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COMMUNICATION

Enantioselective Synthesis of Helical Polydiacetylene in the Visible Light Region

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Herein, we demonstrate for the first time that the enantioselective polymerization of DA monomers could be realized upon irradiation with circular polarized visible light (CPVL), which could effectively provide chiral order in the propagating step of a polymerization reaction.

Helical conformation is a representative secondary structure of biomacromolecules in nature, such as proteins and deoxyribonucleic acids. The origin of homochirality of biomolecules has attracted the interest of a wide range of scientists.¹ Circularly polarized light (CPL), which could be observed in star-forming regions of the Orion constellation,² has long been proposed as one of the origins of single chirality in nature. Right- and left-handed CPL have been used to induce the enantioselective photodecomposition of chiral organic compounds, however, only a small enantiomeric excess (<2%) could be obtained due to their very small anisotropy (g) factors.³ Various asymmetric amplification methods have been proposed to achieve the complete deracemization of chiral organic compounds.⁴ Recently, professor Iwamoto and our group reported the successful enantio-selective synthesis of polydiacetylene (PDA) films upon the irradiation with circular polarized UV light (CPUL).⁵ The left- and right-handed CPUL irradiation definitely yielded opposite chiral PDA films. However, detailed enantio-selective polymerization mechanism with CPUL is still not clear. The interaction between the CPUL and the diacetylene (DA) dimer at the early photo-initiation stages was assumed to play a key role in the enantio-selective synthesis of PDA.^{5a} The visible light is not able to directly initiate the photo-polymerization reaction of DA monomer, whether helical PDA can be enantio-selective synthesized with circular polarized visible light (CPVL) remains a question to be answered by the proposals for both better understanding of the enantio-selective polymerization mechanism and creating new synthesis ways for helical conjugated polymer materials.

PDA is usually prepared via topochemical solid-state polymerization. At low temperature, solid-state polymerization of DA is commonly accomplished by irradiation with short wavelength UV light or high-energy radiation with γ -ray.⁶ It has been reported

that the photo-initiation of polymerization reaction depends on the exciting of DA

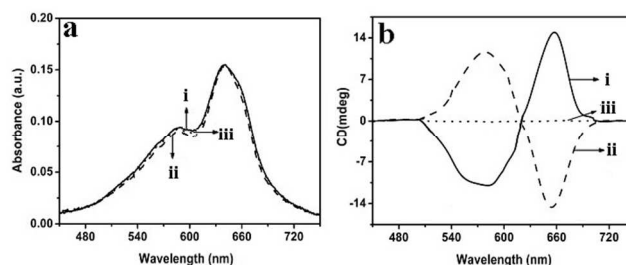


Fig. 1 UV-vis absorption and CD spectra of (a) UV-vis absorption spectra and (b) CD spectra of PCDA film after irradiation with (i) right-handed CPVL and unpolarized UV light; (ii) left-handed CPVL and unpolarized UV light and (iii) unpolarized UV light alone.

monomer, and the wavelength should be less than 310 nm. After formation of DA dimer, there are two ways to propagate the chain. One is the energy transfer from an excited monomer to the active polymer chain. The light should be in the UV-region and the process is a competition between chain initiation and propagation. The other is the excitation of the active PDA chain directly. The essential exciting energy decreases with increasing of the active PDA chain length. When the number of repeat units is more than 5, the excitation wavelength is about 550 nm. Therefore, the visible light is able to accelerate the solid-state polymerization of DA monomer when the UV and visible-light are applied simultaneously.⁷ Moreover, some efforts have been made to sensitize solid-state polymerization of DA in the visible light region.⁸ However, to the best of our knowledge, attempts to synthesize helical PDA with CPVL have not been described to date. Herein, the enantio-selective polymerization of DA had been realized in the visible light region. In this case, chiral source is only CPVL, which could effectively provide chiral order in the chain-propagating process, and direct the handedness of the final PDA chain.

