Organic Materials for Third-Order Nonlinear Optics 4 h 48	Vật liệu hữu cơ cho Quang phi tuyến bậc 3.
The current status of organic low-	Chúng ta điểm lại một số nghiên cứu hiện

molecular weight and polymeric materials for third-order nonlinear optics is re-viewed. The importance of organic materials lies in their promise of large nonlinear optical figure of merit, high optical damage thresholds, ultrafast optical responses, architectural flexibility, and ease of fabrication. Organic materials exhibit-ing interesting third-order nonlinear optical properties are dis-cussed to illustrate the importance of structure-property cor-relations.

Results on emerging organic materials that include liquids, dyes, fullerenes, charge-transfer complexes, ic-conju- gated polymers, dye-grafted polymers, organometallic com-pounds, composites, and liquid crystals are presented. Organic nonlinear optical materials seem promising for a wide range of applications and their potential for integrated optics should be further explored.

1. Introduction

The word "laser" is an acronym which stands for light amplification by stimulated emission of radiation. The first operating laser was developed in 1960 by Maiman11' using a crystal of ruby. One year later, Franken et al.121 demonstrated the frequency doubling of light from a ruby laser by a quartz crystal. This frequency-doubling phenomenon is termed second harmonic generation. These milestone discoveries opened up two fields of research: laser science in one direction and nonlinear optics in the other.

tại về các vật liệu hữu cơ trọng lượng phân tử thấp và polime. Vật liệu hữu cơ có nhiều ưu điểm như hệ số phẩm chất quang phi tuyến lớn, ngưỡng hủy hoại quang cao, đáp ứng quang học cực nhanh, sự linh động của cấu trúc, và dễ chế tạo. Chúng ta sẽ xét những vật liệu hữu cơ có tính chất quang phi tuyến bậc 3 lý thú để minh họa tầm quan trọng của mối liên hệ giữa cấu trúc và đặc tính.

Chúng ta sẽ trình bày kết quả nghiên cứu trên các vật liệu hữu cơ nổi trội bao gồm chất lỏng, thuốc nhuộm, fuloren, phức chất chuyển điện tích, polime liên hợp π, polime ghép thuốc nhuộm, hợp chất hữu cơ kim loại, composite và tinh thể lỏng. Vật liệu quang phi tuyến hữu cơ mang lại hàng loạt những ứng dụng và tiềm năng to lớn trong quang học tích hợp cũng đang được nghiên cứu thêm.

1.Giới thiệu
"Laser" là từ viết tắt của khuếch đại ánh sáng bằng cơ chế phát xạ cảm ứng.
Laser đầu tiên được phát triển vào năm 1960 bởi Maiman11 ' sử dụng tinh thể ruby. Một năm sau, Franken và các cộng sự121 đã tiến hành thành công thí nghiệm nhân đôi tần số ánh sáng từ một laser ruby bằng một tinh thể thạch anh. Hiện tượng nhân đôi tần số này được gọi là sự phát sóng hài bậc hai. Những bước đột phá này mở ra hai lĩnh vực nghiên cứu: khoa học laser và quang học phi tuyến. Sự phát triển nhanh chóng trong nghiên

The rapid growth in laser research has provided a variety of lasers that are commercially available today. Indeed, semiconductor diode lasers are the key elements of the optical recording technique used for compact discs and digital audio discs. The selection of materials for semiconductor diode lasers is vital to explore further their uses in optoelectronic technologies. In the first decade of nonlinear optics, research work was focused on inorganic materials, which led to the development of classical materials such as quartz, potassium dihydrogen phosphate (KDP), lithium niobate, cadmium sulfide, cadmium selenide, cadmium telluride, cadmium germanium arsenide, etc. Progress in nonlinear optical (NLO) materials in the past decade was stimulated by the development of organic mate-rials. First, in the 1970s, Davydov etal.[3'4] demonstrated strong second harmonic generation (SHG) from organic compounds having electron donor and acceptor groups attached to a benzene ring. This turning point aroused considerable interest in searching for new organic molecules possessing large second-order optical nonlinearity, which are the most prevalent nowadays. Secondly, in 1976, Stauteret et al.[5] found large third-order optical nonlinearity in polydiacetylene /^-toluene sulfonate (PDA-PTS), which opened new opportunities for studying organic ^-conjugated polymers. Therefore, present research activities in the field of nonlinear optics have been proceeding in two directions: exploration of organic

cứu laser đã cho ra đời nhiều laser thương mại. Thật vậy, laser bán dẫn là một trong những phần tử quan trọng của kỹ thuật ghi quang được sử dụng cho đĩa compact, đĩa âm thanh kỹ thuật số. Việc lựa chọn vật liệu cho laser bán dẫn là quan trọng để tiếp tục khai thác ứng dụng của chúng trong công nghệ quang điện tử. Trong thập kỷ đầu tiên của quang học phi tuyến, các công trình nghiên cứu tập trung vào vật liệu vô cơ, điều này dẫn đầu sự phát triển các vật liệu cổ điển như thạch anh, kali dihydrogen phosphate (KDP),

vào   và
các cộng sự

các nhóm
cho và nhận điện tử

đó
cũng chính là những

và các cộng sự đã phát hiện ra

polymer liên hợp hữu cơ

nghiên cứu tính
chất của

molecular and polymeric materials for second-order and third-order nonlinear optics. Symmetry considerations show that second-order nonlinear optical effects appear only in molecules that lack a center of symmetry, whereas there are no symmetry requirements for third- order nonlinear optical effects. Therefore, a wide variety of materials can be utilized for third-order nonlinear optics. In the past few years, the development of optoelectronic technology has intensified research on novel materials and devices based on them.

This article provides a comprehensive overview of both the fundamentals and materials aspects of third-order nonlinear optical effects. The field of nonlinear optics is extremely interdisciplinary, with expertise in areas such as chemistry, physics, materials science, and optical engineering being re-quired, which makes reviewing it a challenge. It should also be mentioned that the theoretical aspects and processes determining microscopic and macroscopic third-order NLO parameters are not very well understood yet.

The main aim of this review is to summarize the experimental results on third-order nonlinear optical susceptibilities of various classes of organic materials to show the importance of molecular engineering concepts. It is rather difficult to do justice to organic materials in a review of this length, and therefore mainly recent developments and emerging organic materials will be discussed, including organic materials tailor-made for third-order nonlinear

Qua xem xét tính đối xứng ta thấy không có đó ràng buộc nào đối với về cả khía cạnh lý thuyết và khía cạnh vật liệu điều này khiến cho việc tổng quan nó khó khăn Thật khó để đánh giá được toàn diện các vật liệu hữu cơ trong bài tổng quan ngắn này

optics, which range from nanostructures to giant organic polymers. This review briefly surveys organic materials such as liquids, dyes, fullerenes, ==charge-transfer complexes==, composites, NLO-chromophore functionalized polymers, 7r-conjugated polymers, and organometallic compounds, and in particular, the significant progress made in absorbing organic 7t-conju- gated polymers into the field of nonlinear optics and developing relationships between the chemical structure and nonlinear optical properties of organic materials.

Model compounds of low molecular weight and well-defined 7i-con- jugation length have been used to understand the origin of optical nonlinearity. The final section looks beyond the current state of the art to future developments of third-order nonlinear optical organic materials.

2. Nonlinear Optical Phenomena
The electromagnetic field of a laser beam impinging on a material generates an electrical polarization. In the presence of an external electric field E, the microscopic polarization P induced in an atom or a molecule is given by Equation 1, where P and E are related to the tensor quantities a, ft and y referred to as the polarizability, first hyperpolarizability and second hyperpolarizability, respectively. Similarly, the macroscopic polarization

liên hợp π ... hấp thụ đối với

Các

đề cập đến hướng phát triển trong tương lai của vật liệu hữu cơ quang phi tuyến bậc III

Khi có ... độ ... với nhau thông qua các đại lượng ... có tên gọi tương ứng là ... bậc nhất ... bậc hai ... độ phân cực vĩ mô

induced in bulk media can be expanded in a power series in the external field, Equation 2.

…………………..

Here /(", ~/(2\ and x(3) are the first-, second-, and third-order nonlinear optical susceptibilities and have similar meanings as their microscopic counterparts a, [3, and y, respectively. The even tensor xi2} is zero in centrosymmetric media, whereas the odd tensor x(3) does not have any symmetry restrictions and is a non-vanishing higher-order optical susceptibility. '/n) is frequency dependent, and as a result, resonant and non-resonant parameters differ significantly depending upon the measurement frequencies. The general trend of the corresponding macroscopic NLO coefficients can be estimated from the microscopic nonlinear optical counterparts. The microscopic quantities are related to the macroscopic counterparts through local field factors,161 Equations 3-5.

…………………….

N is the number of molecules per volume unit andis the frequency-dependent Lorentz-Lorenz local field factor arising from the difference between the microscopic and macroscopic electric fields. For isotropic media the Lorentz approximation fa is given by Equation 6, where n is the refractive index of the medium. The theoretical expression, Equation 5, is valid for third-harmonic generation. Similar relationships between /3) and y for other NLO processes can be written as in Equation 7.171 The frequency dependence of the third-order susceptibility can also be written as in

trong vật liệu khối cũng có thể khai triển theo

Phương trình 2

các đại lượng vi mô tương ứng

ràng buộc

nào   chính là độ cảm quang học bậc cao không triệt tiêu

Đại

các đại

hệ số   Lorentz phụ thuộc tần số

đối với các quá trình quang phi tuyến khác   biểu diễn qua phương trình   Sự phụ thuộc tần số

Equation 8.181

Therefore, one can estimate the third-order non-linear optical susceptibility from computed second hyperpolarizability values. Table 1 lists nonlinear optical processes related to the third-order nonlinear susceptibility. Optical phenomena such as the Kerr effect, third-harmonic generation, four- wave mixing, and Raman, Brillouin and Rayleigh scattering arise from ym.

Table 1. Nonlinear optical processes related to the input and output frequencies for measuring third-order nonlinear susceptibility

The change of refractive index with light intensity is another aspect of NLO processes. The intensity-dependent nonlinear refractive index n2 can be written as in Equation 9,m where n0 is the linear refractive index, e. and e0 are the dielectric constant of the material and the permittivity of free space, respectively, c is the speed of light, and E the applied field. The relationship between nonlinear refractive index n2 and third-order NLO susceptibility /(3) is given by Equation 9,

where is a diagonal component of /(3) in the x-direction. x(3) is a fourth-rank tensor that has only three independent components X^xxx, X(xJyyi and •

bậc hai tính được

Các

phụ thuộc cường độ ánh sáng

vận tốc

nằm trên

chỉ

$\chi_{xxxx}^{(3)}$, $\chi_{xxyy}^{(3)}$, and $\chi_{xyxy}^{(3)}$

These components are related as \y}^xx = x%y = 7^XJ

$$\frac{1}{3}\chi^{(3)}_{xxxx} = \chi^{(3)}_{xxyy} = \chi^{(3)}_{xyxy}$$

in an isotropic medium far from the resonance for a purely electronic optical nonlinearity and provide significant information about molecular interactions.

$$n = n_0 + \frac{1}{2}n_2 c(\varepsilon\varepsilon_0)^{1/2}\langle\boldsymbol{EE}\rangle$$

$$n_2 = \frac{\chi^{(3)}_{xxxx}}{cn_0\varepsilon_0}$$

3. Factors Affecting /<3)

The **magnitude** of the third-order optical nonlinearity is **governed** by several factors. For example, third-order optical nonlinear susceptibilities determined by using the third-harmonic generation (THG), **degenerate** four-wave mixing (DFWM), optical Kerr gate (OKG), and self-focusing techniques differ greatly from each other due to the distinct nonlinear optical processes and experimental conditions used, such as the measurement wavelength, pulse conditions, laser power, environment, and materials states.

As a consequence, all these factors make a comparison of third-order NLO data rather difficult. Third-order optical nonlinearity values are often **quoted** as resonant and non-resonant values resulting from their

wavelength **dispersion** within or far from the optical absorption regions of a nonlinear optical material. The resonant third-order nonlinear optical susceptibility can be several orders of magnitude larger than the nonresonant value.

An **extensive survey** of the literature on third-order NLO materials leads to the **conclusion** that the claim that a high optical nonlinearity measured by a FWM technique and relatively low values measured by a THG technique can be **reconciled** from the viewpoints of optical processes, or otherwise, should be cautiously evaluated.

