

π -Conjugated Soluble Nickel–Polyyne Copolymer: Synthesis and Third-Order Optical Nonlinearity

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ABSTRACT: By means of homogeneous stepwise condensation method, both the Ni–polyyne copolymers with PPh₃ and PBu₃ ligands, and modified π -conjugated nickel-containing copolymers have been synthesized and confirmed by infrared (IR) analysis. The Ni–polyyne copolymers obtained are yellow powder having a \bar{M}_w of about $1 \sim 2 \times 10^4$ and a molecular weight distribution (MWD) of less than 3, and they are soluble in tetrahydrofuran (THF), CHCl₃, and toluene. Their third-order nonlinear optical properties have been investigated by a degenerate four-wave mixing (DFWM) technique. The effect of the nature of the ligands attached to the nickel atoms, the structure, and the length of π -conjugation between the 2 metal centers in the main chain on the hyperpolarizability γ of the Ni–polyyne polymers have been discussed. The maximum susceptibility $\chi^{(3)}$ and hyperpolarizability γ of the Ni–polyyne polymers reach 5.17×10^{-12} and 2.30×10^{-30} esu, respectively. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1165–1172, 1998

Key words: nickel–polyyne copolymer; synthesis; modification; third-order optical nonlinearity

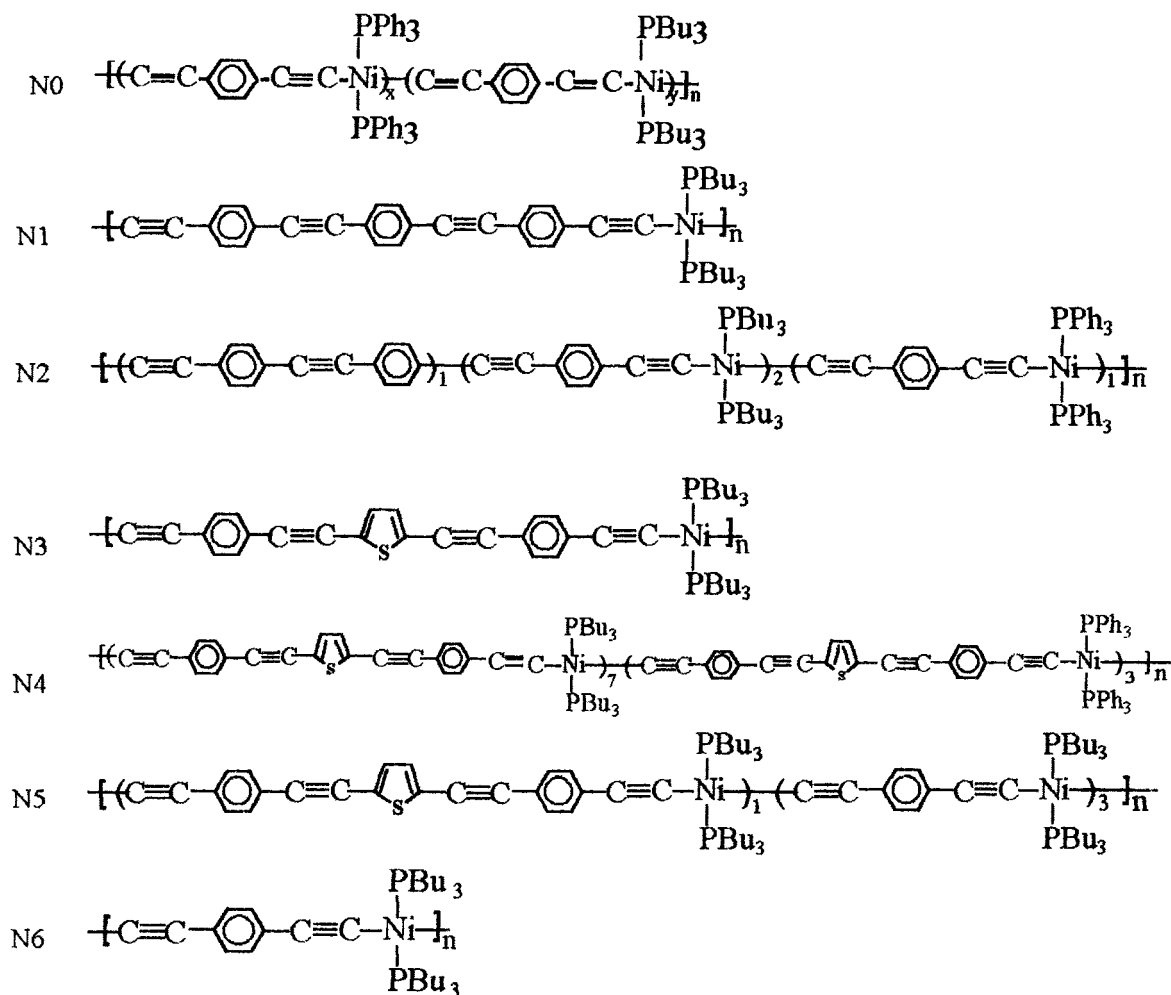
INTRODUCTION

In 1976, Sauteret et al. found large third-order optical nonlinearity in polydiacetylene-*p*-toluene sulphonate.¹ This opened new opportunities for studying conjugated organic polymers. In recent years, there has been a growth of interest in polyne polymers containing transition metal in the main chain in terms of their large third-order optical nonlinearity and low absorption in the visible and the near-infrared ranges, which make them potentially useful for many applications of nonlinear optics.^{2,3} Synthesis of metal–polyne polymers, $[-ML_2-C\equiv C-R-C\equiv C-]_n-$

