Rational design of polymers for optoelectronic interests*

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Abstract: Using organometallic catalysts, two types of polymers containing conjugated moiety and insulating linker are synthesized. The investigations on the photophysical properties of these polymers (photoluminescence, electroluminescence and nonlinear optical properties) are briefly summarized. These polymers represent a new class of materials for optoelectronic interests.

INTRODUCTION

Conjugated polymers exhibit a wide variety of fascinating optoelectronic properties [1]. The burgeoning synthetic methodologies using organometallic catalysts or reagents have provided a powerful arsenal to design and synthesize new conjugated organic materials. It is particularly noteworthy that carbon–carbon bond formation involving a C_{sp}^2 or Csp at the reaction center can readily be achieved [1]. For examples, cross-coupling reactions (e.g., Kumada–Corriu reaction, Stille reaction, and Suzuki reaction) are extremely powerful for the synthesis of C_{sp}^2–C_{sp}^2 single bond. Sonogashira reaction, on the other hand, serves as a useful entry for the preparation of alkynylarenes. Heck reaction furnishes a coupling between an aryl halide and an alkene.

Various model systems suggest that the photophysical properties of certain conjugated polymers can be represented by those of a short fragment of the corresponding oligomeric chromophores [2]. There has been an increasing study on the use of spacers between well-defined conjugated chromophores in polymers. An obvious advantage in this strategy is that polymers can increase the processibility and, in the meantime, the emission wavelength can be predicted [3]. Two approaches using insulating linkers are represented by cartoons shown in Fig. 1. The conjugated moiety can be part of a polymeric backbone as demonstrated in Case a. Ether, ester, alkylidene, as well as silylene linkages are among most commonly used spacers to connect the chromophores [4,5]. The syntheses leading to these polymers rely mainly on condensation or Wittig reaction and, therefore, are not atom-economic. The second method considers the chromophores as pendent to the polymeric skeleton (Case b). In both cases, the photophysical properties of the polymers appear to be the same as those of the corresponding monomeric chromophores. In this account, we summarize our results using the strategy shown in Fig. 1 to design a variety of polymers for optoelectronic interests.

SILYLENE-DIVINYLARENE COPOLYMERS

In line with Case a, there has been an increasing use of tetrahedral silylene moiety as a bridge connecting chromophores in polymers [5]. Our approach uses rhodium-catalyzed hydrosilylation to syn-
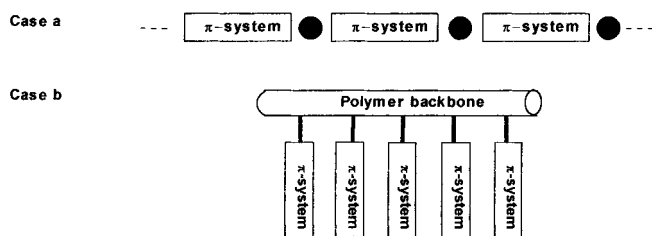

Fig. 1

thesize a variety of silylene-divinylarene copolymers **5** (eq. 1) [6]. The corresponding vinylic silyl hydrides **3** can readily be achieved by the nickel-catalyzed silylolefination of dithioacetals **1** followed by reduction of the Si–O bonds [6]. It is noteworthy that higher concentration and longer reaction time favor the formation of **5** with higher molecular weight. The corresponding monomeric compounds **6** (eq. 2) are prepared in a similar manner.
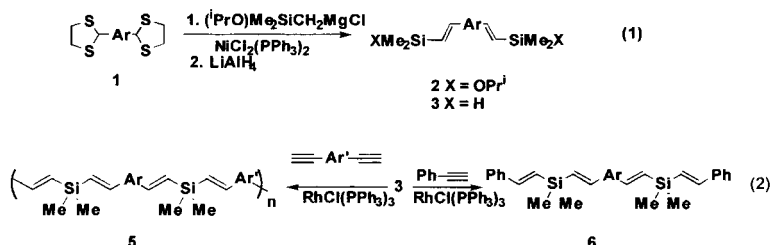
The role of the silicon moiety in **5** depends on the nature of the chromophores. As shown in Fig. 2, the emission properties of the monomer **6a,b** are similar to those of the corresponding polymers **5a,b** having same lumiphores. In these cases, the silylene group can serve as an insulating spacer.

