Strong Luminescence from Poly(1-alkynes)

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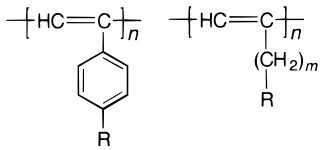
Introduction. Enthusiastic expectation of electronic and optical applications of conjugated polymers has stimulated dynamic research activities in macromolecules with extended π electrons.[1] Polyacetylene [PA; $-(HC{=}CH)_n-$] is a prototypical conjugated polymer and has been the subject of extensive research for decades.[2] Photo- and electroluminescence of conjugated polymers have attracted much interest among scientists and technologists in recent years because of the prospects of constructing all-plastic light-emitting diodes.[3] PA, however, exhibits practically no photoluminescence (PL) in the visible spectral region.[4] Substitution of the hydrogen atoms of PA with other atoms or groups can perturb the electronic structure of the macromolecules, and indeed a variety of PAs with two pendant substituents $-(RC{=}CR')_n-$ (or disubstituted PAs) have been found to be highly luminescent. Emission of intense blue or green light induced by photo- and electroexcitations has been observed in a number of disubstituted PAs including poly(diphenylacetylene) derivatives $-[(C_6H_5)C{=}C(C_6H_4\text{-}p\text{-}R)]_n-$ {R = OC_6H_5, *n*-C_3F_7, *n*-C_4H_9, *t*-C_4H_9, $C_{10}H_{16}$ (adamantyl), $Si(CH_3)_3$, $Si[CH(CH_3)_2]_3$, $Si(C_6H_5)_3$}, poly(1-phenyl-1-alkynes) $-[(C_6H_5)C{=}C(C_mH_{2m+1})]_n-$ (*m* = 1, 2, 6), poly(1-chloro-2-arylacetylene) with the aryl groups being phenyl and naphthyl, and poly(1-methyl-2-naphthylacetylene).[5] The PL of monosubstituted PAs $-(HC{=}CR)_n-$ have also been investigated, but so far only weak luminescence has been observed in such polymers, examples of which include poly(phenylacetylene) and its derivatives $-[HC{=}C(C_6H_4{-}R)]_n-$ with ring substituents of CF_3, $Si(CH_3)_3$, $Si(CH_3)_2C_6H_5$, *i*-C_3H_7, and *n*-C_4H_9 at ortho and para positions and poly(1-propyne) or poly(propargyl) derivatives $-[HC{=}C(CH_2{-}R)]_n-$ with R = diphenylamino and indolyl.[5c,e,f,6] Monosubstituted PAs are thus often referred to as nonluminescent polymers and are generally regarded as unpromising candidates for light-emitting materials.

Compared to disubstituted acetylenes, many monosubstituted acetylenes are readily available from commercial sources or accessible via simple chemical reactions and can be easily converted to the corresponding monosubstituted PAs by various catalyst systems.[7,8] Taking the synthetic advantages, we have recently prepared a wide variety of monosubstituted PAs and investigated their chirality (optical activity), photoconductivity, liquid crystallinity, induced molecular alignment, and light transmission properties.[8c,9] In this work, we studied their light-emitting properties. We here prove that the nonluminescence of monosubstituted PAs is a misconception and demonstrate that the PL efficiency of the polymers can be tuned by changing their molecular structures.

Experimental Section. All the PAs used in this study were prepared in our laboratories and were thoroughly purified and well characterized. The experimental details including synthetic procedures and analytical data can be found in the references given in Table 1. The polymer solutions were prepared by dissolving accurately weighed amounts of the polymers in freshly distilled and degassed spectroscopic-grade tetrahydrofuran (THF) and chloroform. The molar concentrations of the polymer solutions were calculated on the basis of the molecular weights of their repeat units. The absorption spectra of the polymer solutions were recorded on a Milton Roy Spectronic 3000 array spectrometer. The 325 nm line from an Omnichrome helium−cadmium CW laser was used as the excitation source for the PL measurements. The maximum output of the laser was ∼13 mW, but only a small fraction (∼1 mW) of the power was focused onto the samples as a precaution against possible polymer photodegradation. The PL spectra were measured at room temperature in a 1 mm thick quartz cell on a Spex-500M spectrofluorometer. All the polymer solutions were prepared immediately prior to the measurements, and every spectrum was repeatedly measured at least twice.