(M=Pt, Pd, Ni; L=PBu₃, PEt₃, PMe₃), was developed by Takahashi and his coworkers,^{4–6} and their nonlinear optical (NLO) properties were investigated by Frazier et al.² We recently reported the synthesis of nickel–polyne polymer, $[-Ni(PPh_3)_2-C\equiv C-C_6H_4-C\equiv C-]_n-$, in which triphenylphosphine (PPh₃) ligands are attached to nickel atoms.⁷ By comparison with the analogue-containing PBu₃ ligands, the nickel–polyne polymer with PPh₃ ligands would be expected to exhibit large optical nonlinearity based on their different electron characteristics. However, their solubility in common organic solvents are unsatisfactory. In this article, preliminary results on the synthesis of a series of π -conjugated soluble nickel–polyne copolymers (Scheme 1) are described and discussed. Their third-order nonlinear optical properties have

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Scheme 1

been investigated by a degenerate four-wave mixing (DFWM) technique. The maximum susceptibility $\chi^{(3)}$ and hyperpolarizability γ of the Ni-polyynes copolymers obtained reach 5.17×10^{-12} and 2.30×10^{-30} esu, respectively.

EXPERIMENTAL

Materials

p-Diethynylbenzene (H_2PDB), $\text{HC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CH}$, was prepared by a method reported in the literature⁸ and was purified by sublimation immediately before used in the polymerization. *trans*-Bis(triphenylphosphine) dichloronickel, $\text{NiCl}_2(\text{PPh}_3)_2$ was prepared as previously reported.⁷ *trans*-Bis(tri-*n*-butyl-phosphine) dichloronickel, $\text{NiCl}_2(\text{PBu}_3)_2$, was prepared from the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with tri-*n*-butylphosphine (PBu_3) in

an ethanol solution at room temperature to give the product as purple-red crystals in 88% yield⁹. ANAL. Calcd for $(_{24}\text{H}_{54}\text{Cl}_2\text{NiP}_2)$: C, 53.9%; H, 10.10%. Found: C, 53.50%; H, 10.25%.

trans-Bis(triphenylphosphine) dichloropalladium $\text{PdCl}_2(\text{PPh}_3)_2$ was prepared by a procedure in the literature.¹⁰ 2,5-Diiodothiophene was prepared by modifying a reported method.¹¹ Diethylamine (HNEt_2) was distilled from calcium hydride and stored under N_2 . Tri-*n*-butyl-phosphine was purchased from Tokyo Chemical Industry Co. Ltd., Tokyo. All other chemicals were purchased from Shanghai Chemical Reagent Company, Shanghai.