From the chemical point of view, third-order optical nonlinearity is very **sensitive** to the length of π-electron conjugation.

In 1977, Ducuing [10] established relationships 11 and 12 between the **delocalization** length L and the number of electrons N.

$$\alpha \propto \frac{L^4}{N} \qquad (11)$$

$$\gamma \propto \frac{L^{10}}{N^3} \qquad (12)$$

For **the one-dimensional system**, $\alpha \propto L^3$ and $\gamma \propto L^7$ since $N \propto L$. On the other hand, for a two-dimensional system, $\alpha \propto L^2$, and $\gamma \propto L^4$ since $N \propto L^2$. Therefore, **polarizabilities** are **significantly affected** by both the delocalization length and by the **dimensionality** of the molecules.

Later on, Rustagi and Ducuing [11] **estimated** a rather different relationship between

bậc ba trình bày trong các tài liệu thường là

bắt nguồn từ

lớn hơn nhiều bậc về độ lớn so với

Khảo sát chuyên sâu trong những tài liệu nghiên cứu về

tương đối

do các quá trình quang học và chúng ta có thể chấp nhận được   cần phải được đánh giá

nhạy với   liên hợp của electron π

thiết lập

Đối với   bởi vì

microscopic polarizabilities and delocalization length for the **one-dimensional free-electron gas model** $\alpha \propto L^3$ and $\gamma \propto L^5$. Similarly, a tight-binding **approximation** also gave a weaker dependence on delocalization length ($\gamma \propto L^6$).

một hệ thức khác

phép gần đúng liên kết chặt
hệ thức thể hiện

Agrawal et al [12] **suggested** that third-order nonlinear susceptibility $\chi^{(3)}$ in **the optically transparent region** follows a sixth-power dependence on the π-electron conjugation length.

$$\chi^{(3)} \propto \left(N_d \right)^6 \qquad (13)$$

điện tử π

Expression 13 is a good approximation for one-dimensional π-conjugated polymers. There N_d is the π-electron delocalization length at the **Brillouin zone edge**.

biểu thức gần đúng tương đối tốt

One-dimensional tight binding theory for infinite-chain conjugated polymers **predict**s a relationship between the energy gap E, and third-order nonlinear susceptibility to be given by expression 14.

chặt

$$\chi^{(3)} \propto \left(\frac{1}{E_g} \right)^6 \qquad (14)$$

This observation suggests that π-conjugated polymeric structures with small band gap are **potentially** useful materials for third-order nonlinear optics. The **role** of various factors such as π-delocalization length, donor-acceptor groups, dimensionality, conformation and **orientation** to $\chi^{(3)}$ will be **illustrated** to show the structure-property relationships.

Từ đây chúng ta thấy rằng

giữa

At molecular level, second **hyper-polarizability** (γ) is directly related to the third-order nonlinear susceptibility $\chi^{(3)}$, and

cấp độ phân tử   bậc
có liên quan trực tiếp với

therefore, theoretical predicition of γ can **shed light** on the magnitude of $\chi^{(3)}$**.** Many quantum chemistry **approaches** (empirical, semi-empirical and ab initio) have been applied to calculate microscopic third-order optical nonlinearities. A wide range of wavelengths, for example from 0.532 μm to 3.0 μm, is **currently available** with different laser systems for measuring third-order nonlinear optical susceptibility.

This broad range of measuring wavelengths facilitates the determination of the resonant and non-resonant contributions to third-order optical nonlinearity of **an individual material**. The measured third-order nonlinear susceptibility should have either a non-resonant value, when there is no absorption in the medium at the fundamental and harmonic wavelengths, or a resonant value, if the nonlinear medium is absorbing close to these wavelengths, which remarkably enhances $\chi^{(3)}$ values. As a consequence, **due to** non-resonant and resonant processes, the magnitude of $\chi^{(3)}$ may **fluctuate** by several orders of magnitude. We have taken the **precaution**, when reporting $\chi^{(3)}$ values, of describing the conditions of the measurement techniques and measurement wavelength **involved** in the different experimental procedures.

4. Optical Nonlinearities of Model Compounds: Theoretical and Experimental Assessments.

Third-order nonlinear optical properties are sensitive to π-conjugation length, and, therefore, a **systematic study** of the relationship between the π-conjugation length of model compounds and their nonlinear optical response is important for a better understanding of the structure-property relationships. Many **attempts** have been

về   giúp chúng ta có chút thông tin về   Các nhà nghiên cứu đã áp dụng nhiều phương pháp hóa lượng tử

đánh giá các tính chất quang phi tuyến vi mô Hiện nay chúng ta có thể đo độ cảm quang phi tuyến bậc ba bằng các hệ laser khác nhau có bước sóng từ 0,532 μm đến 3,0 μm

Dải bước sóng rộng này tạo điều kiện cho việc

từng vật liệu
đo được sẽ

trong môi trường
                                        môi trường
        điều này làm tăng đáng kể các giá trị $\chi^{(3)}$ là do các

    thay đổi

dễ
thay đổi theo

made to **establish** such relationships by studying different **classes** of organic materials. The **static** dipole polarizability and second hyper-polarizability have been calculated [13] **via coupled-perturbed** Hartree-Fock (CPHF) theory for all-trans polyene molecules in the **series** C_4H_6 to $C_{22}H_{24}$ (1).
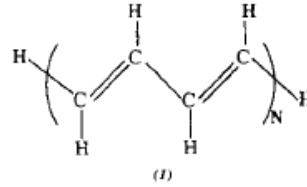

(1)
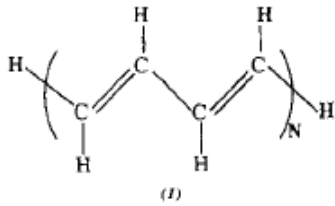
Both α_{xx} and γ_{xxxx} vary with the number of polyene **repeating units N,** increasing significantly with the increase of π-conjugated polyene backbone. The γ values of a $C_{16}H_{18}$ polyene molecule obtained from STO-3G, 6-31G, 6-31G* and 6-31G + PD basis sets were 392074, 808879, 732489 and 976279 **atomic units** (a.u.), **respectively**. The γ value of $C_{20}H_{22}$ polyene is more than an order of magnitude larger than that of $C_{10}H_{12}$ polyene. α_{xx} is **proportional** to $N^{1.40}$ for $N \sim$ 11 and γ_{xxxx} is proportional to $N^{3.98}$ for N ~ 6. The proportionality exponent decreases **sharply** with increasing N, **reducing** to $N^{3.04}$ for $N = 10$ and 11.

The value of static $\chi^{(3)}$ for a poly-acetylene chain from the computed second hyper-polarizability was determined by using Equation 15 [14].

$$\chi^{(3)}(-\omega, \omega_1, \omega_2, \omega_3) = \frac{1}{6} N\gamma(-\omega, \omega_1, \omega_2, \omega_3) f_\omega f_{\omega_1} f_{\omega_2} f_{\omega_3}$$

tiến
hành để thiết lập các

bậc hai

nhiễu loạn liên
kết

dải

(1)

theo
cơ bản

lớn hơn nhiều bậc độ lớn so
với

tĩnh ối với
được tính   bậc   theo

Here N is the number density of molecules and, $f_\omega f_{\omega_1} f_{\omega_2} f_{\omega_3}$ are local field factors; for **isotropic media** Equation 6 holds.

Ignoring the local field factors and using the poly-acetylene **mass density** of 1.2g/cm^3 gives **estimates** for the static χ^C values for a poly-acetylene chain of $4{,}2.10^{-12}$ esu using γ values **obtained** from the 6-31G basis set. The **influence** of the conjugated chain length on the dipole polarizability for trans-1,3,5-hexatriene (2), trans-1,3,5,7,9-decapentaene (3), 1,5-hexadiene-3-yne (4), and 1,5,9-decatriene-3,7-diyne *(5)* was **analyzed** by ab initio CPHF using the STO-3G basis set [15, 16].

For trans-1,3,5-hexatriene-3-yne (2)**,** the α_{xx} and $\langle\alpha\rangle$ were 104.13 and 43.93 a.u. respectively. α_{xx} was 217.25 a.u. for trans-1,3,5,7,9-decapentaene (3) and 44.65 a.u. for 1,5-hexadiene-3-yne (4)**,** and $\langle\alpha\rangle$ was 85.28 a.u. for 1,5,9-decatriene-3,7-diyne (5)**.**

The polarizability of the polyenic backbone is larger because of the more **efficient** delocalization of the π-electrons. The size dependence of α was $N^{1.399}$ and of α_{xx}, $N^{0.958}$.
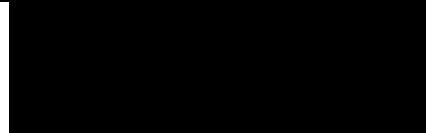
hệ số trường cục bộ luôn đúng

hệ số trường cục bộ

Sự phụ thuộc kích thước của là
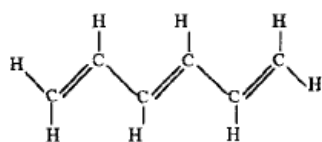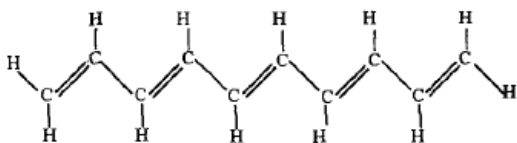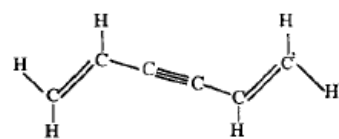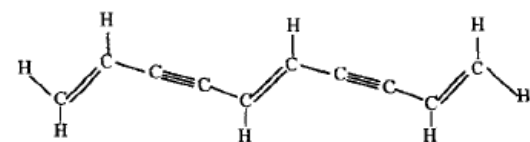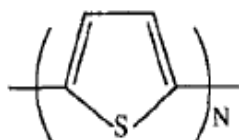
The nonlinear optical properties of a series of α-conjugated thiophene oligomers (α-nT) have been **investigated** to develop structure-property relationships [17]. The α-conjugated thiophene oligomers (number of repeat thiophene units N = 3,4,5,6,8 and so on) have **well-defined** chemical structures and a precise and **controlled** π-conjugation length (6)**.** Second hyper-polarizability and third-order susceptibility of α-nT oligomers increases significantly up to N = 14, while the optical band gap **remains** almost constant after N = 8. The conjugation length dependence of α and γ show exponents of 2.4 and 4.6, respectively, for a series of well-defined conjugated 3-alkyl **substituted**

oligothiophenes $(N = 3,4,5,7,9,$ and 11) [18]. The γ of 3-alkyl substituted oligothiophenes increases up to 11 repeat units, where γ reaches values as high as $4,6.10^{-32}$ esu. The relationship between π-conjugation length and third-order optical nonlinearity for oligomers of polyazine possessing ==terminal electron-donating amino groups== (7) have been reported recently [19-21].

n = 1, 2, 3, 4, or 5

(7)

Figure 1 shows the **optimized geometric structures** in terms of bond lengths and bond angles for the monomer and the trimer azine **derivatives**. The **coordinate** axes x and *z* are **perpendicular** to the π-conjugated polyazine backbone while the y axis is along the **periodicity** direction.

Fig. 1. Optimized geometric structures in terms of bond lengths and bond angles for the monomer (top) and the trimer (bottom) azine derivatives [21].

Table 2 lists the polarizability and second hyper-polarizability **components** of oligomer model compounds of polyazine.

Table 2. Dipole polarizability components of polyazine oligomers obtained from the 6-31G basis set. α is in Å^3 and γ is in 10^{-39} csu units. The orientationally averaged or mean values are $\langle\alpha\rangle = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ and $\langle\gamma\rangle = (1/5)(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})$. The polarizability axes x and z are perpendicular to the π-conjugated backbone while the y axis is along the periodicity direction. N is the number of repeat units in the polyazine chain [21].

