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Theoretical Study of the Nonlinear Optical Properties of Thiophene, Furan, Pyrrole, (1,2,4-triazole), (1,3,4-oxadiazole), and (1,3,4-thiadiazole) Monomers and Oligomers

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PM3 semiempirical calculations were carried out to study the frequency-dependent nonlinear optical properties of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole monomers and oligomers. The longitudinal component, α_{zz} , is the largest of three principle components. On the other hand, the out-of-plane component, α_{zz} , is the smallest. Moreover, the out-of-plane component (α_{zz}) of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole monomers show constant changes with increasing optical frequencies. The frequency-dependent first-order polarizabilities increase in the order: thiophene > (1,2,4)-triazole > pyrrole > furan > (1,3,4)-thiadiazole > (1,3,4)-oxa-diazole monomers and oligomers. The effects of $\beta(-2\omega, \omega, \omega)$ (SHG) shows a larger dispersion compared with $(-\omega, \omega, 0)$ (EOPE) and $\beta(0; -\omega, \omega)$ (OR). The second-order polarizabilities of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-thiadiazole, and (1,3,4)-oxadiazole monomers for the various second-order effects have the order: $\beta(-2\omega, \omega, \omega)$ (SHG) > $\beta(-\omega, \omega, 0)$ (EOPE) > $\beta(0; -\omega, \omega)$ (OR) and thiophene > pyrrole > (1,2,4)-triazole > furan > 1,3,4-thiadiazole > 1,3,4-oxadiazole monomers. The third-order polarizabilities for the various third-order effects have the following order: $\gamma(-3\omega, \omega, \omega)$ (THG) > $\gamma(-2\omega, 0, \omega, \omega)$ (EFISHG) > $\gamma(-\omega, \omega', -\omega, \omega)$ (IDRI) > $\gamma(-\omega; 0, 0, \omega)$ (OKE). The effects of THG increase rapidly with increasing optical frequencies compared with the other effects. In particular, OKE effects increase most slowly with increasing optical frequencies. Also, the effects of THG for thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-thiadiazole, and (1,3,4)-oxadiazole oligomers show the order thiophene > (1,2,4)-triazole > furan > pyrrole > (1,3,4)-thiadiazole > (1,3,4)-oxadiazole oligomers. In particular, the third-order polarizabilities of thiophene and (1,3,4)-thiadiazole oligomers are about four and three times larger than those of (1,3,4)-oxadiazole and (1,2,4)-triazole oligomer, respectively.

Introduction

Materials which exhibit highly nonlinear optical properties are essential for integrated optics, optical data processing, and photonic devices. In particular, organic materials with the large delocalization of the π electrons have been of great interest because they produce very large nonlinear responses.

Heterocyclic five-membered ring polymers (furan, pyrrole, thiophene, etc.) are the most extensively studied of the polyconjugated and conductive polymers.^{1,2} Experimental measurements suggest that organic molecules containing heterocyclic rings (furan, pyrrole, thiophene) exhibit significant nonlinear optical properties. Theoretically and experimentally a new class of second-order nonlinear optical materials which utilize the coupling of electron-rich and electron-deficient aromatic heterocyclic units to provide the charge

asymmetry for the nonlinear optical effect.³

A number of experimental observations of the nonlinear optical phenomena such as electrooptic Pockels effect (EOPE), second harmonic generation (SHG), optical rectification (OR), DC-electric field induced (EFI)SHG, third harmonic generation (THG), optical Kerr effect (OKE), DC-electric field induced (EFI)OR, etc. were reported for new materials with varied structures and dimensions.⁴⁻⁸

Keshari *et al.*⁹ reported *ab initio* self-consistent-field calculations of linear and nonlinear polarizabilities of thiophene, furan, and pyrrole at their theoretically optimized geometries. Also, they reported the dispersion of $\alpha(-\omega, \omega)$ and those of $\beta(-2\omega, \omega, \omega)$ (SHG), $\beta(-\omega, \omega, 0)$ (EOPE), $\beta(0; -\omega, \omega)$ (OR), $\gamma(-3\omega, \omega', \omega, \omega)$ (THG), $\gamma(-2\omega, 0, \omega, \omega)$ (EFISHG), $\gamma(-\omega, \omega', -\omega, \omega)$ (IDRI), and $\gamma(-\omega; 0, 0, \omega)$ (OKE). Using an *ab initio* time-dependent coupled-perturbed Hartree-Fock method, the dispersion of linear and nonlinear optical pro-

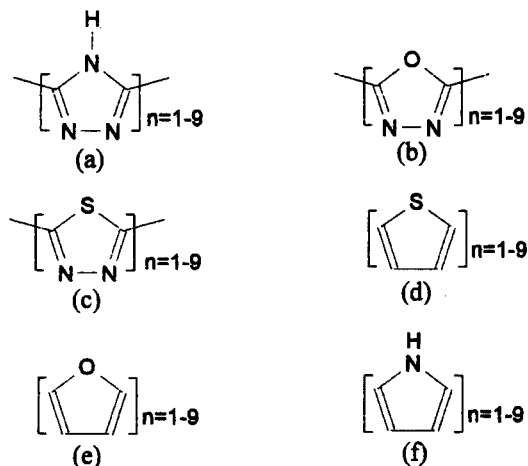


Figure 1. Structures of 1,3,4-triazole(a), 1,3,4-oxadiazole(b), 1,2,4-thiadiazole(c), thiophene(d), furan(e), and pyrrole(f).

Table 1. Values of the coefficients a and b for $X^n_{\alpha\alpha\alpha\cdots\alpha}(\omega)$ in atomic units

Oligomers	α		β		γ	
	a	b	a	b	a	b
1,3,4-triazole	8.830	2.244	8.943(1)	2.813(2)	6.440(3)	6.175(4)
1,3,4-oxadiazole	4.585	1.279	4.192(1)	1.682(2)	1.831(3)	2.445(3)
1,2,4-thiadiazole	5.818	1.194	6.072(1)	2.842(2)	2.795(3)	3.123(4)
thiophene	6.821	1.908	3.253(1)	4.839(2)	2.936(3)	5.234(4)
furan	4.357	0.986	2.117(1)	7.388(1)	3.045(2)	9.426(4)
pyrrole	5.358	1.446	3.379(1)	3.900(2)	3.401(3)	6.018(4)

^a Numbers in parentheses are the powers of ten by which the entry is to be multiplied.

properties of benzene were reported by Karna *et al.*¹⁰ Recently, Li *et al.*¹¹ reported a PPP study of chromophore architecture-frequency doubling efficiency relationships in a series of organic π -electron chromophores.