Preparation of Polymer N0

A solution of $\text{NiCl}_2(\text{PPh}_3)_2$ (444.3 mg, 0.68 mmol) and H_2PDB (189.2 mg, 1.50 mmol) in 55-mL

mixed solvents (DMSO/HNEt₂/CH₂Cl₂ = 6 : 4 : 1 volume ratio) was stirred below 15°C under N₂ for 3 h. The molar ratio of NiCl₂(PPh₃)₂ to H₂PDB is 1 : 2.21. According to design, different contents of ligands in the polymer, a certain amount of NiCl₂(PPh₃)₂ in DMSO/HNEt₂/CH₂Cl₂ or of NiCl₂(PBU₃)₂ in HNEt₂/CH₂Cl₂ (2 : 1 volume ratio) was then injected stepwise to polymerization system every several hours to reach a NiCl₂L₂/H₂PDB ratio of 1 : 1; simultaneously, a solution of cuprous iodide (CuI) (1.4 mg, 0.007 mmol) in 2 mL of HNEt₂ was injected as catalyst. The whole polymerization kept for 14 h or so, then a brown solution was obtained by filtration. Filtrate was evaporated at reduced pressure. The product was dissolved in about 3 mL of THF and precipitated in methanol, filtered, washed with methanol, and dried at room temperature under vacuum for 8 h.

Preparation of Polymers 1 and 3

A mixture (I) of H₂PDB (252.4 mg, 2.0 mmol) and *p*-diiodobenzene (329.9 mg, 1.0 mmol) or 2,5-diiodothiophene (335.9 mg, 1.0 mmol) was stirred at 25°C in 30 mL of HNEt₂ in the presence of PdCl₂(PPh₃)₂ (17.6 mg, 0.025 mmol) and CuI (5.0 mg, 0.026 mmol) as catalysts under N₂ for 2.5 h (for *p*-diiodobenzene) or for 4.5 h (for 2,5-diiodothiophene) in a manner similar to the method in the literature.^{12,13} A solution of NiCl₂(PBU₃)₂ (534.1 mg, 1.0 mmol) in 25 mL of HNEt₂ and of CuI (5.0 mg, 0.026 mmol) in 5 mL of HNEt₂ were then injected to the reacted mixture (I) and stirred at 5–10°C for 24 h (polymer 1) and for 8 h (polymer 3). The resulting mixture was filtered to remove insoluble residue, and the filtrate was concentrated to dryness at reduced pressure. The polymers were then dissolved in 3 mL of THF and precipitated into methanol, washed with methanol, and dried under vacuum at room temperature for 24 h to give a bright yellow polymer 1 and an orange polymer 3 (containing a thiophene ring in the main chain).

Preparation of Polymers 2 and 4

To a reacted mixture (I) described above was injected a solution of NiCl₂(PBU₃)₂ (374.0 mg, 0.7 mmol) in 20 mL of HNEt₂, stirred at 5–10°C for 6 h. A solution of NiCl₂(PPh₃)₂ (196.3 mg, 0.3 mmol) in 6 mL of DMSO was then added and stirred at 5–10°C for 6 h again. The other procedures are the same as described above to give orange polymers 2 and 4.

