Liquid crystalline polyacetylenes: a new class of mesomorphic materials with novel optical and electronic properties

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ABSTRACT

A large number (more than 20 different kinds) of new polyacetylenes with general molecular structures of $-\text{[HC=C(C}_6\text{H}_4\text{-mesogen)]}_p-$ [poly(arylacetylene) type] and $-\text{[HC=C[(CH}_2\text{)}_n\text{-mesogen)]}_p-$ [poly(alkylacetylene) type] are designed and synthesized. Pendant interaction and backbone rigidity in the polymers are tuned through systematic molecular engineering endeavor, and liquid crystalline polyacetylenes (LCPAs) with novel mesomorphic, optical, and electronic properties are successfully developed. The rigid polyacetylene backbones enable ready alignments of the LCPA molecules by simple mechanical perturbations. Upon photoexcitation, the LCPAs with the poly(alkylacetylene) skeleton structure emit strong blue light clearly observable by naked eyes under normal room illumination conditions. The shape and position of the emission peaks and the color of the emitted light can be manipulated by the application of external electrical fields. The LCPAs exhibit excellent intrinsic photoconductivity in the visible spectral region in the undoped (pure) states, and doping with electron acceptor/donor further increases the photoconduction efficiency of the LCPAs.

Keywords: Side-chain liquid crystalline polymers, polyacetylenes, poly(alkynes), poly(phenylacetylenes), mesomorphism, molecular alignment, luminescence, electrical field, photoconductivity, doping, optical and electronic materials.

1. INTRODUCTION

Polyacetylene is a prototypical conjugated polymer and liquid crystals are widely used in modern optical display systems. The development of liquid crystalline polyacetylenes (LCPAs) is of interest because the polymers may possess unique mesomorphic, optical, and electronic properties. The LCPAs, for example, may be macroscopically alignable, optically nonlinear, electrically conductive, and light emissive.

The alternating-double-bond polyacetylene backbone is, however, quite rigid. In the community of liquid crystal research, a rigid polymer backbone is generally regarded as a defect that distorts the packing arrangements of mesogenic pendants in a side-chain liquid crystalline polymer (SCLCP).¹⁻⁴ The standard recipe for designing molecular architecture of a SCLCP given in liquid crystal textbooks is "flexible backbone + spacer + mesogenic group". The SCLCPs with flexible backbones have attracted much interest, but those with rigid backbones have received little attention. Compared to the vast variety of flexible-chain SCLCPs, few of stiff-chain SCLCPs have been developed and their preparations are often for the purpose of giving comparative examples to demonstrate destructive roles of the rigid backbones.

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We have launched a research program with the aim of developing "non-conventional" SCLCPs with rigid conjugated polymer backbones. In this report, we present our recent work on the development of a group of new SCLCPs with novel mesomorphic, optical, and electronic properties originated from their unique molecular structures: conjugated backbone + mesogenic pendant.

2. MOLECULAR DESIGN AND MATERIALS PREPARATION

We first prepared a group of poly(phenylacetylene) (PPA) derivatives containing long methylene spacers and polar cyanobiphenyl mesogens (1; Chart 1) using organorhodium complexes of general structure $\text{Rh}(\text{diene})\text{L}_x$ as polymerization catalysts.^{4,5} The polymers possess high stereoregularity with a predominant *cis* conformation. Unfortunately, however, the polymers show no mesomorphic properties. The non-mesomorphism of **1** may stem from (1) the strong electronic interaction between the cyanobiphenyl mesogens and (2) the high rigidity of the PPA backbones.

Chart 1

To tackle the problem (1), we tried to tune the electronic interaction of the mesogenic pendants. Strong electronic interaction favors direct crystallization from isotropic liquid, and replacing the highly polar cyano tail with a less polar heptoxy group may allow liquid crystalline mesophases to form. The long alkoxy tail may also act as an internal plasticizer, enabling the mesogens to move together and to align along certain direction. We thus designed and synthesized a PPA with heptoxybiphenyl mesogens (**2**). The approach works: **2** undergoes a mesomorphic transition and shows smectic A mesophase at $\sim 130^\circ\text{C}$.