Polarizability component	$N=1$ ($C_2H_6N_4$)	$N=2$ ($C_4H_8N_6$)	$N=3$ ($C_6H_{10}N_8$)	$N=4$ ($C_8H_{12}N_{10}$)	$N=5$ ($C_{10}H_{14}N_{12}$)
α_{xx}	9.08	18.15	26.17	59.60	76.55
α_{yy}	12.48	26.74	44.90	38.92	49.93
α_{zz}	2.41	4.08	5.73	7.39	9.04
$\langle\alpha\rangle$	7.99	16.32	25.60	35.30	45.18
γ_{xxxx}	−683.78	−2159.60	−2668.91	4158.13	12408.28
γ_{xxxy}	−546.35	1143.35	5367.33	28984.31	53186.15
γ_{xxyy}	1086.58	10822.83	29905.89	82439.56	136635.93
γ_{xxzz}	26.76	82.20	144.47	238.30	326.10
γ_{xyyy}	4044.19	30953.39	87658.16	185471.50	293127.52
γ_{xyzz}	7.4391	44.43	105.04	167.33	238.89
γ_{yyyy}	15223.04	79003.62	228382.78	390404.00	592887.31
γ_{yyzz}	−16.83	6.75	62.30	106.97	168.91
γ_{zzzz}	12.73	20.47	27.87	35.34	42.49
$\langle\gamma\rangle$	3349.00	19737.6	57193.41	112033.43	175919.99

The oligomeric polyazine derivatives having 1, 2, 3, 4, and 5 repeat units **exhibit** orientationally averaged $\langle\gamma\rangle$ values of $3{,}34.10^{-36}$, $1{,}97.10^{-35}$, $5{,}71.10^{-35}$, $1{,}12.10^{-34}$ và $1{,}75.10^{-34}$ esu, respectively. The γ values increase by a factor of 6 in going from the monomer to the dimer and by a factor of 17 in going from the monomer to the trimer. The γ value increases by a factor of more than 53 from the monomer to the pentamer polyazine derivative. For the pentamer of polyazine, the estimated chain length is about $35\,\overset{0}{A}$. The increase of γ_{yyyy}, **obeys** an $N^{3.2}$ power law for 3 repeat units ($N = 3$) and then reduces to $N^{3.0}$ for $N = 4$. The orientationally averaged $\langle\gamma\rangle = (1/5)(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})$ obeys an $N^{3.35}$ simple power law for $N = 3$, then reduces to $N^{3.2}$ for $N = 4$ and $N^{3.07}$ for $N = 5$. The increase of α_{xx} obeys $N^{1.66}$ for $N = 5$ and $N^{1.60}$ for $N = 4$, while the orientationally averaged $\langle\alpha\rangle = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ obeys $N^{1.33}$ for $N = 5$, $N^{1.35}$ for $N = 4$, and $N^{2.14}$ for $N = 3$.

Theoretical studies predict a power-law

có giá trị   trung bình theo hướng lần lượt là

lần   tăng lần

hơn 53 lần

quy luật hàm mũ   đối với 3 đơn vị lặp lại

theo

quy luật hàm mũ

quy luật

theo

length dependence of α with an exponent ranging from 1.3 to 3.0 and of γ with an exponent from 3.2 to 5.2, and thus these results on well-defined chain length polyazine are in **agreement**. The averaged γ values of polyazine derivatives were **found** to be larger than those of **regular** polyenes having equivalent numbers of **double bonds**. Second hyper-polarizabilities for regular, and donor-acceptor disubstituted polyenes, poly-diacetylenes and related **species** for **low-lying excited states** have been studied using the CNDO/S-CI method (complete neglect of differential overlap/spectroscopic configuration interaction) [22].

The chemical structures of the monomers of polyacetylene and polyazine having terminal electron-donating amino groups are **illustrated** (8, 9).

$\gamma = 1.86 \times 10^{-36}$ esu $\gamma = 15.2 \times 10^{-36}$ esu

(8)   (9)
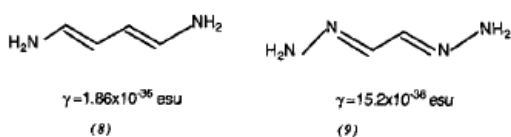
Our studies on polyazine derivatives show that the γ values are at least two orders of magnitude larger than those of regular polyenes ($\gamma = 8{,}87.10^{-37}$ esu) and one order of magnitude larger than those of diamino **substituted** polyenes of the **identical** π-electron delocalization length systems. The log-log plot of γ_{zzzz} **versus** the number of carbon-atom sites yields an exponent of 3.64 for diamino substituted polyenes, which is close to our results on diamino polyazine chains. **Presumably** the presence of the polarizable nitrogen atoms in the conjugated backbone, such as in poly-methineimine and polyazine, plays a **major** role in enhancing optical nonlinearities. The second hyper-polarizabilities of polyenes should begin to
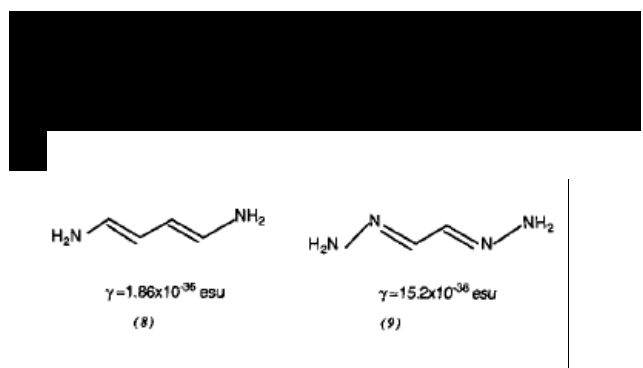
saturate at some length shorter than $60 \overset{0}{A}$, which is **equivalent** to 50 carbon sites for trans-polyene [23, 24]. For large values of third-order optical nonlinearities, chains of **intermediate** length of the order of $100 \overset{0}{A}$, should be **sufficient** and any increment beyond this limit would not be that **significant**. This view was further **supported** by the fact that the maximum optical nonlinearities could be obtained for relatively short oligomeric conjugated **segments** of polyene [25]. The second hyper-polarizabilities of trans-polyenes were found to increase **rapidly** up to 10-15 repeat units and then more slowly up to 40 repeat units. Our studies on the oligomers of polyazine also show that second hyper-polarizability **as well as** third-order nonlinear optical susceptibility do not show any saturation up to the heptamer, and more repeat units are **required** to **optimize** the optical nonlinearity [19-21].

Similarly, third-order optical nonlinearity of thiophene oligomers increases significantly up to $N = 14$, while the optical band gap begins to saturate after $N = 8$ [17, 18]. Computational and experimental studies on a variety of sequentially built oligomers and their corresponding polymers, such as polyenes, poly-yens, polythiophenes, and polyazines, support the view that the magnitude of optical nonlinearity increases with increasing π-electron delocalization length up to an **intermediate chain length** and very long conjugated structures are not **necessary** for large optical nonlinearity.

5. Organic Materials for Third-Order Nonlinear Optics.

sự tăng quá giới hạn này sẽ không có ý nghĩa Quan điểm này được củng cố qua việc

Người ta nhận thấy rằng bậc hai

bậc hai cũng như bão hòa cho đến cần nhiều đơn vị lặp lại hơn để hóa học

của electron π

5.1. Organic Liquids.

The third-order nonlinear susceptibility and hyperpolarizabilities of benzene and stilbene derivatives have been measured to **examine** the effect of π-conjugation length and donor-acceptor groups on optical nonlinearity [26]. The γ values were found to be $1{,}8.10^{-36}$, 51.10^{-36}, 11.10^{-36}, $12{,}2.10^{-36}$, và $15{,}2.10^{-36}$ esu for benzene, nitrobenzene, aniline, benzonitrile and N,N'-dimethylaniline, respectively. The 4-dimethylamino-4-nitrostilbenme olecule shows a hyperpolarizability of 17.10^{-33} esu because of its large π-conjugated system, larger than that of p-nitroaniline ($\gamma = 1{,}0.10^{-33}$ esu). This also **indicates** that large optical nonlinearities can be obtained by introducing electron donor and acceptor groups into a conjugated system. The third-order nonlinear properties of a number of conjugated and non-conjugated organic molecules were investigated to **examine** the effect of the non-conjugated bond additivity on third-order nonlinear properties [27].

Kajzar and Messierr [28, 29] reported the bond-additivity model and the validity of local field factors. The γ values for C-H, C-C, C-Br, and C-I bonds were $2{,}0.10^{-37}$, $1{,}18.10^{-37}$, $7{,}72.10^{-37}$, $13{,}59.10^{-37}$ và $30{,}61.10^{-37}$ esu, respectively. Third-order optical nonlinearities of several **neat** organic liquids were measured by optical third harmonic generation [30]. Table 3 lists the parameters of $\chi^{(3)}$ for various liquids. It is apparent from the **analysis** of the third-order nonlinear parameters of a variety of organic liquids that $\chi^{(3)}$ is **strongly influenced** by the number of carbon atoms, substituents, donor-acceptor functionalities and π-electron systems incorporated in organic molecules

những dẫn xuất

donor-acceptor đến   học

có

là

đánh giá   việc thêm liên kết
không liên hợp đến   quang
bậc ba

hệ số
trường cục bộ   liên kết

đã

được xác định bằng phương pháp

các nhóm thế các nhóm chức donor-

and, in particular, the last two factors play the major role.

Table 3. Third-order nonlinear optical properties of some standard material showing the effect of bond additivity, conjugation and substitution on third order optical nonlinearity [27, 30].

Compound	$\chi^{(3)}$ [10^{-14} esu]	γ [10^{-36} esu]
Benzene	6.33	2.34
Carbon tetrachloride	5.20	2.29
Carbon disulfide	17.8	3.19
1,2-Dichloroethane	12.0	3.39
Methane	-	0.42
Hexane	2.63	2.03
Heptane	2.88	2.40
Dodecane	4.16	4.88
Nitromethane	8.98	1.92
1-Nitropropane	8.26	2.84
2-Nitropropane	6.32	2.76
Nitrocyclohexane	11.3	4.50
Methyl iodide	33.3	6.16
Methylene iodide	48.3	7.32
p-Xylene	5.94	3.08
Toluene	6.80	2.99
o-Diiodobenzene	24.2	6.12
Pyridine	20.6	4.97
o-Fluoronitrobenzene	169.0	45.3
m-Fluoronitrobenzene	107.0	31.4
p-Fluoronitrobenzene	104.0	30.8
Methanol	2.86	0.80
Ethanol	3.65	1.33
2-Propanol	4.11	1.88
2-Propanone	4.41	2.04
Tetrahydrofuran	5.03	2.24
Methylcyclohexane	5.93	3.97
Chloroform	6.73	3.09
Carbon disulfide	23.0	4.4

5.2 Organic Molecular Solids.

In 1973, Hermann et al [31] found that the optical nonlinearities in conjugated trans-β-carotene were three orders of magnitude larger than that of benzene. Conjugated systems of allo-ocimene, trans-retinol, trans-retinal, *trans-β-caro*tene, and dodecapreno-β-carotene that possess 3, 5, 6, 11 and 19 double bonds in their backbone were also studied. The γ values of allo-ocimene and dodecapreno-β-carotene were $9,7.10^{-36}$ esu and $1,7.10^{-32}$ esu, respectively, showing a strong influence of extended delocalized π-electrons on optical nonlinearity. These

studies demonstrate that the third-order nonlinear susceptibility **varies remarkably** with the length of the π-electron system.

Third-order optical nonlinearities of asymmetric carbocyanine dyes (1,1',3,3,3',3'-hexamethyl-2,2'-indotricarbocyanine iodide, 3,3'-diethyl-2,2'-oxotricarbocyaninei odide and 3,3'-dimethyl-2,2'thiatricarbocyanine iodide) were investigated using the DFWM technique [32]. These asymmetric dyes have very large hyper-polarizabilities and the **converted** γ value gives χ^{C} of the order of 3.10^{-8} esu for a 0,1mol/l solution of benzothiazole derivative. The influence of **molecular aggregation** on optical nonlinearity was evaluated from merocyanines [33].