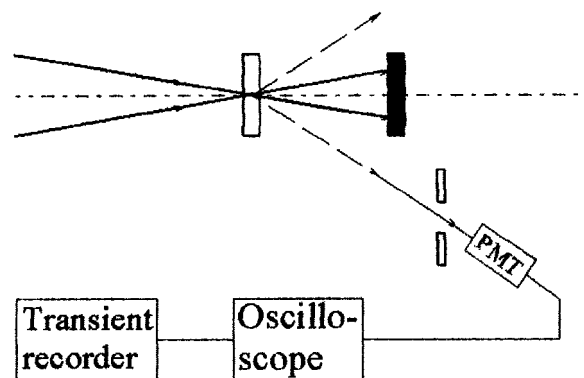


Figure 1 Experimental arrangement for the DFWM measurement.

Preparation of Polymers 5 and 6

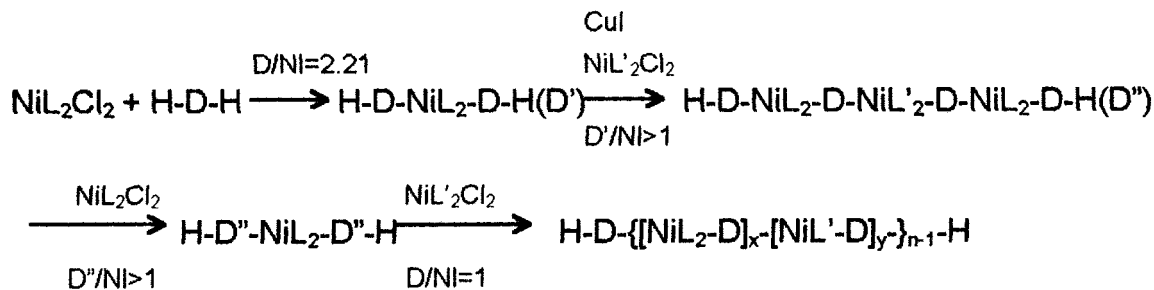
To a reacted mixture of 2,5-diiodothiophene (168.0 mg, 0.5 mmol) and H₂PDB (126.2 mg, 1.0 mmol) described above was injected a solution of NiCl₂(PBU₃)₂ (534.3 mg, 1.0 mmol) in 20 mL of HNEt₂, stirred at 5–10°C for 10 h. Then a solution of H₂PDB (126.2 mg, 1.0 mmol) and NiCl₂(PBU₃)₂ (267.0 mg, 0.5 mmol) in 10 mL of HNEt₂ was injected, and the mixture was stirred at 5–10°C for 15 h again. The treatment of the polymer is the same as described above. The final yellow polymer 5 was obtained. Polymer 6 was prepared in a manner similar to the method in the literature.^{12–13}

Instrumentation

Infrared (IR) spectra were obtained on a PE 983 IR spectrophotometer. Ultraviolet–visible (UV–vis) spectra were taken using a Beckman DU-50 spectrophotometer. Molecular weight determination was carried out on a Waters 208 gel permeation chromatography (GPC) instrument versus a polystyrene standard.

Measurement of the Optical Nonlinearities

Third-order nonlinear optical susceptibility $\chi^{(3)}$ was measured by a DFWM technique. The setup is depicted schematically in Figure 1. A Q-switched Nd : YAG laser with laser pulse width of 8 ns served as the light source. Two beams for DFWM split from the fundamental output of Nd : YAG laser of 1064 nm (or 532 nm) in wavelength were incident on THF solution of the Ni-polyynne polymers. The DFWM signal detected by



Scheme 2 Synthetic route of Ni-polyynes copolymers: L, PPh₃; L', PBu₃; D: —C≡C—C₆H₄—C≡C—; Ni: NiL₂Cl₂ or NiL'₂Cl₂.

a photomultiplier was recorded by an oscilloscope and a transient recorder.

The hyperpolarizability (γ) was calculated by using the equation $\gamma = \frac{\chi^{(3)}}{L^4 N}$ [where $L = \frac{1}{3}(n^2 + 2)$, where n denotes the refractive index of the solvents, and N is the number of the average monomer unit per cubic centimeter].