To tackle the problem (2), we tried to fine-tune the rigidity of the polyacetylene backbone. The polyacetylene backbones consisting of alternating double bonds are much more rigid than the polyolefin backbones consisting of single bonds. This, however, does not mean that the stiffness of the polyacetylene main chains cannot be manipulated by varying the kinds of the substituent pendants, as commonly practiced in the molecular design of vinyl-polymer-type liquid crystals. For example, although poly(1-chloro-1-octyne) $\{-(\text{ClC}=\text{C}(n\text{-C}_6\text{H}_{13}))_p\}$ and poly(1-chloro-2-phenylacetylene) $\{-(\text{ClC}=\text{CPh})_p\}$ have the same number of carbon atoms in the repeat units (i.e., 8), the glass transition temperature of the former (150°C) is lower than that of the latter ($>200^\circ\text{C}$),⁶ suggesting that the backbone of a polyacetylene containing an alkyl (aliphatic) substituent is somewhat less rigid than that of a polyacetylene containing a phenyl (aromatic) substituent.

We thus tried to replace the phenyl group of the phenylacetylene unit in **1** with alkyl groups. We designed and synthesized a group of alkylacetylene monomers with the cyanobiphenyl mesogens directly attached to the acetylene triple bonds through methylenic spacers, instead of through the phenyl rings. We developed an effective polymerization catalyst system

of $\text{WCl}_6\text{-Ph}_4\text{Sn/dioxane}$ and successfully obtained high molecular weight polymers **3** in good yields. The polymers are mesomorphic, with the longer flexible spacer favoring better ordering of the mesogenic groups. The LCPA with a spacer of 8 methylene units displays enantiotropic smecticity with an interdigitated molecular packing arrangement over a wide temperature range ($\sim 110^\circ\text{C}$).

3. INDUCED MOLECULAR ALIGNMENT

We further systematically designed and prepared a series of mesogen-containing poly(alkylacetylenes) of general structure of $-\{\text{HC}=\text{C}[(\text{CH}_2)_n\text{-mesogen}]\}_p-$ (Chart 2). All the polymers are liquid crystalline. The difference between the LCPAs and the "conventional" vinyl-polymer-type SCLCPs is the rigidity of the polymer backbones. The stiff polyacetylene backbone possesses quite a long relaxation time; for example, the chain conformation frozen by the solvent evaporation during the preparation of poly[1-(trimethylsilyl)-1-propyne] films needs more than two (2) weeks to relax back to the most probable conformation.⁷ Thus a mechanically agitated polyacetylene system with a proper viscosity may not quickly return back to the pre-perturbation state, offering the opportunity to generate macroscopic sample anisotropy by the application of mechanical forces. It is of academic interest and practical significance to modulate the molecular alignments of liquid crystalline polymers by external forces and we thus examined the mesomorphic responses of the LCPAs to mechanical perturbations.

Chart 2

$\begin{array}{c} \text{---}[\text{HC}=\text{C}]_p\text{---} \\ \\ (\text{CH}_2)_n \text{---} \boxed{\text{mesogen}} \end{array}$		
n	mesogen	
2, 3, 4, 9	$\text{OCO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_6\text{CH}_3$	4
3	$\text{COO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_6\text{CH}_3$	5
3	$\text{OCO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{OC}_m\text{H}_{2m+1}$ ($m = 4, 5, 7, 9, 11$)	6
3, 4	$\text{OCO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{OCO}(\text{CH}_2)_{10}\text{CH}_3$	7
3	$\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{OCO}(\text{CH}_2)_{10}\text{CH}_3$	8
2, 8	$\text{COO}(\text{CH}_2)_6\text{OCO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_8\text{CH}_3$	9
3, 8	$\text{COO}(\text{CH}_2)_6\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_5\text{CH}_3$	10
3	$\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OCO}(\text{CH}_2)_5\text{CH}_3$	11
8	$\text{COO}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{R}$ ($\text{R} = \text{CN}, \text{OCH}_3$)	12