Since the silylene moiety has a tetrahedral structure, the polymers **5** may be highly folded. Accordingly, the two chromophores may locate in close proximity so that intramolecular interaction may occur. Indeed, certain polymers **5** exhibit dual fluorescence spectra (Fig. 3). The emission profiles remain essentially unchanged with concentration (10^{-2}–10^{-5} M) and with solvents (<8 nm, in MeCy, benzene, or $CHCl_3$). The higher energy emission for **5c** (Ar = Ar$'$ = p-C_6H_4) is compatible with those for **6c**. The relative intensity of the emission in the longer wavelength region (due to excimer formation) increases with the molecular weight of **5c**, and vibronic fine structures were observed in this region. These results suggest that strong intramolecular interaction between the divinylbenzene moieties in **5c** may occur, and such interaction is important even at the ground state. Biphenyl is nonplanar in solution and, therefore, it might be difficult for this moiety to form a stable p-complex with another biphenyl group. Indeed, the weak exciplex spectra indicate that the interaction between two divinylbiphenyl chromophores is less important than other substrates.
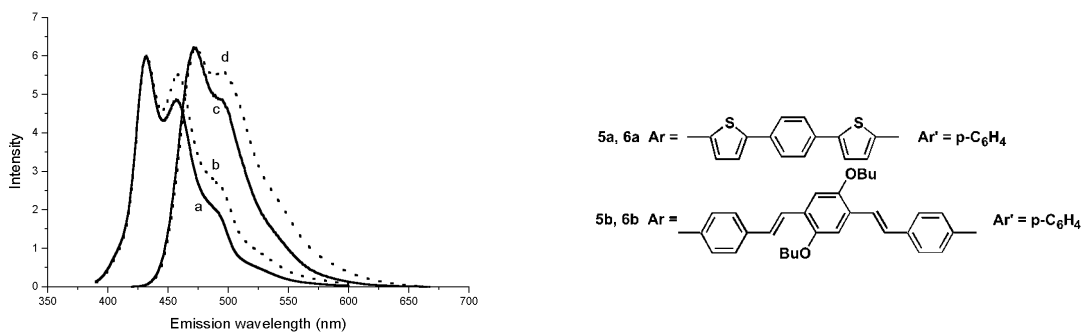
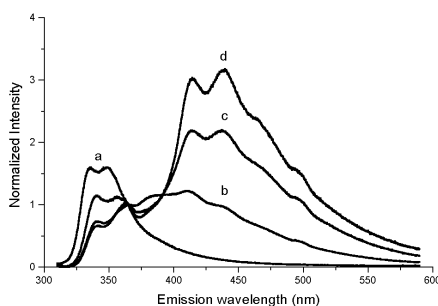**Fig. 2** Photoluminescence of (a) **6a**, (b) **5a**, (c) **6b**, (d) **5b**.
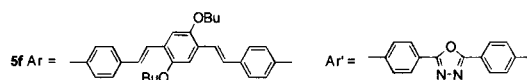
Fig. 3 Photoluminescence of (a) **6c** (Ar = p-C$_6$H$_4$), (b,c,d) **5c** (Ar = Ar' = p-C$_6$H$_4$), where M$_n$ = 2200, 7500, and 10100, respectively.

It is known that the two chromophore linked by a silylene moeity, charge transfer between two chromophores may occur [7]. Accordingly, the neighboring chromophores in **5** may also interact such that energy transfer may occur. The fluorescence spectrum for polymer **5f** occurs at 490 nm attributed to the emission of the ter-phenylene-vinylene (TPV) chromophore. The emission from the distyryloxadiazole moiety apparently transfers the energy efficiently to the TPV chromophore in **5f**. Bright blue electroluminescent properties have been shown in monomer **6b** and the corresponding polymer **5b** having TPV chromophore [8].
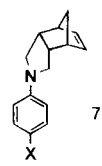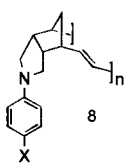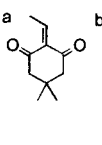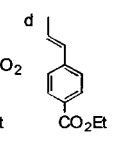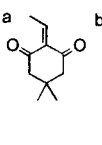
CHROMOPHORE AS PENDENT OF THE POLYMERIC BACKBONE

Second-order nonlinear optical devices can be constructed by arranging the organic chromophores as pendants into a supramolecular backbone [9]. Enhancement of such nonlinearity has been observed when chromophores are organized in a fixed noncentrosymmetric arrangement as side groups of helical polyisocyanide and polypeptide. More recently, using dipolar conjugated moieties as pendants on PNB backbone for the second-order nonlinear optical investigations was executed [10]. Grubb's ruthenium catalyst is employed to prepare the polymers **8** from the corresponding norbornene monomers **7**. Hyper-Rayleigh scattering (HRS) method was employed to measure the β_o values for **7** and **8** in CHCl$_3$. The photophysical properties are summarized in the Table 1.

It is interesting to note that the β_o values are significantly enhanced in **8** in comparison with those of the corresponding monomers **7**. A plot of the β_o(**8**)/β_o(**7**) having the same pendant chromophore versus the average number of repetitive monomeric units, n, in **8** gave a linear relationship with a slope 0.34 and the intercept at the origin. These results indicated that each of the pendant chromphores contributes to approximately 34% of its monomeric β_o values to the second-order optical nonlinearity of the polymers and that the polymers **8** have relatively rigid structure with uniform conformation.

Ring opening metathesis polymerization of norbornenes by the Grubb's ruthenium catalyst gives the polymers having mainly trans double bond (>90%) [11]. The equilibrium structures obtained from molecular dynamics simulation suggest that the isotactic chain results in random coil, whereas the pendant chromophores are aligned fairly well in the syndiotactic form. Introduction of pendant groups may provoke interactions between chromophores that may further stabilize the syn-conformation. In comparison with the experimental results shown in Table 1, it seems likely that the polymers **8** may adopt this syndiotactic structure and each chromophore contributes coherently to the hyperpolarizability of the polymer. The strong enhancement of β_o values observed in the HRS experiments can thus be rationalized.

Table 1

	Mn (PDI)	n	λmax (nm)	ε × 10³ (g⁻¹cm²)	βo × 10⁻³⁰ esu	βo (8) /βo (7)
7a			475		31	
8a	4200 (1.1)	14	469		178	5.7
7b			458	28.2	54	
8b	4900 (1.4)	13	443	27.2	283	5.2
	5200 (1.5)	14	445	27.1	273	5.1
	6200 (1.7)	16	445	26.5	334	6.2
	7200 (1.8)	19	445	26.1	376	7.0
	8800 (2.2)	23	446	24.1	454	8.4
	10000 (1.9)	26	444		459	8.5
7c			495		32	
8c	11700 (2.9)	27	487		283	8.8
7d			393		28	
8d	17000 (1.3)	44	384		459	16.4

CONCLUSIONS

In summary, using organometallic catalysts, two types of polymers containing conjugated moiety and insulating linker are synthesized. The photophysics has been studied in details. These polymers represent a new class of materials for optoelectronic interests.

ACKNOWLEDGMENTS

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