RESULTS AND DISCUSSION

Nickel-Polyynes Copolymers with PPh₃ and PBu₃ Ligands NO

By means of homogeneous stepwise condensation method, the Ni-polyynes copolymers with PPh₃ and PBu₃ ligands were synthesized from the reaction of NiCl₂(PPh₃)₂ and NiCl₂(PBu₃)₂ with H₂PDB in the presence of CuI in DMSO-HNEt₂-CH₂Cl₂ mixed solvent system below 15°C. The condensation route is shown in Scheme 2. A series of copolymers were obtained by the change of feed ratio of NiCl₂(PPh₃)₂ to NiCl₂(PBu₃)₂. The copolymerization results are

given in Table I. It is seen from Table I that the solubility of polymer A, that is, the Ni-polyynes polymer with PPh₃ ligands, is unsatisfactory, but the introduction of unit with PBu₃ ligands into polymer chain resulted in favorable increase of the solubility of Ni-polyynes polymers. Moreover, the yield and molecular weight of those also increased with increasing the component of unit with PBu₃ ligands in the copolymer. In fact, the polymer D with 40% NiCl₂(PBu₃)₂ in NiCl₂L₂ feed is all soluble in THF and CH₂Cl₂.

The series of Ni-polyynes polymers A, B, C, D, E, F, G, and H (Table I) obtained are dark yellow or yellow powder having an \bar{M}_w ranging from 8.8×10^3 to 2.1×10^4 , a MWD of less than 3, and are stable in air. IR spectra of them all show the characteristic absorption of acetylenic bond, C≡C, in the region of 2000–2200 cm⁻¹. The detail IR spectral data in this region are given in Table II. It is seen that the frequency and number of the C≡C absorption band are quite different. There are 4 bands in this region for a polymer-A-containing unit with PPh₃ ligands of 100% and 2

Table I Physical Properties of the Ni-Polyynes Polymers and Copolymers, —{[Ni(PPh₃)₂—C≡C—C₆H₄—C≡C—]_x—[Ni(PBu₃)₂—C≡C—C₆H₄—C≡C—]_y}_n—

Polymer	f_1^a (mol %)	Color	Yield (%)	\bar{M}_w $\times 10^{-3}$	MWD	Solubility (in THF)
A	100	Dark yellow	37.2	9.1	2.00	Partly
B	85	Dark yellow	40.4	8.8	1.78	Mostly
C	70	Dark yellow	29.0	9.5	1.79	Mostly
D	60	Dark yellow	48.6	11	2.20	All
E	50	Dark yellow	58.8	13	2.26	All
F	35	Dark yellow	68.0	16	1.90	All
G	20	Yellow	75.7	19	1.97	All
H	0	Yellow	76.2	21	1.98	All

^a f_1 is feed composition of NiCl₂(PPh₃)₂ in NiCl₂L₂ (mol %). NiCl₂L₂ = NiCl₂(PPh₃)₂ + NiCl₂(PBu₃)₂.