We found that a rotational force applied to **12** (OCH_3) generates unusual high-strength disclinations (s up to 2), which have been reported for a few main-chain liquid crystalline polymers (MCLCPs) with rigid backbones,⁸⁻¹¹ but have never been observed in any conventional SCLCPs with flexible backbones. Translational shear creates inversion walls, solidification of which produces well-ordered parallel bands (Figure 1). The MCLCPs with rigid backbones often display the banded textures, but seldom do the SCLCPs with flexible backbones.¹² Thus, while structurally being a SCLCP, the LCPA mesomorphically resembles an MCLCP in some aspects. At the molecular level, the uniform orientations may be achieved by the alignments of the conjugated polyacetylene main chains along the shear direction. One intriguing possibility is that the bands are the "microtubes" consisting of bundles of stretched polyacetylene "nanowires" clad with the mesogenic jackets. Such microtubes may exhibit anisotropic electrical conductivity and large optical nonlinearity, in addition to excellent thermal stability and high mechanical strength. The novel mesomorphic phenomena have not previously been observed in the SCLCPs with flexible backbones, suggesting that the rigid conjugated polyacetylene backbones play an important role in inducing the molecular alignments aided by the external mechanical force.

Figure 1. (A) Inversion walls observed after a sheared **12** (OCH₃) was annealed at ~140 °C and (B) banded textures observed after the inversion walls were naturally cooled to room temperature. The shear direction was parallel to the long axes of the walls and bands.

4. LIGHT EMISSION

Photoluminescence (PL) of conjugated polymers has attracted much interest among scientists and technologists in recent years. Polyacetylene itself, however, emits no luminescence in the visible spectral region.¹³⁻¹⁵ The PL of monosubstituted polyacetylenes $-(HC=CR)_n-$ have also been investigated, but so far only faint luminescence has been observed in such polymer systems.¹⁶⁻¹⁹ Monosubstituted polyacetylenes are thus often referred to as a group of nonluminescent polymers and are generally regarded as unpromising candidates for light emitting materials.

The LCPAs we developed in this study belong to the category of monosubstituted polyacetylenes (Chart 3). Despite the “bad” nonluminescent reputation of monosubstituted polyacetylenes, we checked the PL behavior of our LCPAs. We are intrigued by the attractive possibility that a polymer with both light-emitting and liquid-crystalline capacities may find innovative applications in the optical display systems. The brightness and contrast of the displays, for example, may be dramatically enhanced and the viewing-angle problems may be well eliminated.

Chart 3

Monosubstituted Polyacetylenes

poly(arylacetylene) poly(alkylacetylene)

We first investigated the PL property of **2**, a PPA derivative. Its emission behavior is, however, really disappointing. The polymer is almost nonluminescent, emitting extremely weak fluorescence (Figure 2). Taking into account the previous findings by other groups for other PPA derivatives,¹⁶⁻¹⁹ the PPAs seem to be a hopeless group of monosubstituted polyacetylenes with some fetal structural defects that effectively quench the PL of the polymers.

Figure 2. Emission and absorption spectra of monosubstituted LCPAs **2** and **4(9)** (the number in the parentheses being the length of the methylene spacer, cf., Chart 2); excitation wavelength for the photoluminescence (PL) measurements: 325 nm; solvent/concentration (mM): THF/0.045 (**2**), chloroform/0.055 [**4(9)**]. The spectra of a THF solution of poly(1-phenyl-1-butyne) (**13**), a disubstituted polyacetylene, with a concentration of 0.039 mM are also shown for comparison.

Figure 3. Emission (solid line) and absorption (dashed line) spectra of some typical LCPAs with poly(alkylacetylene) skeleton structures **4(2–4)**, **4(9)**, **7(4)**, **9(2)**, and **9(8)** (the numbers in the parentheses being the lengths of the methylene spacers, cf., Chart 2); excitation wavelength for the PL measurements: 325 nm; solvent: THF (**4**, **7**), chloroform (**9**); concentration (mM): 0.064 [**4(2)**], 0.089 [**4(3)**], 0.078 [**4(4)**], 0.243 [**4(9)**], 0.143 [**7(4)**], 0.054 [**9(2)**], 0.124 [**9(8)**].