The spin-coated thin films of 3-carboxymethyl - 5 - [2 - (3 - octadecyl - 2 - benzothiazoliny1idene) - ethylidenelrhodanine (referred to as MCS, X = S in **10)** and 3 -carboxymethyl-5 -[2- (3 - 0ctadecyl-2- benzoselenazolinylidene) ethylidene]rhodanine (referred to as MCSe, X = Se in **10)** change their color from red to **bluish purple** when kept in ammonia atmosphere at 60^{0}C for 12h. The **formation** of **J-aggregates** was **evidenced** by the appearance of a new **sharp absorption peak** at 612nm. The χ^{C} values for J-aggregated MCSe films were found to be 3 times larger in the non-resonant region and 10 times larger at resonant frequencies than those of non-aggregated films. Therefore J-aggregation seems to be an effective method of enhancing χ^{C} values.

kể

các thuốc nhuộm không đối xứng

khảo sát bằng

bất đối xứng này

nghịch đảo sẽ cho ra có giá trị đối với

đến cũng được nghiên cứu trên chất

chế tạo bằng phương pháp bằng vật liệu

chứng minh qua sự xuất hiện mới, sắc nét bước sóng

hơn

giúp tăng cường hiệu quả
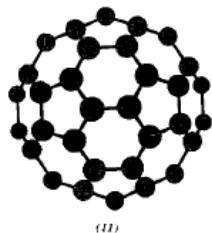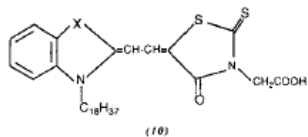
The **highly stable** icosahedral-cage fullerene molecule C_{60} is a new form of carbon which has a soccer ball structure (11)**.** In C_{60} all the atoms are connected by sp^2 bonds and the remaining 60 π-electrons are distributed such that the C_{60} molecule has a highly **aromatic** character [34, 35]**.** C_{60} seems an ideal **candidate** for third-order nonlinear optics because of its interesting π-conjugation. Table 4 lists the third-order nonlinear optical susceptibility and hyperpolarizability of fullerenes measured by different research groups.

Blau et al [36] reported for the first time the $\chi^{(3)}$ and hyperpolarizability of a solution of C_{60} in benzene at 1.064µm using DFWM. $\chi^{(3)} = 6.10^{-8}$ esu was **derived** in the solid state for C_{60} at 1.064µm. The $\chi^{(3)}$ of $2,6.10^{-12}$ esu for a C_{60} toluene solution of 7.10^{-3} mol/l was measured, which gave molecular hyperpolarizability γ of $1,6.10^{-31}$ esu from $\gamma = \chi^{(3)}/(NL^4)$ [38]. The $\chi^{(3)}$ of $3,3.10^{-9}$ esu for the solid C_{60} compound was **deduced** from the **corresponding** C_{60} toluene solution using a density of $1.6 g/cm^3$ and **refractive index** of 2.0. The $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ value of 2.10^{-10} esu for C_{60} thin films at 1.064µm [40] and $\sim 2.10^{-11}$ esu at 1.907µm were measured from THG.
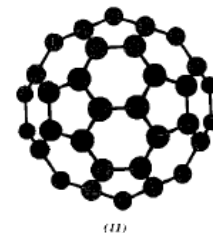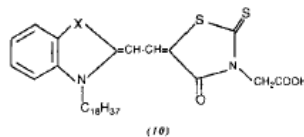
phân bố sao cho

lí tưởng

bằng phương pháp Họ rút ra được

ở bước sóng

Qua phép đo THG, ta được

Kafafi et al [43] conducted time-resolved DFWM experiments on pure C_{60} films vapor deposited onto optical substrates using a 35ps Nd:YAG laser at 1.06µpm. A χ^{C} value of 7.10^{-12} esu was determined and the χ^{C}/α relationship gave a figure of merit of $\sim 1.10^{-12}$ esu/cm.

đã tiến hành thí nghiệm phân giải thời gian chế tạo bằng phương pháp lắng đọng chân không trên các để quang học

cho hệ số phẩm chất

The α value of $7,79.10^{-23}$ cm^3 and γ value of $15,9.10^{-36}$ esu for C_{60} were obtained from local density functional calculations [46]. The calculated γ values of C_{60} of $17,2.10^{-36}$ esu with MNDO (modified neglect of diatomic overlap) and $22,4.10^{-36}$ esu from AM1 parametrization were similar to the PM-3 value [47]. The estimated γ and α values were, respectively, $21,4.10^{-36}$ esu and $6,39.10^{-23}$ esu for C_{60} and $35,6.10^{-36}$ cm^3 and $7,9.10^{-23}$ cm^3 for C_{70}. The average α per carbon atom in C_{70} was found to $0,113.10^{-23}$ cm^3 higher than that in C_{60} ($0,107.10^{-23}$ cm^3).

Theo tính toán hàm mật độ cục bộ,

tính được

phương pháp bỏ qua sự xen phủ nhị nguyên tử hiệu chỉnh bằng theo phương pháp giống tính được

However, controversies remain about the magnitude of χ^{C} and γ, since the magnitude of nonlinearity fluctuates by several orders depending upon the material state, the wavelength used for the measurement, and the technique employed. Both χ^{C} and γ values of C_{60} and C_{70} range over 3 orders of magnitude. C_{70} has more quasi-free electrons, which gives rise to a larger optical nonlinearity than for C_{60}.

vẫn là vấn đề gây tranh cãi sự thay đổi vài bậc độ lớn

đều thay đổi

hơn

5.3 Organic Charge-Transfer Complexes.

The carrier density and delocalization are high in organic charge-transfer complexes and this encourages the study of their third-

Mật độ hạt tải điện và sự bất định xứ đều thúc đẩy chúng ta

order nonlinear optical properties. $\chi^{(3)}$ of the order of $\sim 5.10^{-8}$ esu at 650nm wavelength was measured by DFWM [48] for the one-dimensional complex α-[bis-(ethylenedithio)tetrathiofulvalene] triiodide) (BEDT-TTF)$_2$I$_3$ (12 is BEDT-TTF). The optical nonlinearity also showed strong dependence upon the measurement wavelength. (BEDT-TTF)$_2$I$_3$ is a two-dimensional charge-transfer complex and has a segregated stack structure in which donor (BEDT-TTF) and acceptor (iodine) from separate donor and acceptor stacks.

(12)
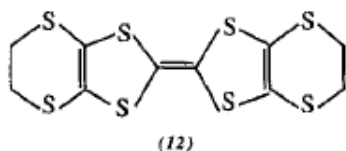
quang phi tuyến
Bằng phương pháp DFWM [48], chúng ta xác định được khoảng trong chiều

phụ thuộc rất nhiều vào bước sóng

chiều
đó

(12)
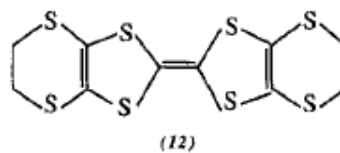
The third-order nonlinear optical properties of organic charge-transfer complexes possessing a mixed structure in which organic electron donors and acceptors stack alternately plane to plane have been tudied [49]. The THG intensities of perylene/tetracyanoethane (TCNE) and perylene/7,7,8,8-tetracyanoquinodimethane (TCNQ) complexes were found to be 4.1 and 2.4 times larger than those of polydiacetylene p-toluene sulfonate (PTS). No noticeable THG intensities were recorded in pure perylene, TCNE and TCNQ molecules but charge-transfer complex formation led to large third-order optical nonlinearities.

The THG intensity of charge-transfer complexes varies with the particle size and

Trong công trình [49], các tác giả đã nghiên cứu

gồm các bó cho và nhận electron hữu cơ xếp theo từng mặt phẳng. Theo tính toán,

không đáng kể
các

làm cho sự
phi tuyến quang học bậc ba lớn

the pump-light wavelength. Typical $\chi^{(3)}$ values of the order of 10^{-13} esu for perylene/TCNE, pyrene/TCNE and naphthalene/TCNE complexes were measured in tetrahydrofuran (THF), taking carbon disulfide as a reference [50]. The estimated $\chi^{(3)}$ values are three to four orders of magnitude larger than the $\chi^{(3)}$ value of CS$_2$. Table 5 lists $\chi^{(3)}$ and γ for several charge-transfer complexes.

Table 5. $\chi^{(3)}$ and γ for charge-transfer complexes [49,50].

Complex	THG intensity ($\times$PTS)	$\chi^{(3)}$ [10^{-10} esu]	γ [10^{-33} esu]
Naphthalene/TCNE	0.6	1.3	7.2
Perylene/TCNE	4.1	10	58
Pyrene/TCNQ	0.4	2.3	12

The THG intensity of the perylene/TCNE complex is a factor of 100 larger along the charge-transfer axis than perpendicular to the charge transfer axis, indicating the anisotropy of the third-order optical nonlinearity. The charge-transfer complexes form an interesting class of NLO materials because of their large optical nonlinearity.

5.4 Organic π-Conjugated Polymers.

A major development of NLO polymeric materials occurred in the 1980s, when the field of organic conjugated polymers was also developing [51]. Both theoretical and experimental results demonstrate that highly conjugated π-electron systems display large third-order optical nonlinearity. For this reason, organic π-conjugated polymers have attracted much attention in the field of nonlinear optics.

Polydiacetylenes (PDAs) are conjugated

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bước sóng ánh sáng bơm vào đối với các đo được làm chuẩn tính được bậc

Table 5. $\chi^{(3)}$ and γ for charge-transfer complexes [49,50].

Complex	THG intensity ($\times$PTS)	$\chi^{(3)}$ [10^{-10} esu]	γ [10^{-33} esu]
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Perylene/TCNE	4.1	10	58
Pyrene/TCNQ	0.4	2.3	12

theo hướng trục chuyển điện tích lớn hơn một trăm lần so với theo hướng vuông góc với trục chuyển điện tích thể hiện tính bất đẳng hướng của hiệu ứng phi tuyến quang học bậc ba hình thành nên một lí thú học

polymers prepared by the solid-state polymerization of diacetylene monomers. Polydiacetylene backbones have a structural formula, R_1-C=C-C=C-R_2 where R_1 and R_2 refer to the substituent side groups (13-27).
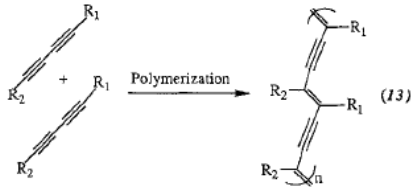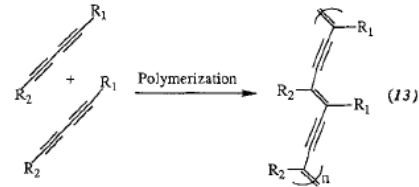

$$R_1 = R_2 = -CH_2-O-SO_2-C_6H_4-CH_3 \quad \text{(PTS)} \quad (14)$$
$$-CH_2-SO_2-C_6H_4-OCH_3 \quad \text{(MBS)} \quad (15)$$
$$-CH_2-O-CO-NH-C_6H_5 \quad \text{(HDU)} \quad (16)$$
$$-(CH_2)_4-O-CO-NH-C_6H_5 \quad \text{(TCDU)} \quad (17)$$
$$-(CH_2)_3-O-CO-NH-CH_2-COO-C_nH_{2n+1} \quad (n\text{-BCMU}) \quad (18)$$
$$-(CH_2)_4-O-CO-NH-C_6H_4-Br \quad \text{(4-PBrPU)} \quad (19)$$
$$-(CH_2)_4-O-CO-NH-(CH_2)_{n-1}-CH_3 \quad (C_4UC_n) \quad (20)$$
$$[CH_3-(CH_2)_{15}-C\equiv C-C\equiv C-(CH_2)_8-COO]_2Cd$$
$$\text{(AFA monomer)} \quad (21)$$
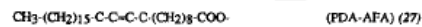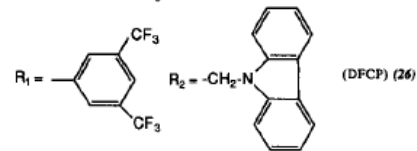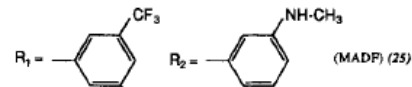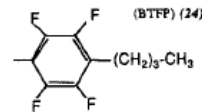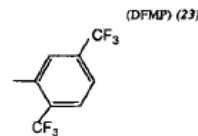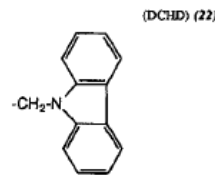
(DCHD) (22)

(DFMP) (23)

(BTFP) (24)

$R_1 = $; $R_2 = $ (MADF) (25)

$R_1 = $; $R_2 = -CH_2-N$ (DFCP) (26)

$CH_3\text{-}(CH_2)_{15}\text{-}C\text{-}C\text{=}C\text{-}C\text{-}(CH_2)_8\text{-}COO\cdot$ (PDA-AFA) (27)

In the polymeric system, the conjugated carbon backbone holds the key for interesting nonlinear optical properties, while the side groups provide structure control and facilitate materials processing. The long alkyl chain

side groups attached to the π-conjugated backbone of the diacetylene monomers, such as in urethane (-O- CONH -), have two advantages: first, they participate in the van der Waals interactions between monomers, and secondly, the incorporated urethane groups lead to a planar structure on polymerization by forming hydrogenbonds between adjacent side groups.