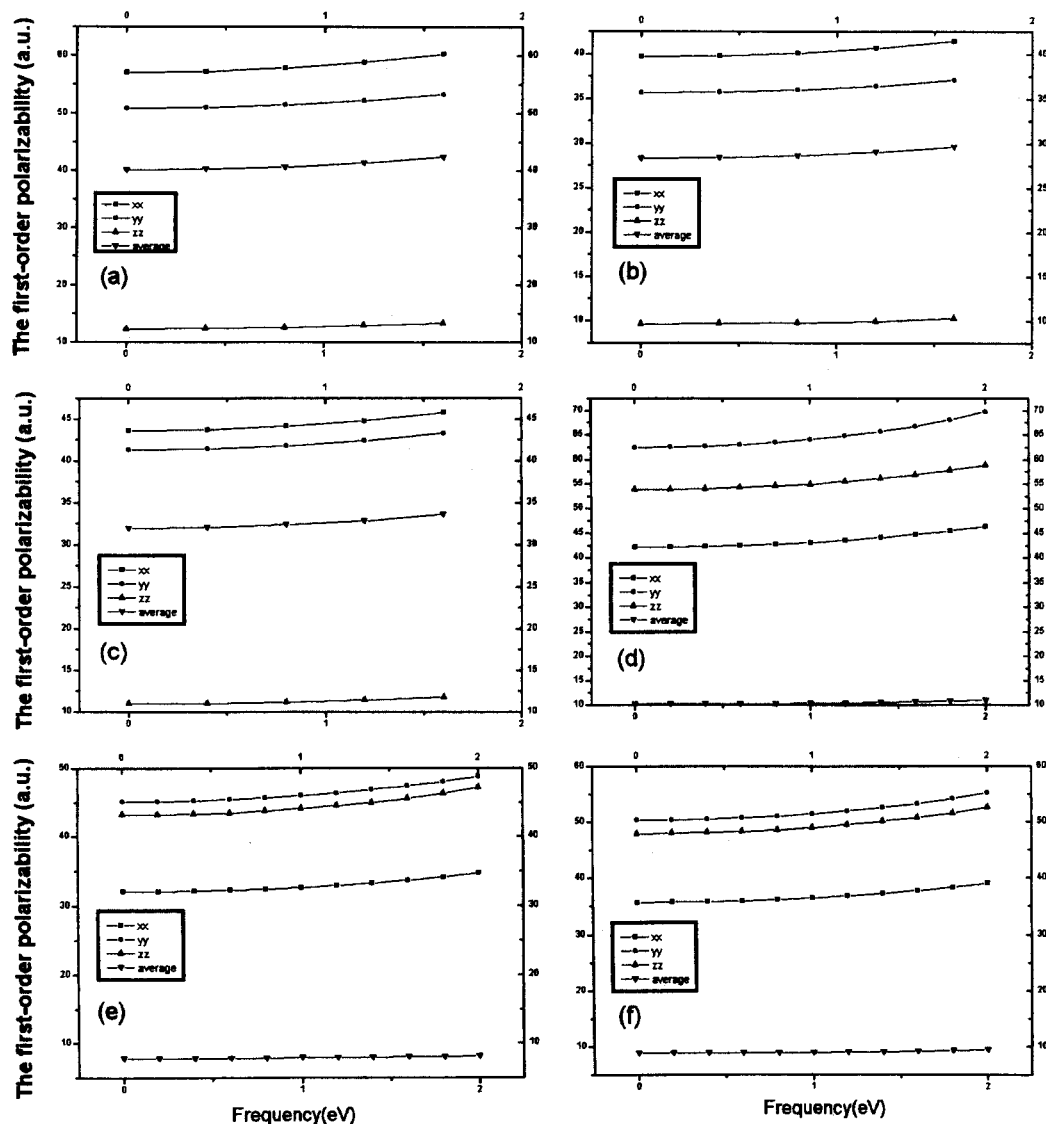


Figure 2. The frequency-dependent various first-order of polarizabilities of 1,3,4-triazole(a), 1,3,4-oxadiazole(b), 1,2,4-thiadiazole(c), thiophene(d), furan(e), and pyrrole(f) monomers.

In this study, to investigate the dispersion properties of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole monomers and oligomers, the nonlinear optical properties corresponding to various nonlinear optical effects at a number of several frequencies were calculated by the TDHF (time-dependent Hartree-Fock) PM3¹² methods.

Methods

All calculations were performed using MOPAC'93 quantum chemistry package. Calculations were carried out at their theoretically PM3 optimized geometries. PM3 calculations on thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole oligomers were performed in C_{2v} (odd-numbered rings) and C_{2h} (even-numbered rings) symmetries as shown in Figure 1.

The elements of the first-order polarizability tensor are denoted by $\alpha(0)$ for dc-electric field ($E=0.0$ eV). The second-order polarizabilities for various second-order effects are de-

noted as follows: $\beta(0;0,0)$ for the static case; $\beta(-2\omega,\omega,\omega)$ for the second-harmonic generation (SHG); $\beta(-\omega,\omega,0)$ for electrooptic Pockels effect (EOPE); and $\beta(0;-\omega,\omega)$ for optical rectification (OR). The molecular third-order response coefficient, γ is referred to as the third-order polarizability. Four different third-order effects can be observed theoretically; they are third-order harmonic generation [THG; $\gamma(-3\omega,\omega,\omega,\omega)$], DC-electric field induced SHG [EFISHG; $\gamma(-2\omega,0,\omega,\omega)$], optical kerr effect [OKE; $\gamma(-\omega;0,0,\omega)$], and intensity dependent refractive index [IDRI; $\gamma(-\omega,\omega,-\omega,\omega)$]. For thiophene, furan, pyrrole, (1,3,4)-thiadiazole, (1,3,4)-oxadiazole, and (1,2,4)-triazole monomers, the first-order polarizabilities, α , and the third-order polarizabilities, γ , are calculated at the various frequencies to investigate their dispersion behaviors. In order to calculate the saturation, the first- and third-order polarizabilities are expressed as a function of the chain length(n):