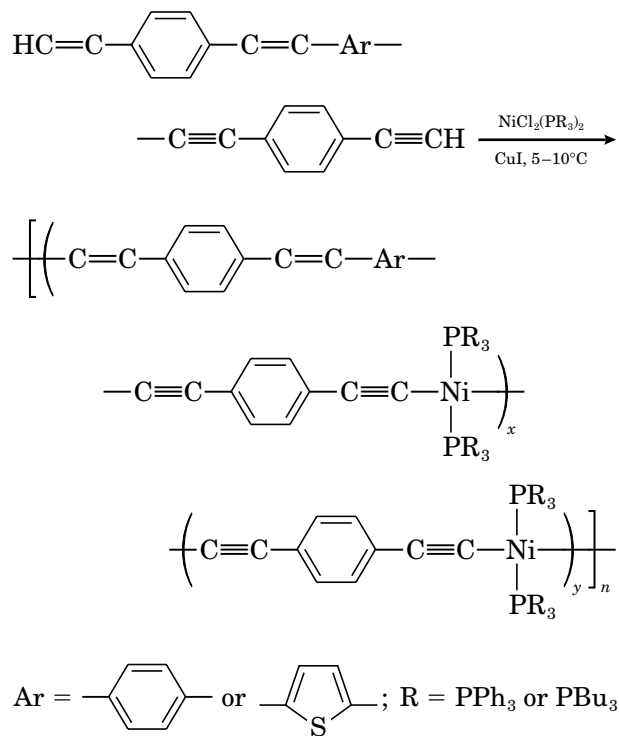
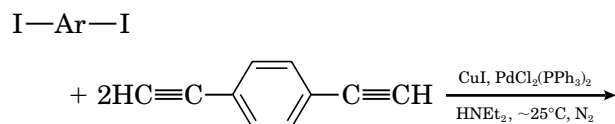
Table II IR Absorption Bands for Ni-Copolymers in the 2000–2200 cm⁻¹ Region

Polymer	$\nu_{C\equiv C}$ (cm ⁻¹)			
A	2208 (m)	2168 (w)	2145 (w)	2092 (s)
B	2209 (m)	2168 (vw)	2140 (w)	2089 (s)
C	2208 (m)	2168 (vw)	2141 (w)	2085 (s)
D	2208 (m)	2168 (vw)	2141 (w)	2083 (s)
E	2209 (w)		2140 (vw)	2083 (s)
F	2208 (w)		2140 (vw)	2084 (s)
G	2208 (w)			2083 (s)
H	2162 (w)			2084 (s)

bands for a polymer-H-containing unit with PBu₃ ligands of 100%; that is, the intensity and number of these absorption bands (C≡C) decrease with the component decrease of the unit containing PPh₃ ligands in polymers going from A to H. It is due to the larger size of the PPh₃ ligand than the PBu₃ that one can introduce steric strain between the adjacent units within the macromolecule. The IR analysis results indicated that the Ni-polyyne copolymers with PPh₃ and PBu₃ ligands were formed.

Nickel-Polyyne-Copolymers-Modified Main Chain N1–N5

Nickel-polyyne-copolymer-modified main chain N1–N5 listed in Scheme 1 were synthesized by a Pd-catalyzed polycondensation reaction in the presence of CuI according to the following equations:



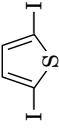

Their physical properties and spectral data are given in Tables III and IV, respectively. They are orange–yellow powders having molecular weights (\bar{M}_w) ranging from 0.49×10^4 to 1.48×10^4 , a molecular weight distribution (MWD) of less than 3, and they are highly soluble in common organic solvents, such as THF, chloroform, and toluene. It is seen from Table IV that the strong terminal $\nu_{(C\equiv C-H)}$ band of the diethynylbenzene at 3264 cm^{-1} is shifted to a higher frequency to about $3278\text{--}3280 \text{ cm}^{-1}$ and becomes weak, which indicated formation of a longer Ni-polyyne polymer chain. Moreover, the $\nu_{(C\equiv C)}$ band of the diethynylbenzene at 2110 cm^{-1} is shifted to $2180\text{--}2200 \text{ cm}^{-1}$, which is

Table III Physical Properties of the Ni-polyyne Copolymer-Modified Main Chain

Copolymer	Color	Yield (%)	$\bar{M}_w \times 10^{-4}$	MWD	Ni (%)	Solubility in THF (%)
N1	Bright yellow	28.6	0.79	1.57	7.76 (7.45) ^a	~ 100
N2	Orange–yellow	42.5	1.48	1.68	7.77 (8.45)	~ 100
N3	Orange–yellow	17.1	0.72	2.63	7.00 (7.39)	~ 30
N4	Orange–yellow	47.4	1.13	1.89	7.53 (7.07)	~ 30
N5	Yellow	49.5	0.49	1.32	9.75 (9.18)	~ 100

^a Calculated values in the parentheses.