The architectural flexibility resulting from modifying the chemical structures of substituted side groups allows PDAs to be prepared in the form of single crystals, Langmuir-Blodgett (LB) monolayers, thin films, and solutions. Some representative examples of diacetylene polymers.

$$\left(\begin{array}{c} \overset{\parallel}{C}-C{\equiv}C-\overset{\parallel}{C} \\ R_1 \qquad R_2 \end{array} \right)_n \text{ are depicted.}$$
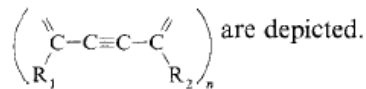
The nonlinear optical properties of PDAs have been investigated by a number of research groups. Table 6 lists the third-order nonlinear optical susceptibilities of a variety of polydiacetylenes; $\chi^{(3)}$ values as high as 10^{-5} esu can be obtained.

Table 6. $\chi^{(3)}$ for polydiacetylenes.

Polymer	$\chi^{(3)}$ [10^{-10} esu]	Experimental technique[a]	Ref.
PDA-PTS (single crystal)	8.5	THG	5
PDA-TCDU (single crystal)	1.6	THG	5
PDA-PTS	90.0	DFWM	52
PDA-PTS	2×10^5	SA	53
PDA-AFA (LB film, blue)	0.56	THG	54
PDA-AFA (LB film, red)	0.08	THG	55
PDA-AFA (thin film)	4.3	EFISH	56
PDA-4-BCMU (thin film)	1.5	EFISH	57
PDA-4-BCMU (red gel)	0.13	DFWM	58
PDA-4-BCMU (thin film)	1.0	THG	59
PDA-5-BCMU (thin film)	2.4	THG	59
PDA-3-BCMU	9.0	DFWM	58
PDA-DCH (thin film)	0.7	THG	60
PDA-DCH (oriented film)	6.0	THG	61
PDA-C₄UC₄ (oriented film)	17.0	THG	62
PDA-BTFP (thin film)	1.2	THG	63
PDA-DFMP (thin film)	0.4	THG	63
PDA-DFCP (thin film)	1.1	THG	63
PDA-MADF (thin film)	8.0	THG	64

[a] SA: saturation of absorption.

The value of $\chi^{(3)}$ for PDAs varies by 5 orders of magnitude depending upon the material, measurement wavelength and technique.

The $\chi^{(3)}$ values of for single crystals of PDA-PTS (14) and PDA-TCDU (17) at 1.89pm are, respectively, $8,5.10^{-10}$ and $0,7.10^{-10}$ esu [5].

bước sóng

$\chi^{(3)}$ of PDAPTS varies with the measurement wavelength from 9.10^{-9} esu at 6515 $\overset{0}{A}$, to 5.10^{-10} esu at 7015 $\overset{0}{A}$ [52]. The response time of the non-resonant $\chi^{(3)}$ is less than 300fs.

nhỏ

At resonance, at 1.99eV, saturation of absorption gave Im $\chi^{(3)}$ of 2.10^{-5} esu for PDA-PTS [53], the largest resonant third-order optical nonlinearity observed so far.

đó là   lớn nhất cho đến thời điểm này

Polyacetylene is one of the most interesting π-conjugated one-dimensional polymers that has trans (28) and cis-isomers (29).

A comparison of $\chi^{(3)}$ in the two isomers indicates that the third-order susceptibility of cis-$(CH)_n$ is more than an order of magnitude (15-20 times) smaller than that of *trans-*$(CH)_n$ as measured on the same.

chúng ta thấy nhỏ hơn một bậc độ lớn đo trong

The difference in $\chi^{(3)}$ for the two isomers results from the fundamental change in polymer symmetry.

là do những thay đổi cơ bản

The magnitude of $\chi^{(3)}$ was $8,1.10^{-9}$ esu at

1.06μm in polyacetylene oriented films, larger than that of a non-oriented sample [66].

Eteinad and Baker [67] measured the $\chi^{(3)}$ spectrum of polyacetylene down to 0.38eV (3.3pm) using an infrared free-electron laser. $\chi^{(3)}$ increases at 0.59eV (2.1pm), reaching 10^{-8} esu, and this is claimed to be the largest electronic $\chi^{(3)}$ in the transparent gap region of any semiconductor.

Poly(ketene), in which the hydrogens of polyacetylene are replaced by hydroxy groups, has a third-order susceptibility of $1,15.10^{-9}$ esu at 532nm [68].

The substitution of a phenyl ring, i.e., poly(phenyl acetylene), PPA, exhibits $\chi^{(3)}$ in the range of $1,2.10^{-12}$ esu, and further substitution at the phenyl ring also increases $\chi^{(3)}$ significantly [69].

The $\chi^{(3)}$ values vary by an order of magnitude according to the substituents. An o-trimethylsilyl-substituted poly(phenyl acetylene) shows a maximum value of about 10^{-11} esu, about an order of magnitude larger than that of one with a phenyl substituent (10^{-12} esu).
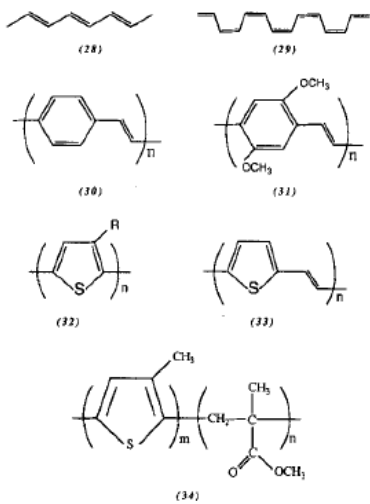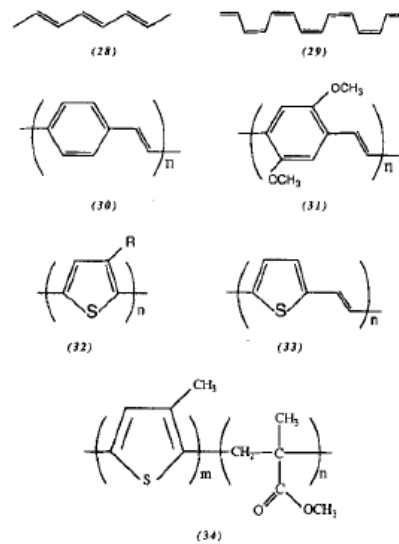

(28) (29) (30) (31) (32) (33) (34)

The effect of increasing π-electron conjugation on χ^{C} of poly(p-phenylenevinylene) PPV (30) has been studied [70].

Thermal conversion of the sulfonium polyelectrolyte precursor at 300°C and 300°C under vacuum for a period of 3h forms PPV polymers that exhibit χ^{C} values of $1{,}6.10^{-11}$ and $7{,}5.10^{-11}$ esu, respectively.

The χ^{C} values in highly oriented poly(2,5-dimethoxy-p- phenylenevinylene) M O-PPV (31) LB films parallel and perpendicular to the orientation axis were $2{,}9.10^{-9}$ esu and $0{,}75.10^{-10}$ esu respectively, at 1.064pm [71].

χ^{C} is $0{,}32.10^{-10}$ esu for an unoriented film, which is about 10 times smaller than that of an oriented MO-PPV film. NLO studies on PPV show that, as in polydiacetylene and polyacetylene, the chain orientation is effective in enhancing the magnitude of third-order optical nonlinearity.

Polythiophene is another conjugated polymer that has created much interest because of its good environmental stability compared to polyacetylenes.

Table 7 lists the third-order optical nonlinearities of a number of poly(3-alkylthiophenes) (32) with alkyl chain ranging from methyl (CH_3) to dodecyl ($C_{12}H_{25}$) and copolymers of polythiophenes.

The polythiophene exhibits a χ^{C} value of about 3.10^{-11} esu at 1.06pm, while the optical susceptibility in the resonant region is about two orders of magnitude larger than that of

Công trình [70] đã nghiên cứu của sự tăng liên hợp electron π đến

áp suất trong không có là

là và

bằng ối với khoảng cũng như trong giúp tăng cường có hiệu quả của hiệu ứng quang phi tuyến bậc ba

cũng được các nhà nghiên cứu rất quan tâm do độ bền trong môi trường

Polythiophene có vào khoảng ở bước sóng 1,064pm

the non-resonant value [72].

Table 7. $\chi^{(3)}$ of polythiophenes and its copolymers.

Polymer [a]	$\chi^{(3)}$ [10^{-10} esu]	Wavelength [μm]	Experimental technique	Ref.
Poly(thiophene)	10.0	0.532	DFWM	72
(R =) H	3.52	1.907	THG	73
R = CH$_3$	0.48	1.50	THG	74
R = C$_6$H$_5$	0.81	1.50	THG	74
R = C$_4$H$_9$	0.20	1.30	THG	75
R = C$_{12}$H$_{25}$	5.0	0.602	DFWM	76,77
PTV	0.32	1.85	THG	78
PBTBQ	2700.0	0.532	DFWM	79
P(3-MeTH/MMA)	0.07	0.602	DFWM	81
PT-PAN	4.0	0.532	DFWM	82

[a] PBTBQ: poly(α-[5,5'-bithiophenediyl]benzylidene-*block*-α-[5,5'-bithiophenequinodimethanediyl]); PTV: poly(thienylvinylene); PT-PAN: poly(thiophene-aniline) copolymer; P(3-MeTH/MMA): copolymer of 3-methylthiophene and methylmethacrylate.

Several copolymers of polythiophenes have also been investigated for third-order NLO effects.

Poly(thiophenevinylene), PTV (33), which consists of thiophene and acetylenic units, exhibits amaximum $\chi^{(3)}$ of 0,3.10^{-10} esu at 1.85pm [78].

A copolymer of polythiophene poly(α-[5,5'-bithiophenediyl]- benzylidene-block-α-[5,5'-bi thiophenequinodimethanediyl]) PBTBQ showed a $\chi^{(3)}$ of 2,7.10^{-7} esu [79].

Polythiophenes are intensely colored materials and therefore random copolymers of 3-methylthiophene and methylmethacrylate (34) were synthesized [80].

A yellow copolymer consisting of conjugated 3-methylthiophene and non-conjugated methylmethacrylate segments shows a $\chi^{(3)}$ value of 7.10^{-12} esu at 602nm [81].

The $\chi^{(3)}$ value of the red copolymer was

measured as $8,7.10^{-11}$ esu, one order of magnitude larger than that of the yellow copolymer under similar measurement conditions.

Although the nonlinear optical responses are somewhat restrained in the copolymer system due to the presence of non-conjugated methylmethacrylate segments, copolymerization leads toward the desired optical transparency.

A copolymer of thiophene and aniline showed third-order susceptibility in the range of 4.10^{-10} esu [82].

The third harmonic response of amorphous poly(3-methyl-4-octyl-2,2'-bithiophene-5,5'-diyl), P3MOT, was measured as a function of wavelength and film thickness [83].

The $\chi^{\mathbb{C}}$ value was found to decrease from $4,4.10^{-11}$ esu at 2.4pm to $1,8.10^{-11}$ esu at 1.06pm. P3MOT showed a laser damage threshold of 30MW/cm^2.

Heteroaromatic ladder polymers constitute another interesting class of π-conjugated polymers that show hightemperature stability and environmental stability [84, 85].

A non-resonant $\chi^{\mathbb{C}}$ value of $1,5.10^{-11}$ esu for the BBL polymer 35 was measured by DFWM at 1.064µm, which is three times larger than that of the semiladder BBB polymer (36) [86].

(35)

(36)
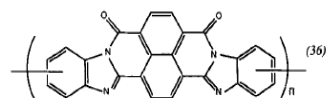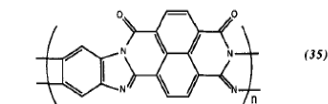
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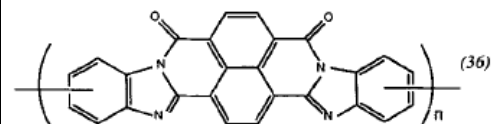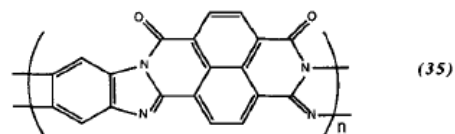hợp quá trình đồng trùng hợp

có vào khoảng

vô định hình theo

Chúng ta thấy

có ngưỡng hủy hoại laser

vòng thơm tạo thành một lớp hợp có

bán

(35)

(36)

The difference observed in optical nonlinearity of BBL and BBB polymer results from the coplanarity arising due to the different structural features, which in turn affect π-electron delocalization.