$$A(n) = n^k$$

where n is the number of thiophene, furan, pyrrole, (1,3,4)-

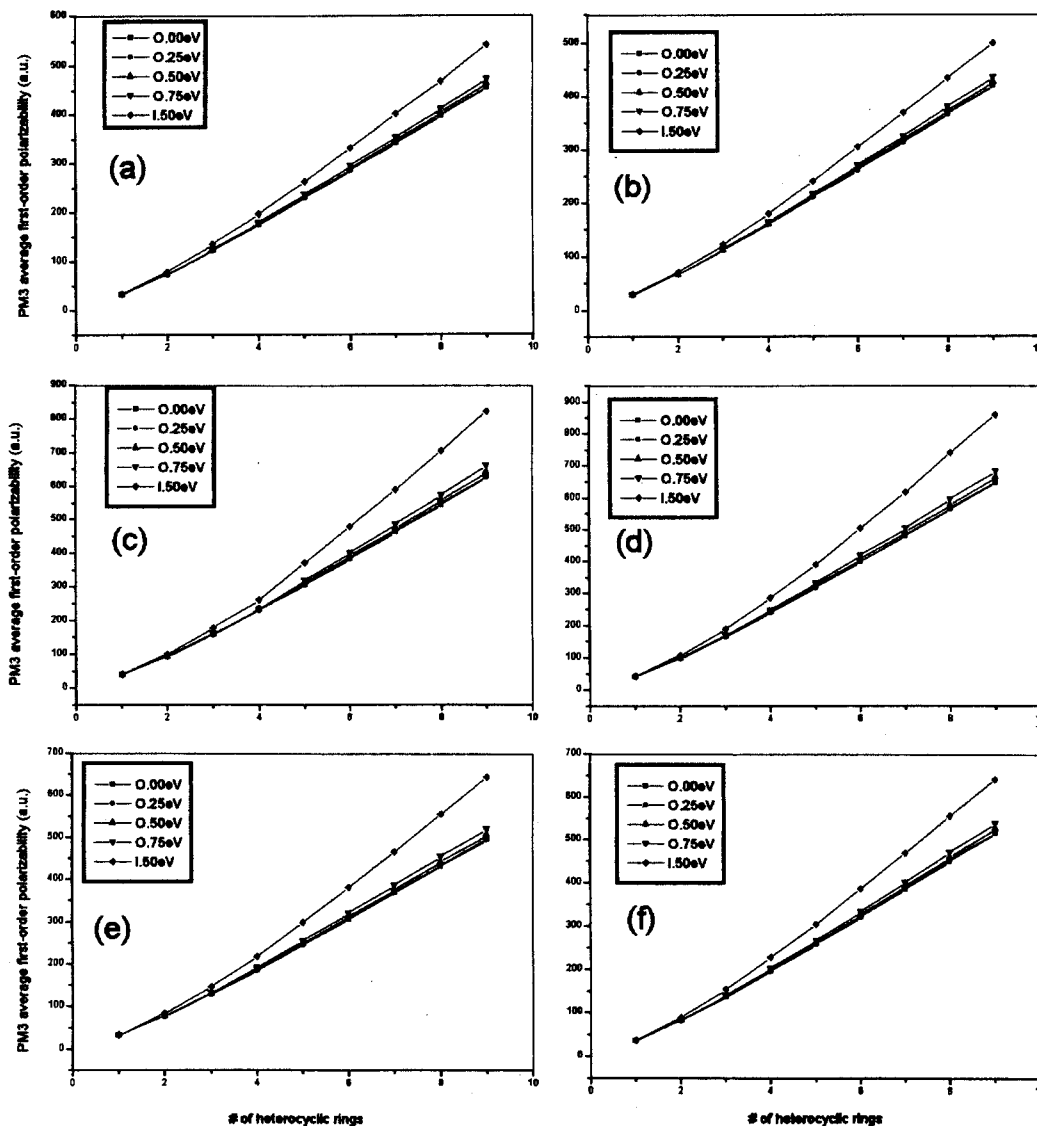


Figure 3. The PM3 calculated average first-order polarizabilities of 1,3,4-triazole(a), 1,3,4-oxadiazole(b), 1,2,4-thiadiazole(c), thiophene(d), furan(e), and pyrrole(f) oligomers.

thiadiazole, (1,3,4)-oxadiazole, and (1,2,4)-triazole monomers, and $A(n)$ is the first- and third-order polarizabilities.

The explicit formulas for the frequency-dependent polarizabilities are derived by Bishop *et al.*^{13,14} They proposed the polarizabilities could be expressed as a single general expansion up to terms which are of the fourth power in the optical frequencies. The general formulas are expressed as

$$X^n_{\alpha,\alpha,\dots,\alpha}(\omega_\sigma;\omega_1,\dots,\omega_n) = X^n_{\alpha,\alpha,\dots,\alpha}(0) + AW_2 + BW^2 + 6B'W_4, \quad (1)$$

where $X^n(0)$ denotes the static polarizability, ω_σ is the sum of the applied electric fields ω_i 's, W_2 is the sum of square of ω_σ and ω_i 's,

$$W_2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 + \dots + \omega_n^2$$

and W_4 is the sum of fourth-order powers of ω_σ and ω_i 's.

$$W_4 = \omega_\sigma^4 + \omega_1^4 + \omega_2^4 + \dots + \omega_n^4,$$

The X^n values denote the polarizabilities, $X^1=\alpha$, $X^2=\beta$, $X^3=\gamma$ etc..