Table IV IR Data for Polymers and Monomers

Compound	ν ($\equiv\text{C}-\text{H}$)	ν ($\text{MC}\equiv\text{C}$)	ν ($\text{ArC}\equiv\text{CAr}$)	IR (cm^{-1})	
				δ ($\text{C}-\text{H}$)	δ ($\text{C}-\text{H}$)
				δ ($\text{C}-\text{H}$)	δ ($\text{C}-\text{H}$)
N1	3282 (w)	2067 (vs)	2136 (w)	830 (vs)	785 (s)
N2	3280 (w)	2072 (vs)	2190 (w)	835 (vs)	
N3	3278 (w)	2070 (s)	2200 (w)	835 (vs)	690 (m), 740 (m)
N4	3280 (w)	2068 (vs)	2195 (w)	838 (s)	
N5	3280 (w)	2072 (vs)	2180 (w)	834 (vs)	690 (m), 740 (m)
N6	3290 (w)	2075 (vs)	2180 (w)	834 (vs)	795 (s)
			2195 (w)	836 (vs)	795 (m)

consistent with a known trend that disubstituted acetylenes give rise to the $\nu_{(\text{C}\equiv\text{C})}$ band at a frequency higher than monosubstituted acetylenes.¹⁴ The IR spectra of N1–N5 exhibit sharp intense $\nu_{(\text{MC}\equiv\text{C})}$ bands at about 2067–2075 cm^{-1} . This also shows that the polyynes containing σ -bond metal are formed. Besides them, characteristic absorption of the thiophene-2,5-diyl group at 795 cm^{-1} are observed for N3–N5 copolymers. In this way, the above IR analysis results support that the Ni-polyynes modified main chain, N1–N5, have been synthesized.

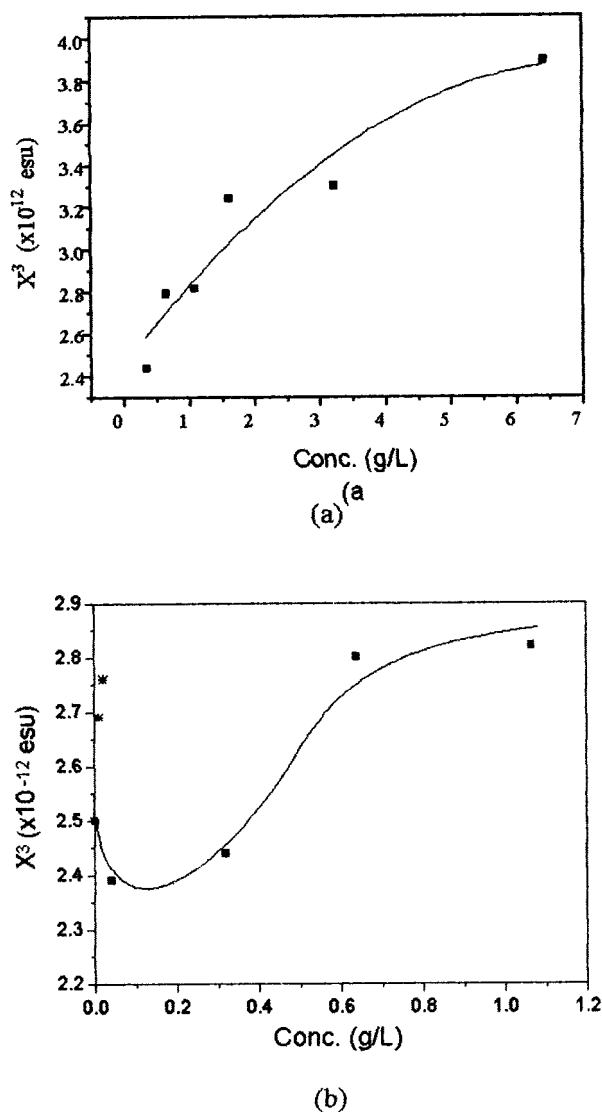


Figure 2 Dependence of $\chi^{(3)}$ on the concentration of polymer D (a) at high concentration range and (b) at a low concentration range.