Table 8 lists the third-order optical susceptibility tensors and refractive indices of polyquinoxaline-based aromatic conjugated ladder polymers (37) [87].
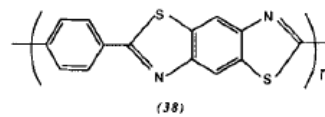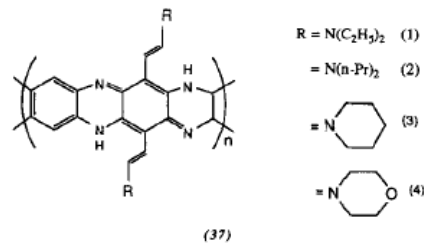
Table 8. Third-order nonlinear optical properties of polyquinooxaline-based ladder polymers [87].

Polymer	$\chi^{(3)}_{1111}$ [10^{-10} esu]	$\chi^{(3)}_{1221}$ [10^{-10} esu]	Refractive index
1	9.78	1.8	1.96
2	8,90	1.9	1.92
3	7.40	1.6	1.92
4	15.5	3.0	1.92

The dispersion of the $\chi^{(3)}$ of thin films of poly(ppheny1enebenzobisthiazole), PBZT (38), and its molecular composites with nylon 66, and poly(trimethylhexamethylene), PTMHT, has been reported [88].

Poly(p-phenylenebenzobisthiazole), PBZT, shows $\chi^{(3)}$ values of $6,0.10^{-12}$ esu.
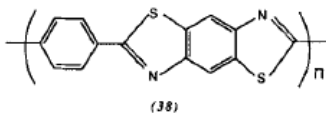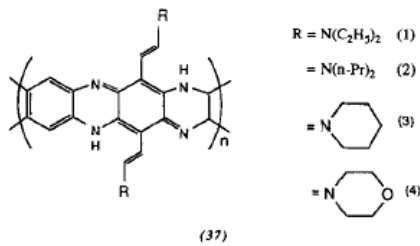
The PBZT/nylon 66 composite shows a linear behavior that is proportional to the mole fraction of the conjugated PBZT polymer. At

50 mol.- %, the $\chi^{(3)}$ of BPZT/PTMHT composite was more than *50%* larger than the corresponding PBZT/nylon 66 composite.

Table 9 summarizes the third-order NLO parameters of n-conjugated polymers.

Table 9. Third-order nonlinear optical properties of π-conjugated polymers

Polymer	$\chi^{(3)}$ [10^{-10} esu]	Wavelength [μm]	Experimental technique	Ref.
Polyacetylene	5.0	1.06	THG	65
	80.0	1.9	THG	65
Poly(ketene)	11.5	0.532	THG	68
Poly(phenylacetylene)	0.07	1.064	THG	69
Poly(p-phenylene vinylene)				
R = H (PPV)	0.75	1.064	THG	70
R = OCH₃ (MO-PPV)	29.0	1.064	THG	71
BBL	0.07	0.602	DFWM	86
	1.5	1.064	DFWM	86
BBB	0.55	1.064	DFWM	86
Polyquinoxaline	45.0	0.532	DFWM	87
PBT	0.09	0.602	DFWM	88
Polyaniline	8.0	0.620	DFWM	90
Polypyrrole	0.02	0.602	DFWM	91
Polyazomethine	0.024	0.602	DFWM	92
Polyquinoline	0.022	2.38	THG	93
Polyazine PMPAZ	0.08	1.5	THG	95

The $\chi^{(3)}$ values of π-conjugated polymers range from 10^{-5} to 10^{-12} esu, depending upon the material, measurement technique and wavelength.

Ginder et al [89] report the resonant $\chi^{(3)}$ of polyaniline (39) and emeraldine salt to be of the order of 10^{-8} esu.

The eineraldine-based polyaniline gave a $\chi^{(3)}$ value of 8.10^{-10} esu from DFWM at 620nm and has a nonlinear figure of merit χ^3/α of 2.10^{-14} esu/cm^{-1} [90].

Pristine polypyrrole (40) film has a $\chi^{(3)}$ value of $3,0.10^{-12}$ esu when measured by DFWM at 602nm [91].

The $\chi^{(3)}$ value increases to $3,9.10^{-12}$ esu for ferric chloride treated polypyrrole films.

đối với

Sắt clorua

Polyazomethine (41) has a $\chi^{(3)}$ value of $2,4.10^{-12}$ esu at $0.602\mu m$ measured by DFWM [92].

bước sóng   khi đo bằng kỹ thuật

Polyquinolines have $\chi^{(3)}$ values of $2,2.10^{-12}$ esu at $2.38\mu m$ from THG measurements [93]. The $\chi^{(3)}$ values of polycarbazole radical cations range from $1,3.10^{-7}$ to $2,72.10^{-7}$ esu according to DFWM measurements [94].

theo
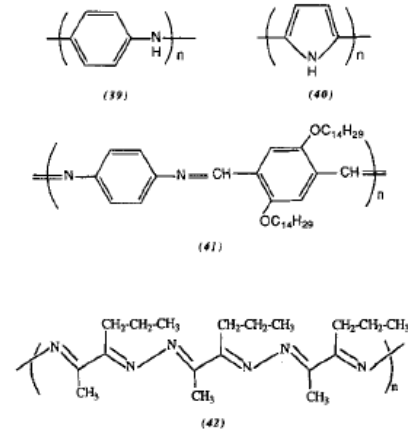ion dương gốc tự do   nằm trong khoảng từ

(39) (40) (41) (42)

(39) (40) (41) (42)
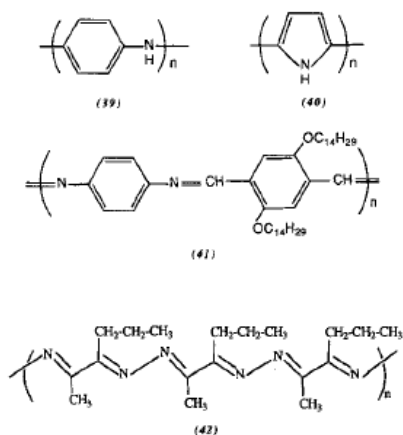
The third-order nonlinear optical properties of polyazine and its oligomers were reported very recently.

cũng được báo cáo trong thời gian gần đây

Third-harmonic generation measurements revealed a non-resonant third-order nonlinear optical susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of $1,53.10^{-12}$ esu for the pentamer and 8.10^{-12} esu for propylmethylpolyazine (42) at $1.5\mu m$ [19, 21, 95].

cho thấy

đối với

đối với
bước sóng

Table 10 lists the polarizabilities and $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of oligomers of well-defined chain length and propylmethylpolyazine.

Table 10. Optical absorption maxima, third-order nonlinear optical susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ at 1.5 µm. The chemical structures of the sequentially built oligomers of polyazine used for $\chi^{(3)}$ measurements are shown in (7) where hydrogens at the carbon atoms are replaced by methyl groups.

Number of repeat units (n)	Linear and nonlinear optical parameters			
	λ_{max} [nm]	$\chi^{(3)}$ [10^{-12} esu]	$\varkappa$ [Å³]	γ [10^{-36} esu]
1	263	0.139	7.9952	3.349
2	265, 295	0.389	16.3253	19.537
3	270, 300	0.867	25.6076	57.193
4	–	–	35.3083	112.033
5	270, 304	1.53	45.1802	175.919
PMPAZ	280, 320	8.0	–	–

The γ values of oligomer model compounds increase much more rapidly than the nonlinear optical susceptibility as the π-electron delocalization length of the polyazine backbone increases.

It should be noted that $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of the oligomers may be diluted to some extent by the methyl pendant groups on the polyazine chain.

Polyazine is isoelectronic with polyacetylene. Both polyacetylene and polyazine have a simple linear chain of atoms with alternating single and double bonds, but polyazine has pairs of nitrogen atoms substituted for pairs of carbon atoms in the polyacetylene chain (Fig. 2).
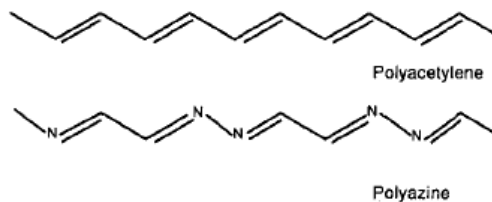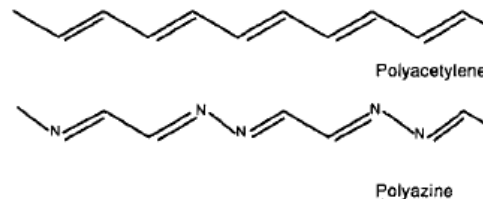
Fig. 2. Relationship between the structures of polyacetylene and polyazine.

This arrangement of carbon and nitrogen atoms in the polyazine π-conjugated backbone offers environmental stability and optical transparency.

The magnitude of optical nonlinearity of π-conjugated polymers in the resonant regions is larger than in non-resonant regions because of the resonant contribution. Although the optical nonlinearity of polyazine is only moderate, its optical transparency is of great advantage.

5.5. NLO-Dye Grafted Polymers.

In particular two types of NLO-chromophore functionalized systems have been investigated: side-chain polymers and main-chain polymers.

Matsumoto et al [96] studied symmetrical cyanines having quinoline rings. The polymers were doped as high as 50% by the dye and transparent films of 0.2-0.3μm were cast from the soluton by spin coating.

The wavelength dependence studies show that a polymer film containing 50% cyanine dye has a $\chi^{\mathbb{C}}$ maximum of 2.10^{-11} esu around 1.9μm.

Meyer et al [97] demonstrated that glasses can be made from a polyelectrolyte (PEL) by adjusting the chemical structures of the ionic polymers (43).

hợp làm cho vật liệu ổn định với môi trường và có độ trong suốt quang học
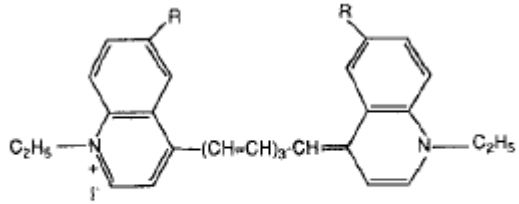
hợp

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chuỗi

cực đại

thủy tinh có thể chế tạo

thủy tinh

The THG efficiency of PEL glasses increases as the dye (44) content increases and reaches a maximum with 62 wt-% dye content.

(43)
Dye 1: R = H, Dye 2: R = Cl

Polymer

Dye
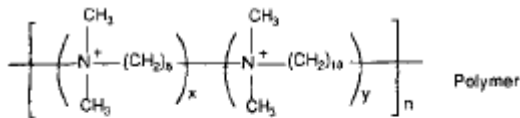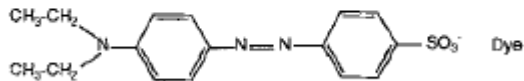
(44)

The use of PEL glasses as nonlinear optical media has been considered due to their good solution processability, incorporation of high dye concentration, optical quality and the structural variations possible by employing various combinations of ionic polymers and appropriate counterions.

The $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of the poly(methylmethacrylate) grafted by 4-dialkylamino-nitrobenzene, 4-dialkylamino-4'-nitrostilbene, 4-dialkylamino-4'-nitrodiphenylbutadiene, and 4-dialkylamino-4-nitrodiphenylhexatriene were in the range of $0,54.10^{-12}$ to $7,42.10^{-12}$ esu at 1.904µm [98, 99].
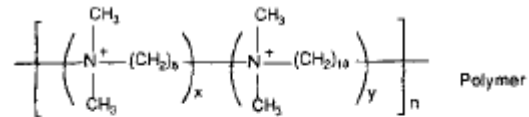
Người ta đã xét đến việc làm do dung dịch của chúng dễ xử lý

những phương thức kết hợp khác nhau của các ion đối thích hợp

bước sóng

The $\chi^{(3)}$ values at 1.904μm and 1.579μm change by a factor of 15 as the conjugation length increases. These polymers show no optical damage threshold up to 1GW/cm^2.