Monosubstituted Polyacetylenes



poly(arylacetylene) poly(alkylacetylene)

Results and Discussion. We first checked the PL behavior of poly(arylacetylenes) or, more specifically, poly(phenylacetylene) derivatives $-[HC{=}C(C_6H_4\text{-}p\text{-}R)]_n-$ with R = biphenyl, amino acid, crown ether, sugar, and oligo(ethylene glycol).[8b,9b,k,10] The PL behavior of the polymers was, however, really disappointing. All the polymers were almost nonluminescent, an example of which is given in Figure 1. The poly(phenylacetylene) derivative with a biphenyl mesogen (**1**) emitted extremely weak fluorescence signals. Our molecular engineering effort in tuning the quantum yields of light emission from the poly(phenylacetylenes) was thus unfortunately failed. Taking into account the previous findings by other groups,[5c,e,f,6] the poly(arylacetylenes) seem to be a hopeless group of monosubstituted PAs with some fetal structural defects that effectively quench the PL of the polymers. We thus turned our attention to other monosubstituted PAs with different molecular scaffolds.

Poly(*alkyl*acetylenes) often show permeability, photoconductivity, mesomorphism, radiolysis susceptibility, and mechanical properties[8−11] distinctly different from those of poly(*aryl*acetylenes) because of the replacement of the *aromatic* rings directly attached to the polymer backbones by the *alkyl* chains. We thus tested a poly(1-alkyne) with a biphenyl mesogen at the end of the alkyl side chain (**5**) to see whether the polymer will behave differently from its poly(arylacetylene) cousins. Delightfully, **5** emitted strong deep-blue light with its PL spectrum maximum located at 380 nm (Figure 1).

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Table 1. Preparation of Substituted Polyacetylenes[a]

	monomer RC≡CR′			polymer −(RC═CR′)$_n$−			
no.	R	R′[b]	catalyst[c]	yield (%)	M_w[d]	M_w/M_n[d]	ref
1	H	Ph-*p*-$CO_2(CH_2)_6$OCO-Biph-OC_7H_{15} (**1**)	$[Rh(cod)Cl]_2$	85.7	385 400	4.60	9b
	H	$(CH_2)_m$OCO-Biph-OC_7H_{15}					
2		m = 2 (**2**)	WCl_6-Ph_4Sn	72.4	40 800	2.22	9h
3		m = 3 (**3**)	WCl_6-Ph_4Sn	85.2	74 770	2.38	9h
4		m = 4 (**4**)	WCl_6-Ph_4Sn	87.3	112 900	5.01	9h
5		m = 9 (**5**)	WCl_6-Ph_4Sn	82.2	41 200	2.21	9h
	H	$(CH_2)_mCO_2(CH_2)_6$OCO-Biph-OC_9H_{19}					
6		m = 2 (**6**)	WCl_6	16.0	14 500	1.45	9f
7		m = 8 (**7**)	WCl_6	10.0	22 600	1.69	9f
8	H	$(CH_2)_4$OCO-Biph-$OCOC_{11}H_{23}$ (**8**)	WCl_6-Ph_4Sn	82.3	59 000	1.85	9g
9	C_2H_5	Ph (**9**)	WCl_6-Ph_4Sn	98.5	201 800	4.88	12

[a] The polymerization reactions were carried out under an atmosphere of dry nitrogen for 24 h; solvent: THF/Et_3N (no. 1), dioxane (no. 2−8), toluene (no. 9); temperature: rt (nos. 1, 6, 7), 60 °C (nos. 2−5, 8), 80 °C (no. 9). For more detailed information on the reaction conditions, see the cited references. [b] Abbreviations: Ph = phenyl, Biph = 4,4′-biphenylyl. [c] Abbreviation: cod = 1,5-cyclooctadiene. [d] Estimated by GPC in THF on the basis of a polystyrene calibration.

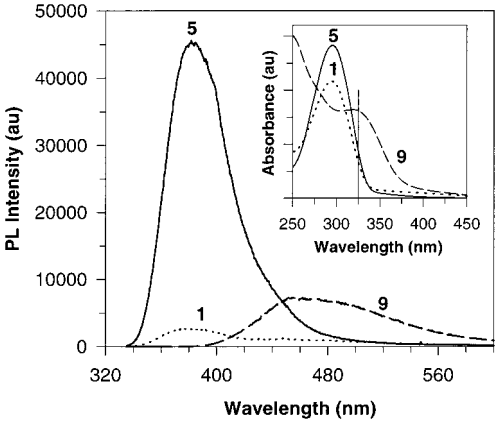

Figure 1. Emission and absorption (inset) spectra of poly(alkylacetylene) **5** and poly(arylacetylene) **1** excited at 325 nm. Solvent/concentration (mM): chloroform/0.055 (**5**), THF/0.045 (**1**). The spectra of a THF solution of a disubstituted polyacetylene (**9**) with a concentration of 0.039 mM are also shown for comparison.