Figure 4. Effect of electrical field on the photoluminescence of a THF solution (5.68 mM) of a typical LCPA, **4(9)**, excited at 325 nm with the E-field applied across a 3-mm-thick quartz PL cell.

Poly(alkylacetylenes) often show permeability, radiolysis susceptibility, and mechanical properties distinctly different from those of poly(arylacetylenes) [with PPA being a typical example of this kind of polymers] because of the replacement of the aromatic rings directly attached to the polymer backbones by the alkyl chains (cf., Chart 3).^{1-3,20-36} We thus investigated the PL property of **4(9)**, a LCPA with a poly(alkylacetylene) skeleton structure, to see whether it would behave differently from **2**, its poly(arylacetylene) cousin. As a delightful surprise, **4(9)** emits strong deep-blue light with its PL spectrum centered at ~385 nm (Figure 2). The emission from **4(9)** is ~18 times more intense than that from **2**, although their absorbance at the excitation wavelength (325 nm) is similar. The PL efficiency of **5** is even higher than that of poly(1-phenyl-1-butyne) (**13**), a well-known photoluminescent disubstituted polyacetylene¹⁶⁻¹⁹ with a higher absorbance at 325 nm. Indeed, the emission from **4(9)** is so strong that it can be clearly observed even by naked eyes under normal room illumination conditions.

Encouraged by the results of **4(9)**, we further investigated PL behavior of other LCPAs of similar structures. As can be seen from Figure 3, although the spectral profile and emission intensity vary with the mesogenic pendants, all the LCPAs strongly luminesce upon photoexcitation, confirming that the intense emission is a general property of the LCPAs with the poly(alkylacetylene) scaffold structure.

When the concentration of the THF solution of **4(9)** is very high (5.68 mM; more than 23-fold higher than that used for the same LCPA in Figure 2), its PL spectrum becomes bimodal, displaying two emission peaks at ~380 and ~400 nm (Figure 4). Application of an electrical field changes the shape of the PL spectrum and shifts the position of the emission peak: the peak at the shorter wavelength weakens and the one at the longer wavelength intensifies. At the high electrical field of 1200 V (or 0.4 V/ μm), the two peaks merge into one with its maximum located at ~385 nm. The concentration and electrical-field effects may be associated with the aggregation states and molecular alignments of the LCPA in the THF solution. The novel concentrato- and electrochromism provides a versatile means for tuning the color of the light emitted from the LCPA solution.

5. PHOTOCONDUCTIVITY

The mesogenic groups in the LCPAs are packed in an ordered fashion. The molecular alignments may help enhance the charge generation and carrier transportation efficiencies in the illuminated LCPAs. We thus studied the photoconductivity of the LCPAs using a photoinduced xerographic discharge technique^{37,38} in function-separate single-layer photoreceptor devices.

The devices were prepared by casting onto polyamide (PAm)-coated aluminum plates, the 1,2-dichloroethane solutions of the LCPAs, 1-phenyl-1'-(α -naphthyl)hydrazine (BAH), and polycarbonate (PC). The resultant polymer films were heated at 80 °C for several hours to remove the residual solvent. In the photoreceptor devices, the LCPAs act as charge-generation materials and BAH as a charge-transportation medium, while the PC resin serves as a polymer matrix and the PAm coating as an interface layer.

Table 1. Intrinsic Photoconductivities of Undoped PVK, PPA, and Some Typical LCPAs^a

polymer ^b	V_o (V)	V_r (V)	R_d (V/s)	ΔV_1 (%)	$t_{1/2}$ (s)	S ($10^{-3} \text{ lux}^{-1} \text{ s}^{-1}$)
PVK	700	342	9	8	8.625	1.93
PPA	781	292	10	13	6.313	2.64
2	808	282	10	14	5.813	2.80
4(9)	656	117	18	22	3.063	5.43
9(2)	707	98	20	40	1.438	11.63

^a Exposed to 573-nm light with an exposure intensity of 60 lux. Abbreviations: PVK = poly(9-vinylcarbazole), PPA = poly(phenylacetylene), V_o = charged initial potential, V_r = residual potential, R_d = dark decay, ΔV_1 = percentage of potential discharge after 1 s of exposure, $t_{1/2}$ = half-discharge time, S = photosensitivity. ^b The numbers (9 and 2) in the parentheses are the lengths of the methylene spacers in the LCPAs (cf., Chart 2).