5.6. Organometallic Compounds.

Organometallics have two types of charge-transfer transitions, i.e., metal-to-ligand and ligand-to-metal. The metalligand bonding displays large molecular hyperpolarizability due to the transfer of electron density between the metal atom and the conjugated ligand systems.

Furthermore, the overlapping of the electron orbitals of ligands with the metal ion orbitals leads to larger intramolecular interactions in organometallic complexes. The diversity of central metal ato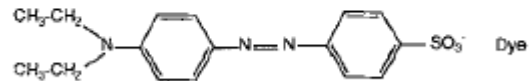ms, oxidation states, their size, and the nature of ligands helps in tailoring materials in order to optimize the chargetransfer interactions. Nalwa" "1 has reviewed organometallic materials for nonlinear optics.

The first report on the third-order nonlinear optical properties of metallophthalocyanines (MPcs) appeared in 1987. The x<3) values of phthalocyanines with Ga, Al, In, V, Ti, Pb, Pt, Pd, Co, Ni, and Cu as the central metal atom, and their derivatives, have been summarized in a review on organo¬metallic materials.11001 The thin films of chlorogallium phtha- locyanine

15 lần do sự tăng chiều dài liên hợp có ngưỡng hủy hoại quang

dịch chuyển chuyển điện tích phối tử kim loại có do sự trao đổi electron hợp

(GaClPc) and fluoroaluminum phthaloyanine (AlFPc) show x<3) values of the order of 2.5 x 10-11 and 5.0 x 10" " esu, respectively, at 1.064 (imj1011 Shirk and co-workers11021 measured the third-order nonlinear susceptibil¬ity of H2Pc, PbPc, and PtPc. The x{3) values of metal-substituted Pc were about 2 to 45 times larger than that of a metal-free phthalocyanine. The metal substitution on the Pc ring and the molecular packing also have a significant effect on the optical nonlinearity.1103,1041 The second hyperpolar¬izability and x<3) values of lanthanide bis(phthalocyanines) M(Pc)2 (where M is Sc, Lu, Yb, Y, Gd, Eu, and Nd) and their anions range from 15 x 10"32 to 48 x 10"32 esu and from 5 x 10"10 to 2 x 10"9 esu, respectively, at 1.064 (rm, depend¬ing upon the metal atom.11051 The y values were found to decrease in the order ScPc2 > YbPc2 >LuPc2 > YPc2 > EuPc2 > GdPc2 > NdPc2.

Third-order nonlinear optical susceptibilities -/3) of naph- thalocyanines (Ncs) 45 containing as the central metal atoms vanadyl (VO), copper (Cu), zinc (Zn), palladium (Pd), nickel (Ni), indium (In), iridium (Ir), ruthenium (Ru), and rhodium (Rh) were measured by thG.[106"1081 Table 11 lists the nonlinear optical parameters for MNc thin films. The x<3)- (—3CO;CO,OJ,CO) values of VONc, CuNc, ZnNc, PdNc, and NiNc possessing terminally tetrakis-(w-pentoxycarbonyl)

Table 11. Third-order nonlinear optical suspectibility data of phthalocyanine
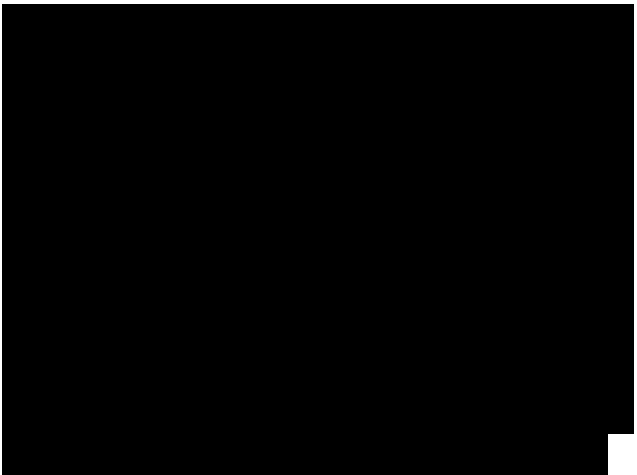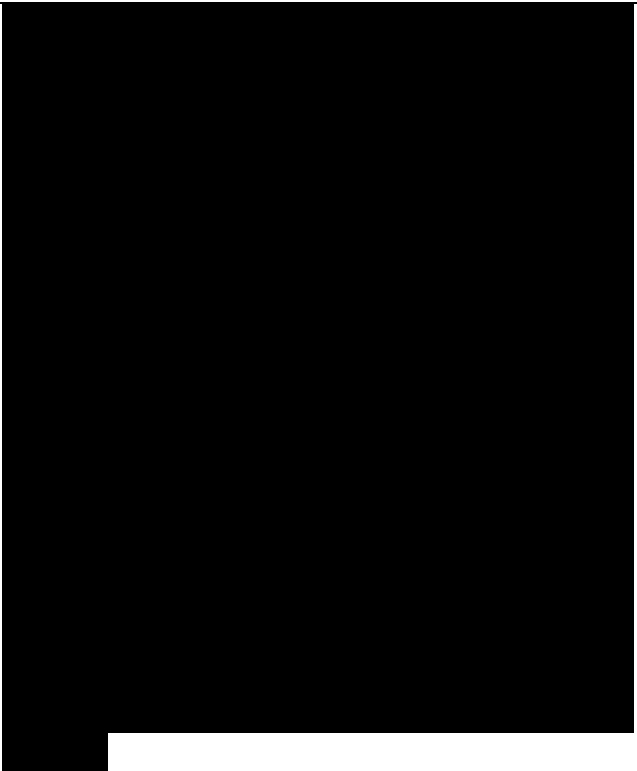
compounds181 [100].
faI Pc: phthalocyanine; Nc: naphthalocyanine; TB: ter/-butyl, CP4 = tetrakis- (cumylphenoxy).

(COO-CgHj L)4 substituents on peripheral sites of the macrocycle were found to lie in the range 86x10"12 to 1.28 x 10"12 esu at 2.1 ^im. On the other hand, the /3) (— 3co;co, co, co) values of InCINc, IrNc, RuNc, and RhNc possessing terminally tetrakis(fcr/-butyl) [C(CH3)3]4 substituents were between 4.21 x 10"12 and 1.0 x 10"12 esu at the same measurement wavelength. The x<3)(~ 3co;co,co,co) values were also found to be affected by the nature of the central metal atoms, although the effect was not so pronounced. Although the terminal long-chain bulky groups on the naphthalocyanine ring dilute the magnitude of optical nonlinearity, the x<3)(— 3ct>; ct>, co, co) values of metallonaph-thalocyanines were found to be quite large, arising from the extended ii-electron conjugated system introduced by benzo- isoindole units. VONc(COO-C5Hu)4 showed third-order optical nonlinearity one order of magnitude larger than that of other metallonaphthalocyanines. Figure 3 shows the dispersion of x<3,(— 3co;co,co,co) for VONc(COO-CsHn)4, along with the electronic spectrum. The value of x<3> is maximum at 2.1 nm and decreases toward lower wavelengths. The z<3) apparently changes with absorption intensity because it is influenced by the three-photon (3co) resonance effect. At lower wavelengths, the resonance effect is smatler and hence

partially affects the x(3) values between 1.5 and 1.74 (im. Therefore, the large difference noticed in x<3) values of VONc(COO-C5Hu)4 occurs due to the dispersion of the X(3) in resonant and non-resonant regions. The dispersion of the third-order optical nonlinearity of VONc(COO-C5H, ,)4 over the fundamental wavelength range of 1.5 to 2.1 |im is similar to other organic molecular and polymeric materials.

Pumpine Wavelength (/urr\)

Wavelength (nm)

Fig. 3. The dispersion of /(3)(— 3to;o>,o>,«) for VONc(COO-C5Hn)4 [107].

The x(3) values of spin-cast films of soluble oligomeric bridged (phthalocyanato)ruthenium(n) complex ['Bu4PcRu- (dib)],,, which is axially linked by />-diisocyanobenzene (dib) bridging ligands and in which four ferf-butyl groups are substituted for a phthalocyanine ring, were measured by THG at 1.064)im and by DFWM with laser wavelengths varied over the complete range of the Q-band.11091 The THG measurements yielded an absolute value of X(3)(— 3co; c»,co,ct>) = 3.7 x 10-12 esu with a phase of 155° + 10°. The i^\ — (0',co,co,—co) value obtained by DFWM was more than four orders of magnitude larger than X(3) (— 3ft); co, co, co) obtained by THG because of the different optical processes. The DFWM measurements showed a fast relaxation time of 70 ps in ['Bu4PcRu(dib)],, thin films at a laser wavelength of 600 nm, which probably has an electronic origin.

Like   metallophthalocyanines,

metalloporphyrins (M-PPs), 46, are another class of two-dimensional 7i-electron conjugated systems. Table 12 lists the third-order nonlinear optical susceptibilities of various metalloporphyrins. The x<3) measurements on metal-free (H2TPP), zinc-containing (ZnTPP), and cobalt-containing (CoTPP) tetraphenylporphyrins were studied by using DFWM at a wavelength of 532 nm.11101 Sakaguchi etal.[lul measured values in the range of 10~11 esu of mesogenic tetraphenylporphyrin, 5,10,15,20-te-trakis(4-«-pentadecacylphenyl)porphyrin and its metal com-

nonlinear optical effects. The third-order optical susceptibility '/3) was found to be higher with the polarization of the fundamental light parallel to the dipping direction than with the polarization perpendicular. The angular dependence of X(3) of polysilane with bis(m-butoxyphenyl) groups showed that x(3) is influenced by the oscillator strength of the polysilane backbone rather than by the phenyl ring absorption. Furthermore, annealing of the samples at elevated temperatures produces a strong increase in anisotropy, and the largest absolute x(3) value of 4 x 10"12 esu was determined for an annealed sample. Polysiloxane having bis(m- butoxyphenyl) substituents showed the largest third-order susceptibility associated with the effective conjugated length along the polysilane backbone.

Third-order nonlinear optical properties of transition metal poly-ynes were extensively studied by the research team at Martin Marietta Laboratories as early as

1987.[1112111221] In order to establish a relationship between polymer structure and optical nonlinearities, very wide variations in the polymeric structures were made mainly on the benzene ring substituents of poly-ynes and related oligomers containing the transition metals platinum and palladium. The second hyperpolarizabilities of metal-poly-ynes were measured using THG, four-wave mixing, optical Kerr gate, and self-focusing techniques. These materials show hyperpolarizability values of the order of 5 x 10-33 esu. The increase in conjugation length between the two metal centers results in three- or four-fold increase in y. The y values of fluoro, methoxy, and ethyl substituted polymers are slightly larger than that of the unsubstituted polymer. The y values of palladium polymers are lower than their platinum analogues. The platinum and palladium polymers with two diethynylbenzenes in the repeat unit were found to have larger hyperpolarizability val-ues than the analogous polymers without diethynylbenzene.

Black plate-like single crystals of 10 |i,m thickness of the organic metal (BEDT-TTF)4Re6Se5Cl9 showed a y(il value of 1.6 x 10-s esu.[11231] In this organic metal, the single sheets of BEDT-TTF donors alternate with layers of all-inorganic cluster anions. The high delocalization in the donor plane is probably favorable for large optical nonlinearity. Metallocenes are another interesting class of third-order nonlinear optical materials.[1124,1251] The nonlinear refractive indices of metallocenes change with metal
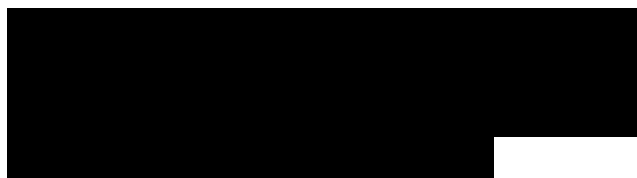
substitution and range from 2.6x 10-13 esu (for nickel) to l.Ox 10-11 esu (for platinum).

