37 (m, 16H), and 0.88-0.92 (t, J = 6.4 Hz, 6H).

¹³C NMR (CDCl₃) δ (ppm): 189.54, 160.66, 133.63, 131.65, 125.59, 124.60, 112.83, 68.49, 31.51, 29.02, 28.94, 28.79, 25.77, 22.37, and 13.83.

Preparation of Naphthalene 1,5-bis(methyl triphenyl phosphonium) dibromide

The procedures for the preparation of 1,4-*bis*(methyl triphenyl phosphonium) dibromide, and their 1,5 and 2,6 isomers were conducted as described in our earlier paper [29].

General Procedure for Wittig Reaction

Wittig polycondensation method was used for the synthesis of the polymers P1-P5 as shown in Scheme I. Dialdehyde (1 mmol) and triphenyl phosphine salt (1 mmol) was dissolved in anhydrous THF in a 200 mL RB flask. Freshly prepared sodium ethoxide (10 mL) was added dropwise to the solution and refluxed with stirring under nitrogen atmosphere for 48 h. The solvent was evaporated to a minimum volume and the content was poured into 100 mL of methanol to obtain a powdery precipitate of the polymer. The polymer was purified by the repeated dissolution in THF and precipitation using methanol.

P1: Poly[(4,4'-dioctyloxy-3,3'-biphenylenevinylene)*alt*-(1,4-naphthalene vinylene)]

¹H NMR (CDCl₃) δ (ppm): 6.8-8.2 (br), 3.8-4.1 (br), 0.9-1.9 (br).

P2: Poly[(4,4'-dioctyloxy-3,3'-biphenylenevinylene)*alt*-(1,5-naphthalene vinylene)] ¹H NMR (CDCl₃) δ (ppm): 6.7-8.2 (br), 3.8-4.1 (br), 0.9-1.9 (br).

P3: Poly[(4,4'-dioctyloxy-3,3'-biphenylenevinylene)*alt*-(2,6-naphthalene vinylene)] ¹H NMR (CDCl₃) δ (ppm): 6.7-7.9 (br), 3.9-4.1 (br), 0.8-1.9 (br).

P4: Poly[(4,4'-dioctyloxy-3,3'-biphenylenevinylene)*alt*-(9,9'-dioctyl-2,7-fluorenylene vinylene)] ¹H NMR (CDCl₃) δ (ppm): 6.7-7.8 (br), 4.0 (br), 0.48-1.9 (br).

P5: Poly[(4,4'-dioctyloxy-3,3'-biphenylenevinylene)*alt*-(1,2-bis(2-thienylethylene)-5,5'-vinylene)]





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¹H NMR (CDCl₃) δ (ppm): 7.6-7.7 (br), 7.3-7.4 (br), 6.8-7.0 (br), 4.0 (br), 1.3-1.9 (br), 0.9 (br).

Methods of Analysis

Thermogravimetric analysis (TGA) of alternating copolymers was carried out using a thermal analyzer instrument (SDT Q600, TA Instruments, USA) at a heating rate of 20°C/min in nitrogen. FTIR spectra of the polymers and the monomers were recorded using a Bruker spectrophotometer (Tensor 27, USA). ¹H NMR spectra of the monomers as well as the polymers were measured by a 400 MHz multiprobe Bruker spectrometer (USA) using CDCl₃ as solvent and TMS as internal standard. The optical absorption spectra of the polymer samples were recorded in THF solution using Varian Cary 500 UV-Vis-NIR spectrophotometer, USA. The PL emission and excitation spectral data were obtained using a Varian Cary eclipse fluorescence spectrophotometer, USA. The molecular weights of the synthesized polymers

were measured by gel permeation chromatography (GPC) using a Shimadzu HPLC-GPC system (LC-20AD, Japan). Polystyrene was used as the calibration standard and THF was used as the solvent for the measurement.

RESULTS AND DISCUSSION

The synthesis of the precursors is shown in Scheme II. Alkylation of 4,4'-dihydroxy biphenyl was carried out with sodium hydroxide as the base in 1-butanol using 1-bromo-octane as alkylation agent. The 4,4'-dioctyloxy biphenyl was then bromo-methylated with (HCHO)_n/AcOH and HBr/AcOH to obtain product 2 with 70% yield. Oxidation of bromo-methyl group into aldehyde was achieved using hydrogen peroxide as an oxidizing agent and ethanol as a solvent. During the course of reaction, the completion of formation of dialdehyde was confirmed by TLC. Excess addition







Figure 1. ¹H NMR Spectrum of DOBPDA.

of hydrogen peroxide and impurities in the bromo-methyl compound was found to decrease the yield of the product. The formation of dialdehyde was confirmed by ¹H NMR and ¹³C NMR. The disappearance of the peak at 4.63 ppm (-CH₂Br) and

the appearance of a singlet at 10.55 ppm corresponding to -CHO in ¹H NMR spectrum of the dialdehyde (Figure 1) are indications of the conversion of -CH₂Br to -CHO. The ¹³C NMR spectrum of dialdehyde is shown in Figure 2 where the





Polymer	$\overline{M_n} \times 10^3 *$	$\overline{\mathrm{M}_{\mathrm{w}}}$ ×10 ³ *	PDI	T _g (°C)	Residue (%) at 800°C
P1	2.197	2.849	1.29	67	10.9
P2	3.527	5.642	1.59	62	8.4
P3	2.881	3.421	1.19	65	18.9
P4	3.109	3.689	1.19	73	7.8
P5	3.460	5.436	1.57	49	5.3

Table 1. Physical properties of the polymers.