In the photoconductivity measurements, the samples were negatively corona charged to initial potential (V_o) and then kept in the dark for 3 s. When a sample is exposed to light with an intensity of I , the electron-hole pairs are generated in the charge-generation material. The holes then migrate through the charge-transportation medium towards the charged surface, recombining with the surface charges and thus discharging the surface potential. This photoinduced discharge process forms the basis of the electrophotographic industry. From this process, we can obtain several parameters: charged initial potential (V_o), dark decay (R_d), percentage of potential discharge after 1 s exposure [$\Delta V_1 = [(V - V_1)/V] \times 100\%$, V and V_1 being respectively the surface potentials before illumination and after 1 s exposure], time from V to half value under exposure ($t_{1/2}$), residual potential (V_r), and half-discharge exposure energy ($E_{1/2} = I \times t_{1/2}$). The photosensitivity (S) is defined as reciprocal of the half-discharge exposure energy ($1/E_{1/2}$). The larger the S value, the higher the photosensitivity. A good photoconductor should have a high value of ΔV_1 and small R_d , $t_{1/2}$, and V_r values when the sample is charged to a comparable initial potential (V_o).

Figure 5. Photosensitivity spectra of LCPAs, PPA, and PVK.

The photoconductivities of some typical LCAs along with those of PVK and PPA exposed to 573-nm light are summarized in Table 1. PVK is the best-known photoconductive polymer,³⁹ and its photosensitivity in the undoped state in the single-layer device is $\sim 2 \times 10^{-3} \text{ lux}^{-1} \text{ s}^{-1}$. PPA is a well-studied photoconductive polyacetylene,^{37,40-43} and for comparison, we also checked its intrinsic photoconductivity in the single-layer device. When the device is initially negatively charged to a surface potential of 781 V, the polymer shows a negative residual potential (V_r) of 292 V, a dark decay (R_d) of 10 V/s, 13 % of potential discharge after 1 s of exposure (ΔV_1), a half-discharge time ($t_{1/2}$) of 6.313 s, and a photosensitivity (S) of $2.64 \times 10^{-3} \text{ lux}^{-1} \text{ s}^{-1}$. Thus, the intrinsic photosensitivity of the PPA is superior to that of PVK, possibly due to the better absorption of the visible light by the conjugated polymer. The photosensitivity of the LCA **2** is slightly better than that of the parent PPA. In contrast, the LCAs with the poly(alkylacetylene) skeleton structure, i.e., **4(9)** and **9(2)**, perform much better as photoconductors. A 6-fold increase in photosensitivity is observed in **9(2)** when compared with that of PVK.

Figure 5 shows photosensitivity spectra of the LCAs. For comparison, the spectra of PPA and PVK measured under the same experimental conditions are also given. Clearly, **9(2)** and **4(9)** outperform the PPA and its derivative **2** as well as PVK in the whole visible spectral region. So far, the photoconductivity studies on polyacetylenes have been concentrated on PPA derivatives. We here demonstrate that the poly(alkylacetylene)-type LCAs are much better photoconductors even without doping, opening up a new avenue in the search for more efficient polyacetylene-based photoconductors.

As described above, **9(2)** is the best photoconducting polymer among the LCAs investigated in this study. The excellent photoconductivity may be associated with the ordered packing of the biphenyl mesogens in the polymer. Since **9(2)** is a LCA with a transition temperature of $\sim 74^\circ\text{C}$,³⁰ the temperature employed in the film-forming process (80°C) brings the polymer into its liquid crystalline state. Upon cooling to room temperature, the biphenyl mesogens may align in a stack, along which the charge transportation is easy, thus making the LCA a good photoconductor. The transition temperature of **4(9)** ($\sim 83^\circ\text{C}$)³² is, however, higher than that used in the device manufacturing process, and the chances for the biphenyl mesogens to align well are lower. Its photoconductivity is thus lower than that of **9(2)**. On the other hand, it is quite difficult, if not impossible, for the mesogens in **2** to move together to pack because its LC transition occurs at a much high temperature ($\sim 130^\circ\text{C}$), and **2** is thus a poor photoconductor. The enhanced photoconductivity has also been found in the ordered polymeric phthalocyanine thin films oriented in an electric field.⁴⁴