The coefficients A, B, and B' would be independent of NLO process. They indicate the coefficient B' is smaller than B, and then the last term in Eq(1) can be ignored. The resulting formulas for the frequency dependent polarizabilities can be expressed as the appropriate frequencies in W_2 and W_4 and reduce to

$$X^n_{\alpha,\alpha,\dots,\alpha}(\omega) = X^n(0) + a\omega^2 + b\omega^4. \quad (2)$$

The coefficients were evaluated by frequency expansion of polarizabilities on the basis of the sum over state (SOS) technique. Thus we can obtain the coefficients by fitting the above equation. The results of the coefficients are represented in Table 1.

The dispersion coefficients A, B, and B' given in Eq. (1) essentially result from the oscillator strength of the tran-

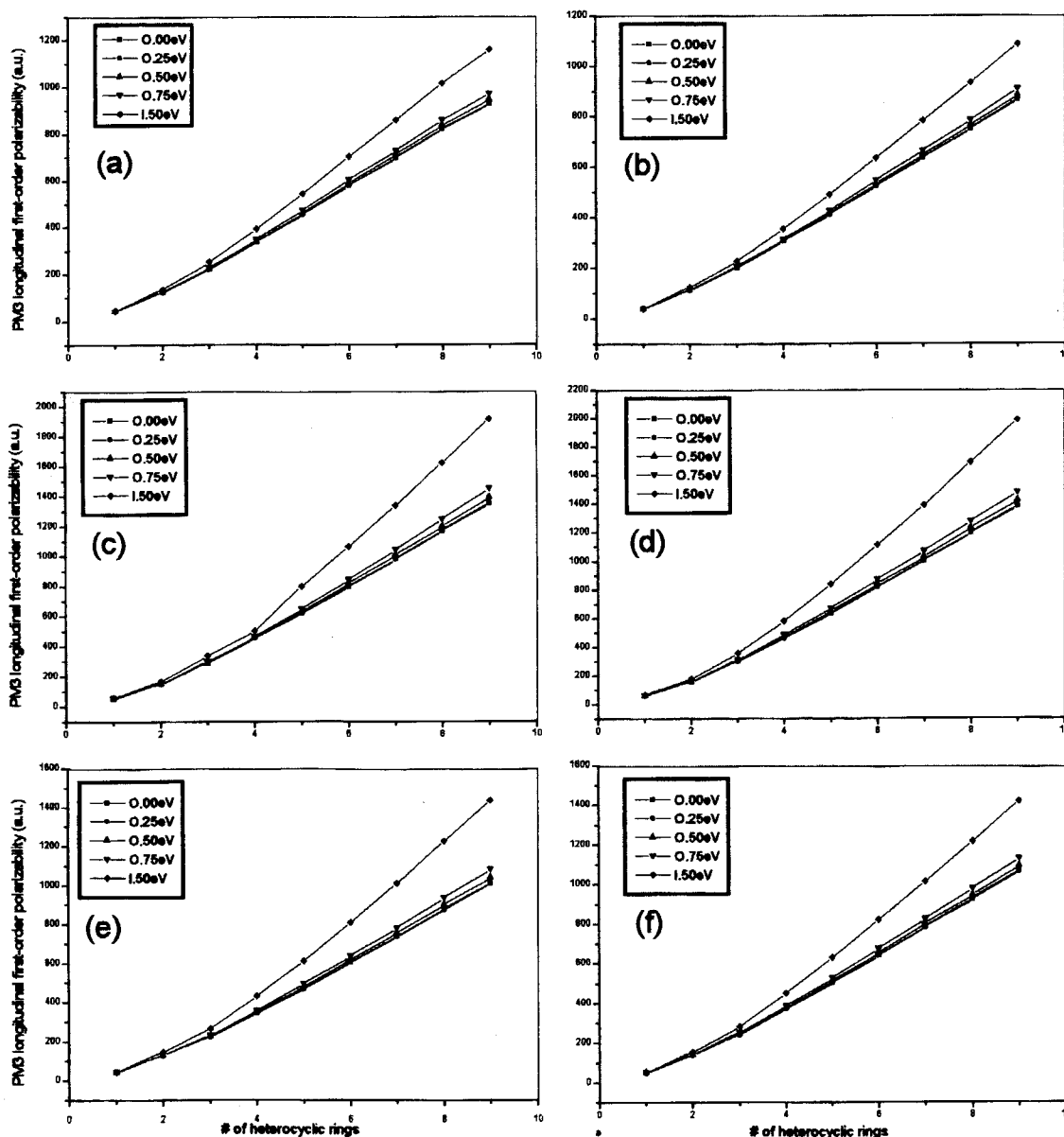


Figure 4. The PM3 calculated longitudinal first-order polarizabilities of 1,3,4-triazole(a), 1,3,4-oxadiazole(b), 1,2,4-thiadiazole(c), thiophene(d), furan(e), and pyrrole(f) oligomers.

sition and the change in dipole moment between ground state and excited states. The coefficients are originally evaluated by splitting into nonsecular and secular components of polarizabilities by Bishop *et al.*^{13,14}

The coefficients (a and b) which are indirectly related to the dispersion coefficients(A and B) are evaluated by fitting the frequency dependent polarizabilities as shown in Table 1. Although the fitted coefficients cannot be correctly analyzed as molecular properties, the tendency for the polarizabilities to increase with the frequency can be reasonably explained.

Results and Discussion

PM3 calculated frequency-dependent first-order polarizabilities of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-

oxadiazole, and (1,3,4)-thiadiazole monomers as a function of optical frequencies are shown in Figure 2. Three principle components, α_{xx} , α_{yy} , and α_{zz} , show the parallel dispersion behavior with increasing optical frequencies. The longitudinal component, α_{xx} , is the largest of the three principle components. On the other hand, the out-of-plane component, α_{zz} , is the smallest. Moreover, the out-of-plane component (α_{zz}) of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole monomers shows constant changes with increasing optical frequencies. These trends are consistent with ab initio calculated results.¹⁵ The average first-order polarizabilities increase in the order: thiophene > furan > pyrrole > (1,2,4)-triazole > (1,3,4)-thiadiazole > (1,3,4)-oxadiazole monomers.