(*) Polystyrene was taken as the standard.

appearance of a new peak at 189.54 ppm confirms the formation of the dialdehyde.

Polymerization was carried out using the dialdehyde and the corresponding bis(methyltriphenyl phosphonium) dibromide in THF using NaOEt as a base. The initiation of the polymerization reaction was through the formation of the 'ylide' as seen from the formation of a blue colour in the reaction mixture. The colour disappeared immediately due to the reaction of the 'ylide' with the -CHO functional groups.

The number and weight average molecular weights of the alternating copolymers were determined by GPC using polystyrene standards and THF as the solvent. The weight average molecular weights of the alternating copolymers were found to be in the range of 3000-5000 Da. The low molecular weights of these polymers may be due to the



The thermal stability of the polymers was characterized by TGA (Figure 3). It was found that all the polymers are thermally stable up to 250°C. Two fragmental decompositions could be observed, the first by the loss of alkyl chains and the other due to degradation of the main chain of the polymers. Polymer P5 has a lower decomposition temperature compared to other samples, which may be ascribed to the bisthiophene part of the molecule.

DSC data show that the glass transition temperatures of the polymers lie between 50-70°C. P5 has the lowest T_g (49°C) while P4 has the highest





Figure 3. TGA Plots of of polymers P1-P5 in nitrogen atmosphere.

Figure 4. FTIR Spectrum of polymer P4 in KBr.

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Figure 5. ¹H NMR Spectrum of polymer P5.

(73°C). The generally low T_g values of these polymers are due to the presence of long alkyl chains in the biphenyl backbone. Values of the T_g and the percentages of residue at 800°C are presented in Table 1.

The FTIR spectrum of the polymer P4 (Figure 4) shows -CH vibrations at 3018 cm⁻¹ (aromatic), 2923 cm⁻¹ and 2856 cm⁻¹ (aliphatic). Absorption signals at 1607 cm⁻¹ (*trans* CH=CH stretching mode) and 965 cm⁻¹ (*trans* CH=CH out-of-plane deforming mode) reveal the formation of the polymer.

¹H NMR spectrum of polymer P5 is shown in Figure 5. The broadening of peaks and the absence of the aldehydic peak at 10.5 ppm in the ¹H NMR spectra of the polymers imply completion of polymerization.

The optical absorption spectra of the polymers (P1-P5) are presented in Figure 6. It can be seen that P1, P2 and P3 absorb at 348, 357 and 359 nm, respectively, suggesting that there is no significant shift in the absorption maxima. The absorption maxima of P4 and P5 lie around 347 and 452 nm, respectively. It may be noted that the polymers P1-P3 have biphenylene vinylene naphthalene building blocks with varying positional linkages of the naphthalene segments, ca., 1,4, 1,5 and 2,6. P4 is a biphenylene

fluorene vinylene system and P5 is a biphenylene bisthiophene vinylene system. Hence, it is inferred that the absorption maxima depend on the nature of the copolymer block. Naphthalene and fluorene systems are similar to each other, and hence the absorption maxima are in the same range, with marginal blue shifts for the biphenylene fluorene system.



Figure 6. Absorbance spectra of polymers in solution (solvent: THF).

Polymer	λ _{max} soln (nm)	λ _{max} film (nm)	λ _{emi} soln (nm)	λ _{emi} soln (nm)	Φ^{f} *soln
P1	348	348	463	511	0.180
P2	357	358	435	468	0.340
P3	359	359	428	470	0.330
P4	347	379	430	562	0.300
P5	452	509	515	573	0.036

Table 2. Optical properties of the polymers.

(*) Quinine sulphate in sulphuric acid was taken as the standard (Φ^{f} = 0.546).

The common building unit in all the polymers is 4,4'-dioctyloxy-3,3'-biphenylene group. It is worthy to note that the linking or the polymer chain originates from the 3,3'-position of the biphenyl system. These positions are strained as compared to the 4,4'-linking positions of the biphenyl or the phenylene systems.

The optical spectra of the spin-coated thin films were recorded. In the case of P1-P3, there is no significant change in the absorption maxima (Table 2) in transition from solution state to film form. However, in the case of P4 the absorption maximum is red shifted to 379 nm (a 32 nm shift), while in the case of P5 film it shifts to 509 nm (a 57 nm shift). The extended red shift in the absorption maxima for the films may be due to the long alkyl chain in P4 and the additional vinylene group in P5. This may result in aggregation in the thin film. However, in the case of the biphenylene naphthalene system, such interactions may not be so effective, which means that no significant change is expected in the absorption maxima of the polymer.