The CPVL (generated by 532nm ND:YAG CW Semiconductor laser) was applied simultaneously with unpolarized UV light (16W UV lamp, $\lambda = 254$ nm) to realize the enantio-selective polymerization

(Figure S1a). The light intensity of CPVL and UV light were about 30mWcm^{-2} and 15mWcm^{-2} , respectively. As the reference sample, PCDA films were irradiated with unpolarized UV or CPVL alone for 20 min. PCDA films could be polymerized upon irradiation with the combined light (the CPVL and unpolarized UV light simultaneously) or unpolarized UV light alone (Figure 1a), while not upon irradiation with CPVL (532 nm) alone (Figure S2). When above samples were subjected to CD measurement, it was interesting to note that significant CD signals at the absorption band for PDA backbone could be observed for the sample upon the combined light irradiation, while not for the sample upon the irradiation with unpolarized UV light alone (Figure 1b). By rotating the sample within the film plane, the change of CD intensity could be neglected, thus confirming that the above CD spectra were free from linear dichroism (LD) (Figure S3).^{9a,9b} To further evaluate the degree of CD, we defined the absorption dissymmetry factor (g) as $g = (\epsilon_L - \epsilon_R) / [(\epsilon_L + \epsilon_R) / 2] = \Delta\epsilon / \epsilon$, where $|g| < 2$.¹⁰ The ϵ_L and ϵ_R are defined as the absorption coefficients of left- and right-handed polarized light, respectively. As shown in Figure S4, the samples irradiated with left- and right-handed CPVL clearly exhibited opposite g -factor values at the corresponding absorption band for PDA chains. Namely, left- and right-handed CPVL distinguishably induced the formation of helical PDA with opposite handedness. However, upon irradiation with normal UV light alone, no macroscopic chirality for PDA could be observed. All above results indicated that the enantio-selective polymerization of PCDA with CPVL should be a deterministic process and the handedness of the applied CPVL directed the helical direction of the prepared PDA chains.

It was reasonable to use the chronological development of the absorption maxima to determine the polymerization reaction kinetics.^{8e} Figure 2a showed time-resolved development of the absorption maximum at 650 nm for pure DA film. The kinetics curves clearly showed that the polymerization process under the combined light irradiation could be described as a first order reaction, the same as that of the sample upon UV irradiation alone. And the polymerization rate constants k was $8.3 \times 10^{-3} \text{ s}^{-1}$, higher than that of the sample upon UV irradiation ($k = 7.7 \times 10^{-3} \text{ s}^{-1}$, in Figure 2a). All above results indicated that the irradiation with CPVL could excite chain propagation and accelerate the polymerization process.⁷

As mentioned above, the helical PDA chains exhibited typical g -factor maxima at 650 nm, therefore it was reasonable to use the chronological development of the g -factor maxima to evaluate the enantio-selective polymerization kinetics for the helical PDA chains with CPVL. The kinetics curves clearly showed that the enantio-selective polymerization process could also be described as a first order reaction (Figure 2b). The rate constants k was determined to be $4.5 \times 10^{-3} \text{ s}^{-1}$. Moreover, the kinetics constants k was found to be proportional to the light intensity of the applied CPVL (as shown in Figure 2c), which revealed that the formation mechanism of the helical PDA chains with CPVL may involve asymmetric carbene radicals as the primary species, different from the commonly proposed biradical mechanism for DA enantio-selective polymerization in the UV region.^{5b} As the light intensity for the applied CPVL increased, the g -factor value of the final PDA films increased, gaining the maximum value of 1×10^{-4} , when the light intensity of the CPVL increased to 30 mWcm^{-2} (Figure 2d). As mentioned above, there are two ways to propagate the active PDA chains. One is the energy transfer from the excited monomers to polymer chains. The light should be in the UV-region and the CPVL irradiation seemed no effect on this chain propagation process. In this case, the formed PDA chains made no contribution to the CD signals of the final films. The other is excitation of the PDA oligomer chain directly. The wavelength of CPVL was lower than

550 nm and it could excite the PDA oligomer chain directly. The thus-formed oligomer radical might be aligned in a suitable

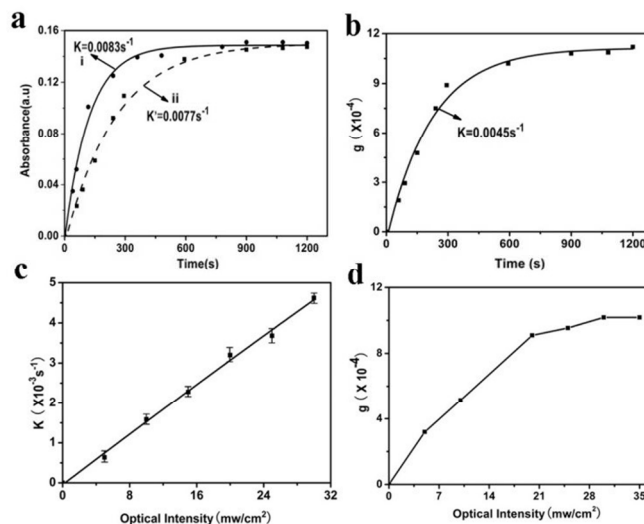
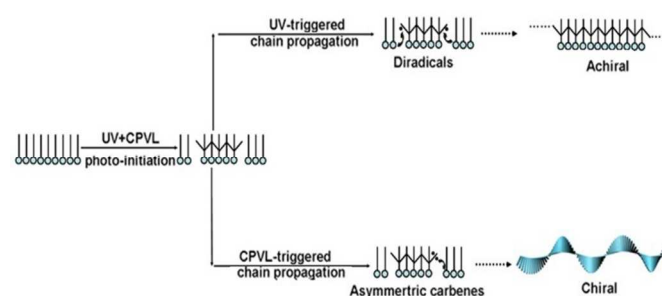