The average and longitudinal first-order polarizabilities of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole,

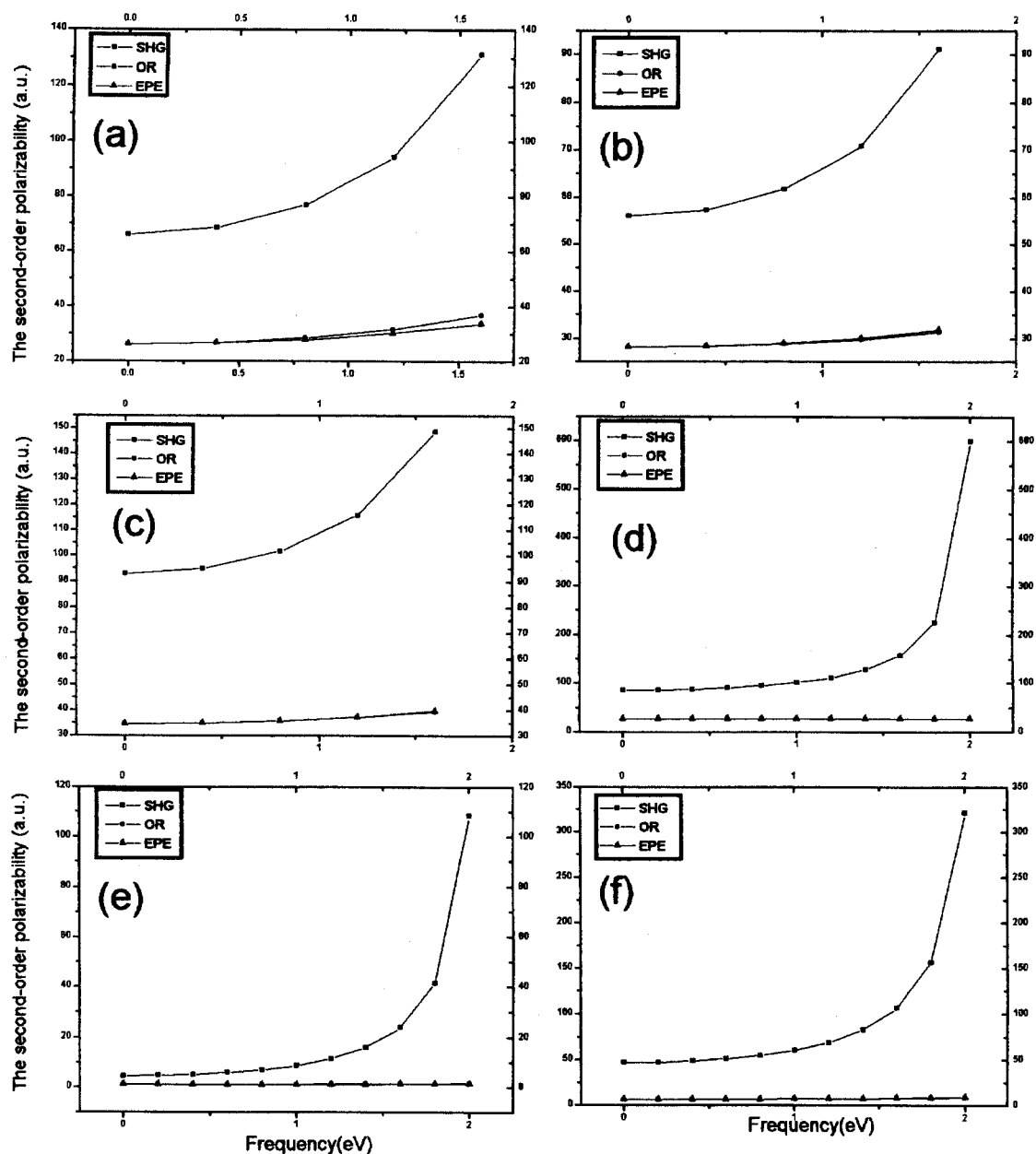


Figure 5. The frequency-dependent various second-order effects of 1,3,4-triazole(a), 1,3,4-oxadiazole(b), 1,2,4-thiadiazole(c), thiophene(d), furan(e), and pyrrole(f) monomers.

and (1,3,4)-thiadiazole oligomers for the various optical frequencies as a function of heterocyclic rings are shown in Figures 3 and 4, respectively. The average and longitudinal first-order polarizabilities increase in the order: thiophene > (1,2,4)-triazole > furan > pyrrole > (1,3,4)-thiadiazole > (1,3,4)-oxadiazole oligomers.

The average and longitudinal first-order polarizabilities of thiophene oligomers are the largest among the six oligomers. In the case of (1,3,4)-thiadiazole oligomers, the average first-order polarizabilities are similar to the values of thiophene oligomers, while the longitudinal first-order polarizabilities are slightly smaller than those of the thiophene oligomers.¹⁶

The average and longitudinal polarizabilities of thiophene and (1,3,4)-thiadiazole oligomers are about two times larger

than those of 1,2,4-triazole and 1,3,4-thiadiazole oligomers and 1.5 times larger than those of furan and pyrrole, respectively.

The exponent values (k) of the average and longitudinal first-order polarizabilities show the order: thiophene (1.5 eV; 1.37, 1.58) > (1,3,4)-thiadiazole (1.5 eV; 1.37, 1.6) > furan (1.5 eV; 1.36, 1.56) > pyrrole (1.5 eV; 1.3, 1.5) > (1,3,4)-oxadiazole (1.5 eV; 1.30, 1.49) > (1,2,4)-triazole (1.5 eV; 1.28, 1.48) oligomers. The saturation of average first-order polarizabilities for thiophene and (1,2,4)-triazole oligomers appear faster than the other oligomers. The exponent values of (1,2,4)-triazole, (1,3,4)-thiadiazole, and (1,3,4)-oxadiazole oligomers are smaller than those of thiophene, furan, and pyrrole oligomers, respectively. However, the exponent