The photoluminescence spectra of the polymers in solution states and thin film forms are shown in Figures 7 and 8. In solution all the polymers except P5 emit blue-green light whereas P5 emits orange light. Figure 7 shows the photoluminescence spectra of naphthalene positional polymers P1-P3 in both solution state and thin films. The effect of the position of the naphthalene linkage on the emission behaviour



Figure 7. Photoluminescence emission spectra of polymers: P1, P2, P3 in solution and P1', P2', P3' in thin film forms.



Figure 8. Photoluminescence emission spectra of polymers: P1, P4, P5 in solution and P1', P4', P5' in thin film forms.

was studied. From Figure 7 it can be seen that while P1 and P2 show emission maxima at 463 and 435 nm, respectively, P3 shows blue shift to 428 nm in its emission maximum.

As compared to P2 ($\lambda_{emi} = 435$ nm), P3 was 7 nm blue shifted and P1 was 28 nm red shifted, suggesting that electronic structure and strain in polymer chains affect photophysical properties. It is clear that P3, with a 2,6-linked naphthalene, is less conjugated because of its poor π -electron delocalization as compared to P1 and P2 [34]. The emission maxima of polymers in thin film form are red shifted from the values in their solution states. This red shift is attributed to long side chains in each polymer backbone that enhances inter-chain interactions in polymer thin films.

Figure 8 shows the photoluminescence spectra of polymers P1, P4 and P5 in solution state and film form. If one considers the effect of aromatic moieties, P1 (with the naphthalene moieties) and P4 (with the fluorene moieties) give light emission in the same range, 430-460 nm, but P5 (with the bisthiophene moieties) gives an orange emission ($\lambda_{emi} = 515$ nm) in solution. The red shift in the emission maxima of P5, as compared with P1 and P4, is due to the long conjugation path of the bisthiophene polymer. All the polymers showed red shifted emission maxima in thin film forms due to long side chains in the polymere.

The polymer P4 shows absorption at 347 nm and emission at 430 and 562 nm in the solution state and film form, respectively. It is worth comparing the optical properties of P4 with those of poly(phenylene vinylene fluorene vinylene) and poly(biphenylene vinylene fluorene vinylene). Recently, Mikroyannidis et al. reported the synthesis of alternating polyfluorene vinylenes with phenylene and biphenylene segments by Heck coupling reaction [35]. According to these workers, poly(4,4'-biphenylene vinylene fluorene vinylene) absorbs at 371 nm and shows emission at 454 and 462 nm, respectively, in solution and film forms [35].

Poly(*p*-phenylene vinylene fluorene vinylene) absorbs at 378 nm and displays emission maxima at 464 and 474 nm in solution and thin film, respectively. The blue shifted absorption, emissions in solution and film forms of poly(4,4'-biphenylene vinylene fluorene vinylene) in comparison with poly(*p*-phenylene vinylene fluorene vinylene) is due to insertion of biphenyl that disrupts π conjugation by its non-planar and twisted structure. The blue shift in absorption and emission of P4 as compared to poly(4,4'-biphenylene vinylene fluorene vinylene) is caused by meta linkage of biphenylene which further decreases the conjugation path of the polymer. Moreover, the profound red shift in the emission maxima of P4 thin film at 562 nm is due to aggregation of P4 in film form brought about by the longer alkyl chain.

The polymer P5 has absorption at 452 nm and its solution state and film form emissions are at 515 and 573 nm, respectively. The red-shifted absorption and emission of P5 as compared to P1-P4 are due to the 2,5-linking positions of thiophene in the bisthiophene moieties which also contribute to the lower quantum efficiency of P5 [30]. Aggregation in thin film results in close proximity of polymer inter-chains that may enhance the deactivation of the excitons by decreasing the emission efficiency [36]. As compared to the planar poly(*p*-phenylene vinylene), the other, more rigid biphenylene vinylene shows lower quantum yield. The twisted conformation of the polymer chains should favour non-radiative relaxation processes in solution [26].

CONCLUSION

The synthesis of 4,4'-dioctyloxy biphenyl 3,3'dialdehyde was carried out by conversion of bromomethyl group to aldehyde in the presence of hydrogen peroxide and a series of polymers having 4,4'-substituted 3,3'-biphenylene with different aromatic moieties, viz., naphthalene, fluorene and bisthiophene. The effects aromatic moieties in the polymer backbone as well as linking positions were characterized by polymers' optical properties. Insertion of 4,4'-biphenyl in the polymer chain leads to a blue shift in emission. This shift is more pronounced if the linkage is made through the 3,3'- position. However, this linkage introduces strain in the system and leads to a red shift in thin film form of the polymer. Photophysical properties of the polymers reveal that they are promising materials for PLED.

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