5.7.   Organic Composites

A. 100 \im thick film of boric acid glass containing fluorescein shows a large xi3) of the order of ~ 1 esu and a response time of 0.1 s.11261 These composites have low durability and poor homogeneity of the boric acid host, which limit the practicality of the composite system. In this context, Tomp- kin et al.11271 recently developed new composite materials based on lead-tin fluorophosphate glass containing acridine yellow 48 and acridine orange 49 dyes. The tin content is the major factor which provides tailoring of physical and optical properties. The glasses with a tin content between 35 and 75 cation mol.- % form clear transparent glasses. These composites have %(3) values of ~0.1 esu, saturation intensities of ~100mW/cm2, and a response time of ~1 ms. The low melting temperature of lead-tin fluorophosphate glass allows doping with many organic dyes without any decomposition. These composites are useful in nonlinear devices where very large optical nonlinearities and a millisecond response time are required. The calculated ^<3) value of the lead-tin fluorophosphate glass composite doped with acridine yellow was 5 x 10-3 esu.11281 The laser induced fluorescence studies indicate the three-photon excitation flu-orescence. The molecules of acridine yellow dye are randomly oriented in the host matrix and held rigidly. In the case of THG, both bulk and surface enhancements contribute to large y}3) values. Organic

dyes dispersed in glass showed the largest optical nonlinearity, but the response time of these materials is of the order of milliseconds. Therefore they should be useful when an ultrafast response is not a prerequisite.

5.8. Liquid Crystals

Liquid crystals are an interesting class of NLO materials because their physical properties can be controlled by achieving orientation by means of a modest field. An excellent review on the NLO response of liquid crystals has been published by Palffy-Muhoray.11291 The nonlinear refractive indices for 4-cyano-4'-«-pentylbiphenyl (5CB), 50, 4-cyano- 4'-«-octylbiphenyl (8CB) and a mixture of biphenyl with ter- phenyls (E7) measured by the Z-scan technique were —175 x 10-11, — 77 x 10" n, and —115 x 10"11 esu, respectively, at 24°C.11301 A x(3) of 6.2 x 10"19 m2V"2 for 5CB was

determined close to the phase transition temperature at 55.1 °C at 632.8 nm.11311 Liquid

6. Summary and Prospects

In the last 15 years, since the discovery of PDA-PTS,151 much progress has been made in exploring the various class

es of organic materials and in understanding the origin of optical nonlinearities. This survey concludes with a discussion of a very wide variety of organic materials, ranging from liquids, dyes, 7t-conjugated polymers and dye-grafted polymers to liquid crystals, organometallics and composites, for third-

order nonlinear optics. After almost a decade of evolution of 7t-conjugated polymers as third-order NLO materials, a new trend in understanding of the basic requirements for large third-order NLO effects seems to be emerging. It has become clear that the third-order optical nonlinearities can be significantly enhanced by increasing n-electron density and by chain orientation in polydiacetylene, polyacetylene and PPV. The following factors have been found to affect the magnitude of y}3\ and examples have been provided in previous sections:

• Ti-delocalization length (e.g. 7i-conjugated polymers)

• donor-acceptor functionalities (e.g. polyazines, polyenes)
• chain orientation and packing density (e.g. polyacetylene, polydiacetylene, PPV)
• conformation (e.g. polyenes)
• dimensionality (e.g. phthalocyanines, porphyrins)

Figure 4 shows the y(3} scale of various classes of organic materials. The /<3) of organic materials range over more than eight orders of magnitude, from 10 "5 esu to 10 ~13 esu in the resonance and off-resonance regions, respectively. Although many organic materials show y{3) of the order of 10" 8 esu, the largest x<3) of 2x10"5esu was measured for polydiacetylene /"-toluene sulfonate (PDA-PTS) single crystals at ~ 2.0 eV.

OOQ O   OO   O   O
h   CD   C7>£»   NJ   °
£»   M   O
| organic composites   j
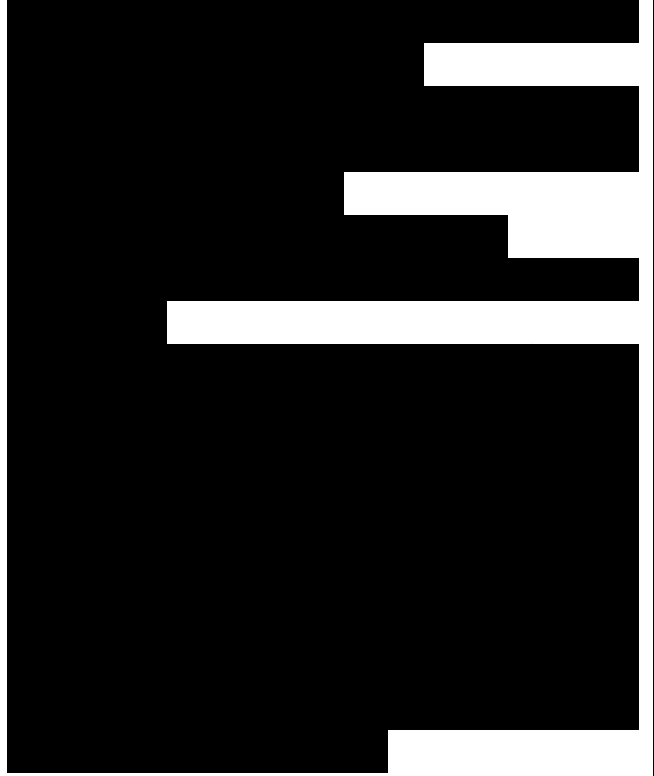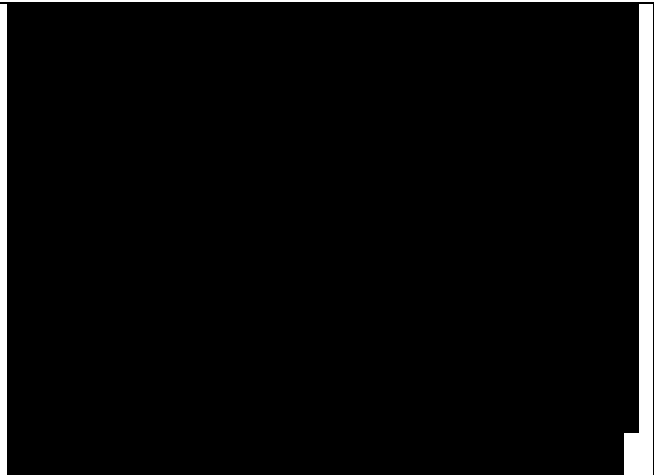
dyes, dye-grafted polymers, fullerenes, charge-transfer complexes, polysilanes, liquids organometallic compounds, liquid crystals

Fig. 4. Scale of x<3) for various classes of organic materials.

The device concepts are at an early stage, hence a good understanding of NLO processes and materials requirements is still lacking. The possible applications of third-order NLO materials are widespread and include frequency conversion, optical bistability, optical waveguides, image processing, optical computing, and optical fiber telecommunication. Several prototype devices have already been fabricated, especially using polydiacetylene materials. An optical bistable device has been made from PDA LB films.11321 Thermal optical bistability with a Fabry-Perot cavity filled with a PDA-PTS solution has been reported.11331 It is advantageous because of its ultrafast switching and memory storage. A directional coupler has also been fabricated from PDA-4-BCMU thin films,11341 and a nonlinear Bragg mirror has been fabricated from ultrathin layers of the saturably absorbing copolymer of siliconphthalocyanine and methylmethacrylate.11351 Optical limiting at an intensity of 5 — 10 MW/cm2 for 6 ns pulses was demonstrated at a wavelength of 688 nm from a 23-layer stack. All-optical phase modulation in waveguides from a single-crystal film of PDA-PTS has been demonstrated.11361 Single-crystal PDA waveguides demonstrate the tremendous potential of rc-conjugated polymers in
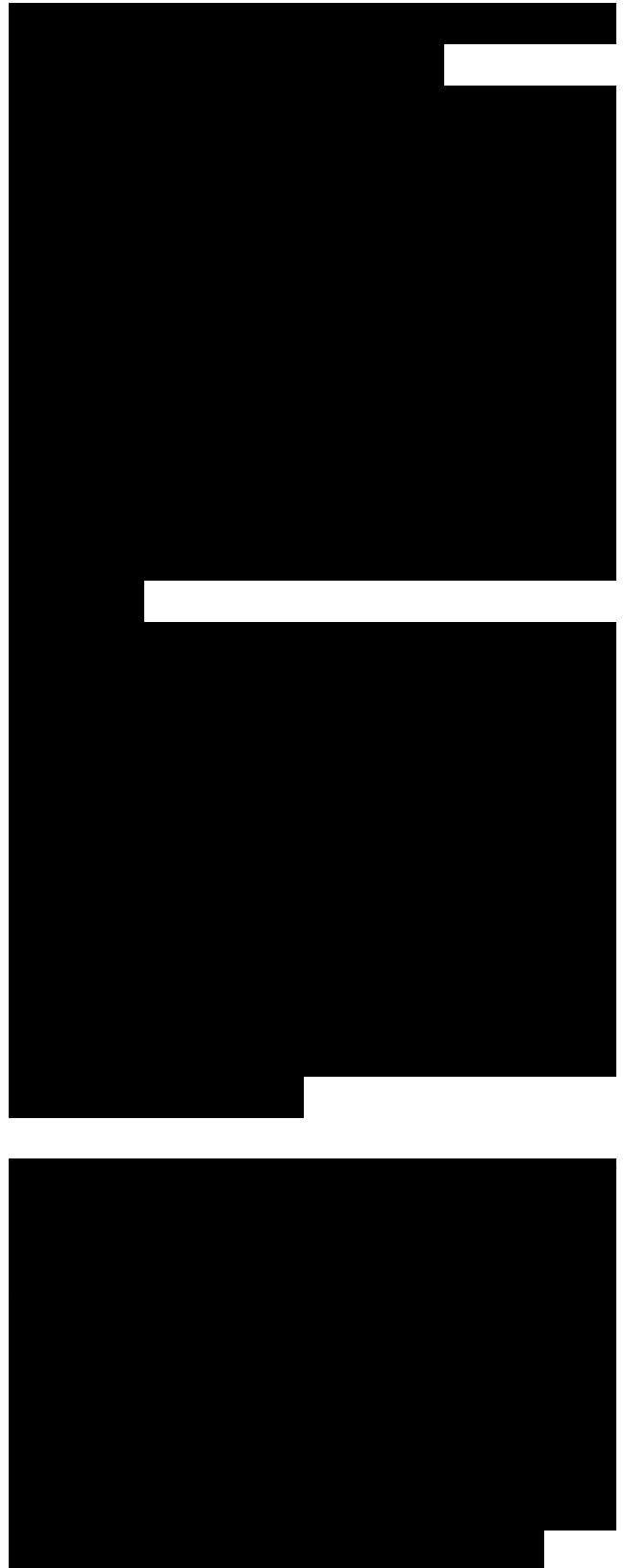
photonic technology.

Large third-order NLO susceptibility coupled with optical transparency are the key points in fabricating novel devices. Propagation losses of about 1 dB/cm and a linear absorption coefficient a of 2 cm"1 for PDA-PTS and 2-20 dB/cm and a of 0.5 cm-1 for PDA-4-BCMU have been recorded.11371 The nonlinear figure of merit (FOM) can be written as y(3)jcc, therefore further reduction of optical losses would yield a good candidate material for NLO devices. Currently two combinations of NLO materials for third-order nonlinear optics are available: i) materials possessing large optical nonlinearity and high optical losses, such as PDA polymers («2 = 10"11 cm2/W and a =10 'cm'1), and ii)materials possessing small optical nonlinearity and low optical losses, such as silica glass fiber (n2 =10"16 cm2/W and a =10-6 cm"1).11361 The latter class ofNLO material would provide devices to be used for long length optical processing whereas the PDA polymers should be useful for short length applications. The real limits of y<3) and a for an ideal NLO material are still difficult to set, although several criteria have been proposed. Do we really need NLO materials with off-resonance ^(3) = 10-7 esu? Such harsh conditions for an NLO material will be difficult to meet in practice. In order to utilize organic materials in technological applications, a y}3) of 10"7 esu should be sufficient if it is combined with the desired optical transparency and subpicosecond response time. The architectural flexibility of organic molecules assists in optimizing the

optical nonlinearities and material performance by molecular engineering approaches. A well-designed finite-sized conjugated system of either n-conjugated polymers or organometallic complexes should be sufficient for achieving large third-order optical nonlinearities and subpicosecond response time, although the optical losses need to be reduced as much as possible. This combination is a challenging task for the scientific community involved in this fast-growing field of technical endeavor. The demand for high-performance NLO organic materials possessing particular optical and nonlinear optical functions will continue.