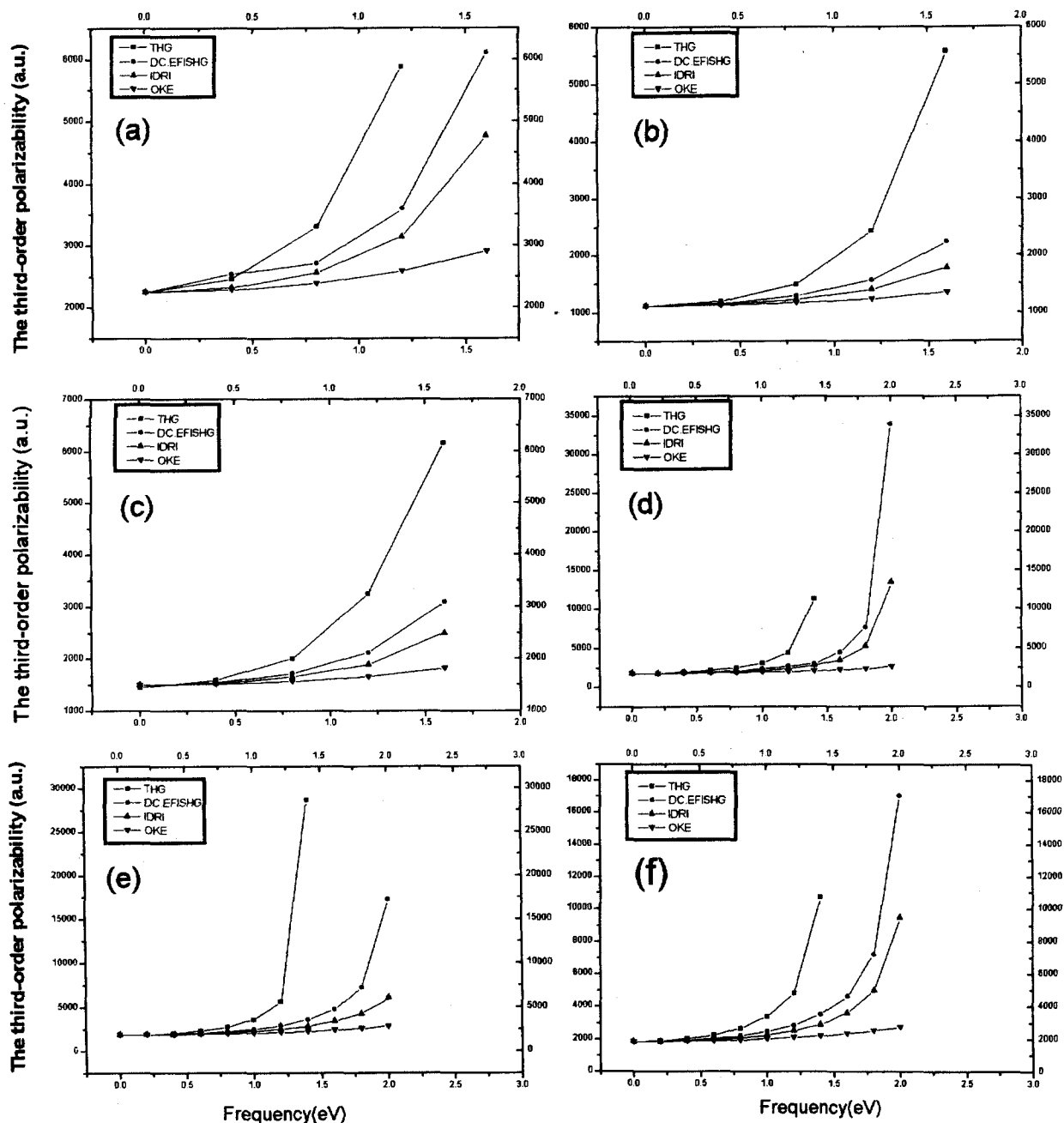


Figure 6. The frequency-dependent various third-order effects of 1,3,4-triazole(a), 1,3,4-oxadiazole(b), 1,2,4-thiadiazole(c), thiophene(d), furan(e), and pyrrole(f) monomers.

values of six oligomers are nearly similar to each other. These values are about two times smaller than previous experimentally estimated exponent values for π -electron polyenic systems.^{17,18} However, the exponent values of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole oligomers are larger than those of thiophene- and furan-TTF¹⁶ and -TCNQ¹⁹ systems.

Figure 5 shows the frequency-dependent second-order polarizabilities of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole monomers for the various second-order effects. Thiophene shows the largest SHG, EOPE, and OR effects. The calculated values of $\beta(-\omega, \omega, 0)$ (EOPE) and $\beta(0; -\omega, \omega)$ (OR) are not too different from $\beta(-2\omega, \omega, \omega)$ (SHG) at lower frequencies. However, the effects of SHG increase rapidly with optical frequencies. Also, $\beta(-2\omega, \omega, \omega)$ (SHG) shows a larger dispersion compared with $\beta(-\omega, \omega, 0)$ (EOPE) and $\beta(0; -\omega, \omega)$ (OR), and the differences increase with the optical frequencies. $\beta(-\omega, \omega, 0)$ (EOPE) and $\beta(0; -\omega, \omega)$ (OR) show the small dispersion behavior in the calculated range of the various frequencies. The calculated β values in thiophene, furan, pyrrole, (1,2,4)-

triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole have the following order: $\beta(-2\omega, \omega, \omega)$ (SHG) > $\beta(-\omega, \omega, 0)$ (EOPE) > $\beta(0; -\omega, \omega)$ (OR). This behavior is similar to the benzene,¹⁰ *p*-nitroaniline,²⁰ and other organic molecules.¹⁵

The average and longitudinal third-order polarizabilities of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole monomers for the various third-order effects increase in the order: $\gamma(-3\omega, \omega, \omega, \omega)$ (THG) > $\gamma(-2\omega, 0, \omega, \omega)$ (EFISHG) > $\gamma(-\omega, \omega, -\omega, \omega)$ (IDRI) > $\gamma(-\omega, 0, 0, \omega)$ (OKE) as shown in Figure 6. The effects of THG increase rapidly with optical frequencies compared with the other effects. In particular, OKE effects increase most slowly with optical frequencies. These results are consistent with the ab initio calculated results with the time-dependent coupled perturbed Hartree-Fock approach²⁰ and CNDO-CI calculated results reported by Morly *et al.*²¹

PM3 calculated average and longitudinal third-order polarizabilities of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole oligomers are shown in Figures 7 and 8, respectively. The average and longitudinal third-order polarizabilities have the order: thiophene