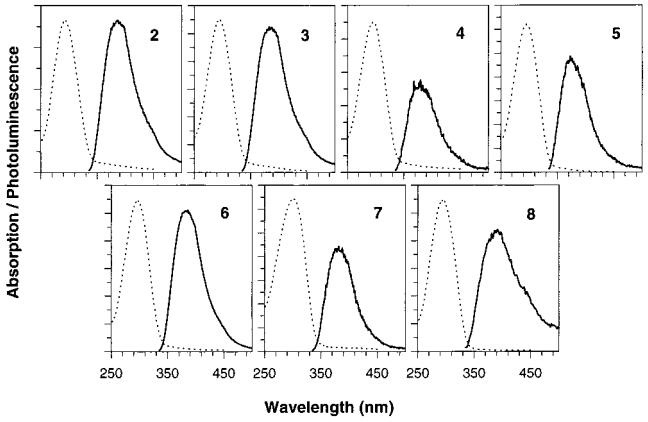

Figure 2. Emission (solid line) and absorption (dashed line) spectra of poly(alkylacetylenes) **2**−**8**. Solvent: THF (**2**−**4**, **8**), chloroform (**5**−**7**). Concentration (mM): 0.064 (**2**), 0.089 (**3**), 0.078 (**4**), 0.243 (**5**), 0.054 (**6**), 0.124 (**7**), 0.143 (**8**). Excitation wavelength: 325 nm.

The emission from **5** was ∼18 times more intense than that from **1**, although their absorbance at the excitation wavelength (325 nm) was similar. The PL efficiency of **5** was even higher than that of poly(1-phenyl-1-butyne) (**9**), a well-known luminescent disubstituted PA[5] with a higher absorbance at 325 nm. Indeed, the emission from **5** was so strong that it could be clearly observed even by naked eyes under normal laboratory lighting.

Encouraged by the results, we further investigated PL behavior of other poly(alkylacetylenes) of similar structures. As can be seen from Figure 2, although the spectral profile and emission intensity vary with the pendant groups, all the polymers strongly luminesce upon photoexcitation, confirming that the intense emission is a *general* property of the poly(alkylacetylenes). Close inspection of the PL spectra reveals that the emission maximum slightly blue-shifts with an increase in the length of the alkyl chain (m).

The reasons for the high PL efficiencies of the poly(alkylacetylenes) are not clear at the present time but may be associated with the confinement effect induced by the alkyl pendants. The saturated alkyl chains directly attached to the polymer backbone form a nonconjugating boundary, preventing the excitons in the polymer main chains from moving to the side chains. The confined excitons thus have less chance to encounter nonradiative sites, contributing to the high quantum yields of the light emission. On the other hand, the conjugation of the π-electrons of the alternating double bonds in the poly(arylacetylene) main chains and those of the aromatic rings directly attached to the polymer backbones may allow the photogenerated charges to flow into the pendant benzene rings, taking into consideration our recent finding that the PA backbone is electron donating in nature.[9b] This may convert some of the benzene rings from benzenoid forms to quininoid ones, thus separating the charged carriers. The photoinduced electron transfer and charge separation hamper the recombination of electrons and holes, leading to the weak light emission.[13−15] In the case of poly(propargyls),[5e] the π-electrons of the polymer backbone can communicate with those of the aromatic rings via the allylic conjunctions, inducing charge separation and hence quenching the PL of the polymers. The aromatic rings in our poly(alkylacetylene) systems are well separated from the polymer backbone by the alkyl spacers. The photogenerated charge carriers confined by the aliphatic cages may have good chances to participate in the recombination process, and the polymers thus can emit strong luminescence.

Conclusion. In contrast to the "general" belief that monosubstituted PAs are a group of nonluminescent polymers, in this work, we found that monosubstituted PAs with poly(1-alkyne) skeleton structure were highly luminescent. Indeed, the poly(alkylacetylenes) **2**−**8** emitted strong deep-blue light, whose intensities were higher than that of the highly luminescent disubstituted PA **9**. Our finding thus opens up a new avenue in the search for new light-emitting polymers with PA struc-

tures and may lead to the development of new theories for conjugated polymers.

It is worth pointing out that all the luminescent poly(1-alkynes) investigated in this study are also liquid crystalline[9] and photoconductive;[16] polymers with such attributes may find attractive technological applications in display and imaging industries. The polyacetylenes, for example, may be used for the construction of spatial light modulators[17] and optical display systems with the advantages of both liquid crystal devices and light-emitting diodes, showing high brightness and contrast but with minimal viewing-angle constraints.[16] Our preliminary results show that a thin film of **5** sandwiched between ITO and Ag electrodes luminesce upon applying an electrical field;[18] detailed studies on the electroluminescence of the polyacetylenes are under way in our laboratories and will be published in a separate paper in due course.

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