Table 2. Photoconductivities of C₆₀-Doped LCAs

LCA	C ₆₀ (wt %)	wavelength ^a (nm)	<i>I</i> (lux)	<i>V</i> ₀ (V)	<i>V</i> _r (V)	<i>R</i> _d (V/s)	ΔV_1 (%)	<i>t</i> _{1/2} (s)	<i>S</i> (10 ⁻³ lux ⁻¹ s ⁻¹)
2	0	400–800	800	882	140	18	48	1.063	1.18
	1.5	400–800	800	621	82	33	77	0.313	4.00
	1.5	500	60	562	109	15	27	2.625	6.35
	1.5	573	60	636	136	18	36	1.750	9.52
	1.5	601	60	585	148	10	18	4.313	3.86
	1.5	762	60	554	171	11	15	5.188	3.21
4(9)	0	400–800	800	623	131	62	52	0.875	1.43
	1.5	400–800	800	539	70	34	75	0.375	3.33
	1.5	500	60	527	97	16	22	3.125	5.33
	1.5	573	60	589	101	15	25	2.750	6.06
	1.5	601	60	609	128	15	18	4.063	4.10
	1.5	762	60	664	300	14	7	>10	<1.67

^a An halogen lamp was used as the light source, whose radiation is mainly in the visible spectral region (400–800 nm). The monochromatic wavelengths of 500, 573, 601, and 762 nm were isolated from the lamp beam through the use of optical filters.

Doping of photoconductors with electron acceptors and donors has been a widely used methodology for enhancing the photosensitivity via the mechanism of charge transfer complex formation. As can be seen from Table 2, **2** and **4(9)**, whose intrinsic photoconductivities are relatively low, show enhanced photosensitivities in the whole visible spectral region upon the addition of a small amount of C₆₀ (1.5 wt %) to the single-layer devices, possibly due to the photoinduced electron

transfer from the polymer chains to the C₆₀ cages.⁴⁵⁻⁴⁸ Even bigger (up to ~14-fold) enhancements in the photosensitivity are observed when **2** are doped with either I₂, an electron acceptor, or CV, an electron donor (Figure 6).

Figure 6. Doping effects of iodine (I₂; A) and crystal violet (CV; B) on photosensitivity of **2** illuminated by 573-nm light with an exposure intensity of 60 lux.

6. CONCLUSION

In summary, in this study, we have successfully developed a number of new LCPAs with novel mesomorphic, optical, and electronic properties. The rigid conjugated polyacetylene backbones endow the LCPAs with unique mesomorphic and orientational properties. The LCPAs show high photoluminescence efficiency and excellent photoconductivity, thanks to the synergistic contributions from the conjugated backbones and the mesogenic pendants. The light emission from the LCPAs can be tuned by the application of electrical fields, and their photosensitivity can be boosted by doping with either electron acceptors or donors.

We here propose a new recipe for designing molecular structures of non-conventional SCLCPs: *rigid* backbone + spacer + mesogenic group. The study on the SCLCPs with conjugated backbones is a little explored research area, partly owing to the common belief that the rigid main chains interfere the packing of the mesogenic pendants and disturb the growth of the ordered domains. Our work presented here thus may trigger intensive molecular engineering efforts in the design of conjugated-backbone SCLCPs and help develop a new class of liquid crystalline conjugated polymeric materials with combined advantages of SCLCPs (e.g., excellent processibility) and MCLCPs (e.g., superb orientability). Noticing that many conjugated polymers are electrically conductive, optically nonlinear, and light emissive, the development of the SCLCPs with conjugated polymer backbones should contribute to the search for the advanced materials with intriguingly novel electronic and optical properties. Such materials are expected to find a wide range of attractive applications in the high technology industries.

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