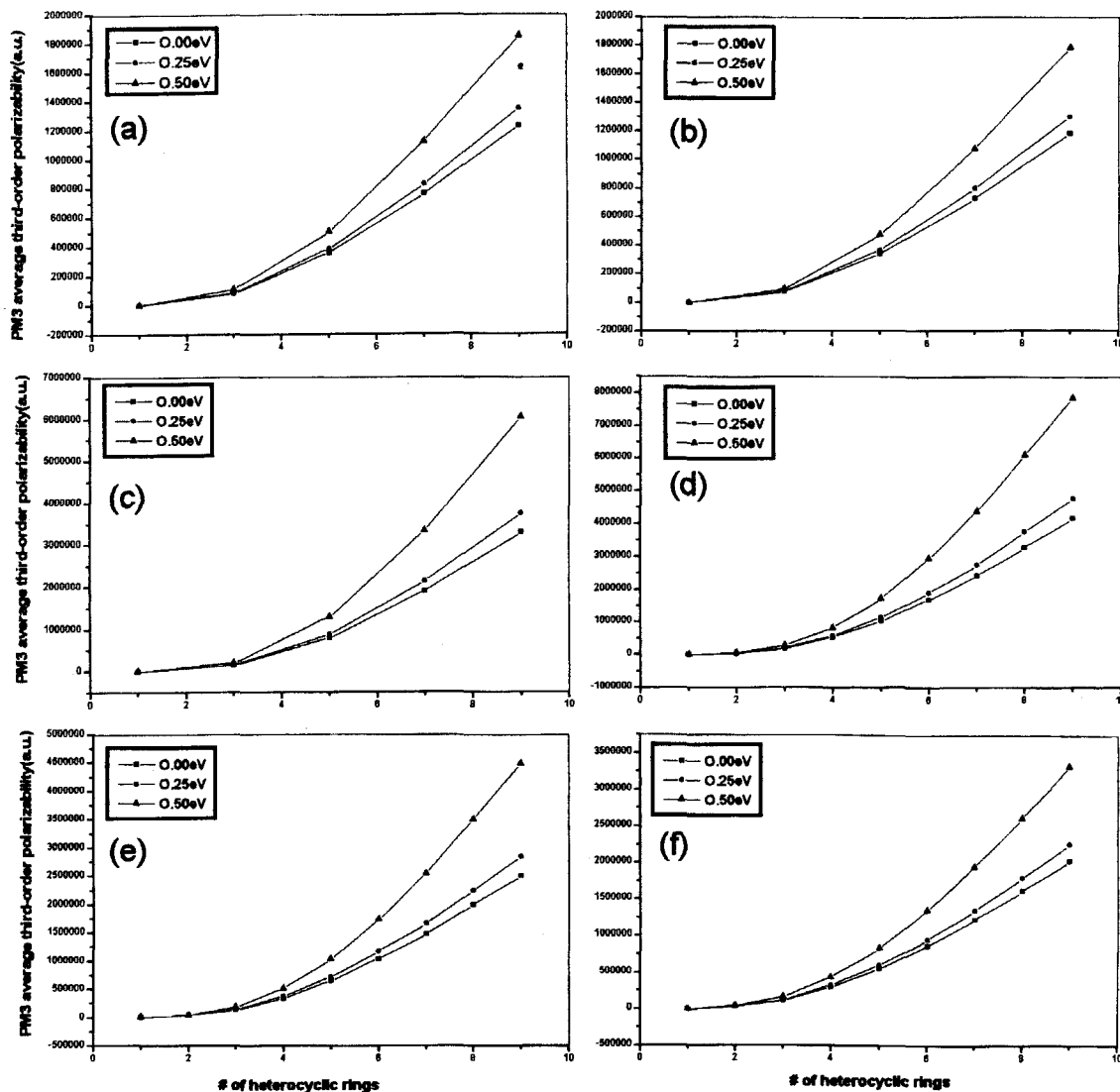


Figure 7. The PM3 calculated average third-order polarizabilities of 1,3,4-triazole(a), 1,3,4-oxadiazole(b), 1,2,4-thiadiazole(c), thiophene(d), furan(e), and pyrrole(f) oligomers.

> (1,2,4)-triazole > furan > pyrrole > (1,3,4)-thiadiazole > (1,3,4)-oxadiazole oligomers.

A number of theoretical studies have been performed on the investigation of the γ evolution as a function of chain length in polyenes.²² The results provided exponent values between 3 and 5.4 for the short chains. PM3 estimated exponent values of the γ value for thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole oligomers in the static electric field are similar to Valence-effective Hamiltonian(VEH)/sum-over-states calculated exponent value(3.3)²³ in polyene chains containing 2-15 double bonds(n). Also, these values are similar to EFISH measuremental exponent value(3.2) on the copolymers and Craig *et al.*²⁴ reported experimental exponent value(3.2) for polyenes. The exponent values of the γ value for thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-oxadiazole, and (1,3,4)-thiadiazole oligomers are 1.5 times smaller than those of regular (neutral) polyene (around 4.25) calculated by de Melo and Silbey.²⁵ Moreover, the exponent values of the γ

value for thiophene, furan, pyrrole, 1,2,4-triazole, 1,3,4-thiadiazole, and 1,3,4-oxadiazole oligomers are much smaller than those of charged soliton(4.8), polaron(6.3), and bipolaron(6.1). Also, these values are slightly smaller than those results reported by Beljonne *et al.*,²⁶ Prasad *et al.*,²⁷ and experimental data reported by Meijer *et al.*²⁸

The exponent values of the average and longitudinal third-order polarizabilities for the energy of frequencies have the following order: thiophene (0.5 eV; 3.74, 4.32) > 1,3,4-thiadiazole (0.5 eV; 3.58, 4.06) > furan (0.5 eV; 3.46, 4.40) > pyrrole (0.5 eV; 3.33, 3.85) > 1,2,4-triazole (0.5 eV; 3.23, 3.47) > 1,3,4-oxadiazole (0.5 eV; 3.35, 3.42) oligomers. The exponent values of 1,2,4-triazole, 1,3,4-thiadiazole, 1,3,4-oxadiazole oligomers are slightly smaller than those of thiophene, furan, and pyrrole oligomers, respectively. On the other hand, the exponent values of thiophene, furan, pyrrole, (1,2,4)-triazole, (1,3,4)-thiadiazole, and (1,3,4)-oxadiazole oligomers are larger than those of hetero (X=O,S,Se)-TTF¹⁶ and -TCNQ¹⁹ systems.