Fig. 2 Polymerization rate constants and g values at 650 nm for PDA films. (a) Time-resolved development of absorption maximum at 650 nm for DA films upon irradiation with (i) right-handed CPVL and unpolarized UV light simultaneously; or (ii) unpolarized UV light alone. (b) Time-resolved development of g value maximum at 650 nm for DA films upon irradiation with right-handed CPVL and unpolarized UV light simultaneously. (c) The enantio-selective polymerization rate constant as a function of the light intensity of CPVL. (d) The measured g value maximum for the final PDA films as a function of the light intensity of CPVL.

orientation and reacted with the neighbor DA monomer, eventually resulted in the formation of helical PDA chains. The interaction between CPVL and PDA oligomer was assumed to play a dominant role, which could effectively provide chiral order in the chain-propagating process and direct the handedness of final PDA chain. Therefore, definite CD signals for PDA backbone could be obtained, followed by the handedness of CPVL. On the basis of above discussion, the formation mechanism of helical PDA chains in visible light region was illustrated in Scheme 1.

In order to prove above idea, the enantio-selective polymerization of DA films was further performed with CPVL irradiation alone by employing the ruthenium(II) complexes to sensitize solid-state polymerization of DA in the visible light region.^{8e} Here, the enantio-selective polymerization of DA was performed upon CPVL irradiation alone (Figure S1b). The chain initiations were realized through photo-induced electron transfer from the ruthenium(II) complexes to DA monomers. And the CPVL could excite chain propagation and was utilized here to realize the enantio-selective



Scheme 1. Scheme of enantio-selective polymerization mechanism for DA films in the visible light region.

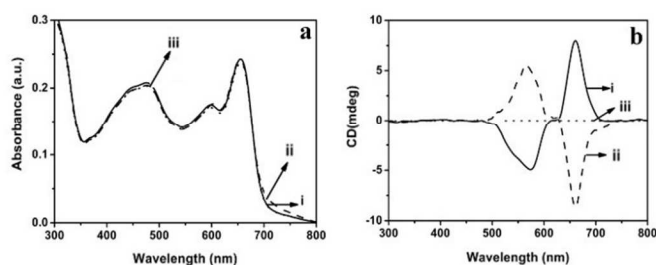


Fig.3. UV-vis absorption and CD spectra of (a) UV-vis absorption spectra and (b) CD spectra of PCDA/[Ru(dpphen)₃]Cl₂ hybrid film after irradiation with (i) right-handed CPVL; (ii) left-handed CPVL and (iii) unpolarized visible light, respectively.

polymerization of DA monomer. The DA hybrid films with 3.4mol% [Ru(dpphen)₃]Cl₂ were prepared by spin-coating technique. Upon irradiation with CPVL or unpolarized visible light for 20min, all films turned blue and exhibited typical intense absorption maxima at about 580 and 650 nm. As expected, the samples irradiated with left- and right-handed CPVL clearly exhibited opposite CD signals at the corresponding absorption band for PDA chains (Figure 3). However, no obvious CD signals could be observed for the sample under the irradiation with unpolarized visible light. Left- and right-handed CPVL distinguishably induced the formation of left- or right-handed helical PDA chains. All above results well confirmed that the enantio-selective polymerization of DA could be realized in the visible light region by employing the CPVL as the chiral source.

In summary, the enantio-selective polymerization of DA units was realized in the visible light region for the first time. The interaction between the CPVL and the PDA oligomer was assumed to play a dominant role, which could effectively provide chiral order in the chain-propagating process and direct the handedness of the final PDA chain. The formation mechanism of the helical PDA chains in the visible light region may involve asymmetric carbene radicals as the primary species, different from the commonly proposed biradical mechanism in the UV region. This work is not only of great fundamental value for the understanding of the enantio-selective polymerization mechanism for chiral PDA materials but also provides a promising asymmetric synthesis method for fabricating the conjugated polymer, towards with the practical applications in enantio-sensing and so on.

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