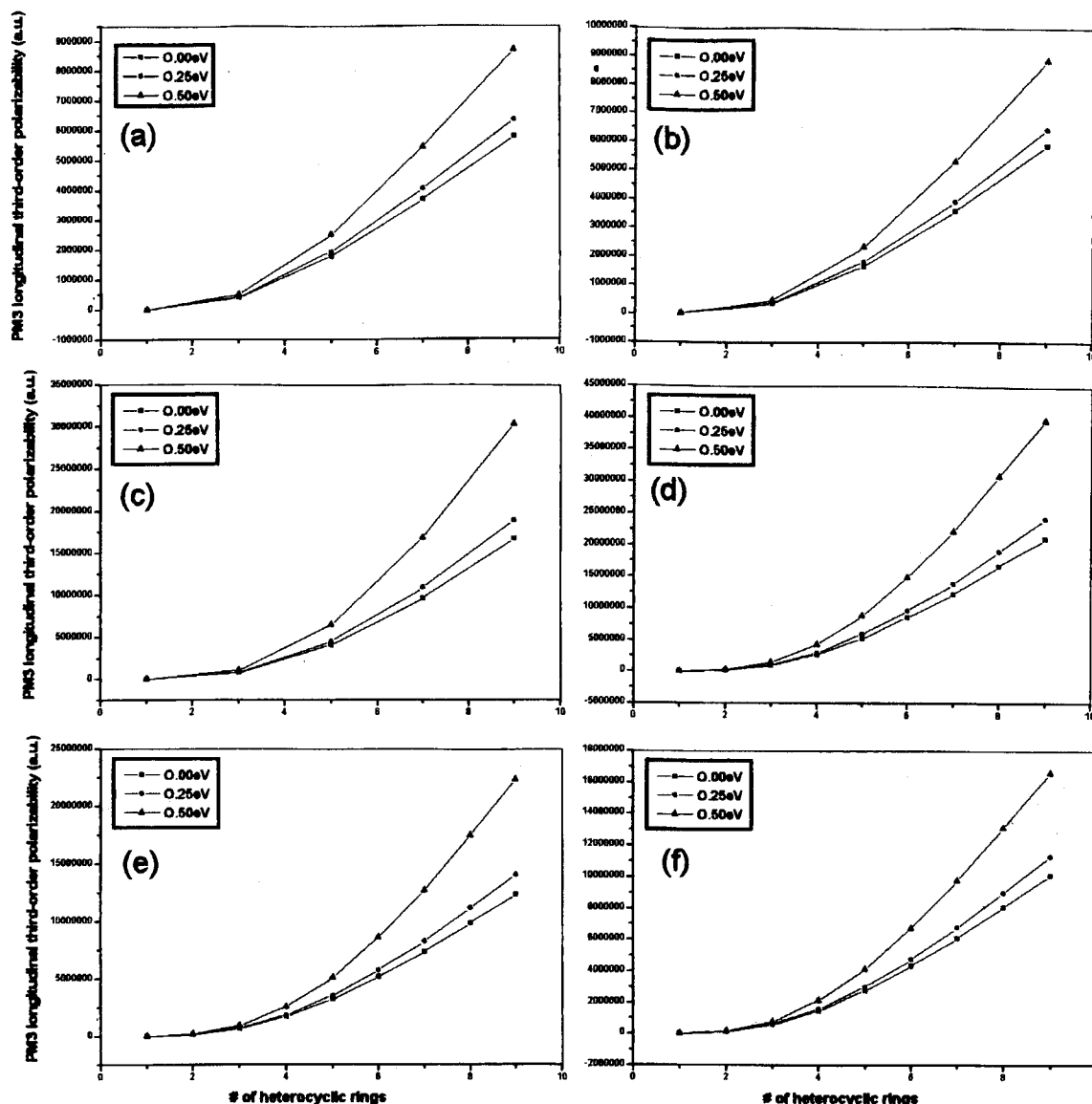


Figure 8. The PM3 calculated longitudinal third-order polarizabilities of 1,3,4-triazole(a), 1,3,4-oxadiazole(b), 1,2,4-thiadiazole(c), thiophene(d), furan(e), and pyrrole(f) oligomers.

From the above discussion, we find that the first-order polarizabilities increase in the order: thiophene > (1,3,4)-thiadiazole > furan > pyrrole > (1,2,4)-triazole > (1,3,4)-oxadiazole monomers and oligomers. The second-order polarizabilities for the various second-order effects have the order: $\beta(-2\omega, \omega, \omega)$ (SHG) > $\beta(-\omega, \omega, 0)$ (EOPE) > $\beta(0; -\omega, \omega)$ (OR) and thiophene > pyrrole > (1,2,4)-triazole > furan > 1,3,4-thiadiazole > 1,3,4-oxadiazole monomers. The third-order polarizabilities for the various third-order effects have the following order: $\gamma(-3\omega, \omega, \omega, \omega)$ (THG) > $\gamma(-2\omega, 0, \omega, \omega)$ (EFISHG) > $\gamma(-\omega, \omega, -\omega, \omega)$ (IDRI) > $\gamma(-\omega, 0, 0, \omega)$ (OKE) and thiophene > (1,3,4)-thiadiazole > furan > pyrrole > (1,2,4)-triazole, and (1,3,4)-oxadiazole oligomers. In particular, the average and longitudinal third-order polarizabilities of thiophene oligomers are four times larger than those of (1,3,4)-oxadiazole and (1,3,4)-thiadiazole and are 1.5 and 2 times larger than those of furan and pyrrole, respectively. Therefore, we suggest that sulfur containing heterocyclic ring systems show the largest nonlinear optical properties among the various heterocyclic ring systems.

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