Table V Hyperpolarizability (γ) of Ni-Polyynene Copolymers Containing PPh₃ and PBu₃ Ligands

Copolymer	D	E	F	G
f_1^a , mol fraction	0.60	0.50	0.35	0.20
$\gamma^b \times 10^{31}$ esu	5.95	5.57	5.16	5.14

^a See Table I.^b Measurement at 1064 nm.

Third-Order Optical Nonlinearity of Nickel-Polyynene Polymers N0–N6

The third-order nonlinear optical (NLO) properties for the soluble Ni-polyynene polymers have been investigated by means of a DFWM technique. Figure 2 shows the third-order nonlinear optical susceptibility $\chi^{(3)}$ of solution of the Ni-polyynene copolymer in THF as a function of its solution concentration (g/L). The maximum concentration of the copolymer in THF adopted was 6.4 g/L. A strong dependence of $\chi^{(3)}$ on solution concentration was observed. $\chi^{(3)}$ decreases as concentration does at the high concentration range, then falls below the level of the pure solvent (THF) at the low concentration, subsequently showing a parabolic dependence, which indicates that the susceptibility of the solute ($\chi_{solu}^{(3)}$) has an opposite sign to that of solvent ($\chi_{solv}^{(3)}$), that is, $|\chi_s^{(3)}| = |\chi_{solu}^{(3)}| - |\chi_{solv}^{(3)}|$. A similar behavior was observed for the dialkynyl complex.¹⁵ Notably, while the solution concentration is decreased further, a $|\chi_s^{(3)}|$ higher than $|\chi_{solv}^{(3)}|$ was observed as suggested that multiphoton resonant enhancement may exist.¹⁶

The effect of ligand bonded to nickel in the main chain on the molecular hyperpolarizability (γ) is shown in Table V. With the increase of component (f_1) containing PPh₃ ligands in the

feed of NiCl₂(PPh₃)₂ and NiCl₂(PBu₃)₂, that is, the component increase of the unit containing PPh₃ ligands in the copolymer, the γ value increases and reaches 5.95×10^{-31} esu ($f_1 = 0.60$). It is seen that PPh₃ ligand shows greater contribution than PBu₃ ligand to the second-order hyperpolarizability (γ) of Ni-polyynene polymers, which may be due to the fact that with the increasing composition of the unit with PPh₃ ligands, the electron density in the main chain increases and the electrons delocalize easier.

As shown in Table VI, there is significant influence of the structure and length of π -conjugation between the 2 metal centers in the main chain of metal-polyynene polymer on their third-order nonlinear optical properties ($\chi^{(3)}$ or γ). Comparison of polymers N1–N5 with N6 shows that introducing phenylene-di-ethynylene and 1,4-phenylene or thiophene-2,5-diyl to the main chain gives rise to the increase in π -conjugated length between the 2 metal centers and to rearrangement of the π -electrons within the polymer chain, bring about the alternating high-band-gap conjugated structures with low-band-gap structures^{17,18} and therefore leads to the increase in γ . Particularly, inserting more thiophene rings into the main chain of the nickel-polyynene polymers, such as polymer N4, leads to a large enhancement of γ value. The γ value of polymer N4 reaches 2.30×10^{-30} esu, which is 7 times larger than that for polymer N2 without containing a thiophene ring in the main chain. It is due to the introduction of the thiophene ring into the polymer chain, which might lead further to the nondegenerate ground-state system.^{19–21} A further increase in the conjugation chain length between the 2 metal centers by inserting more phenylene-diethynylene and thiophene-2,5-diyl (or *p*-phenylene) groups into the polymer main chain should give rise to large

Table VI The Values of λ_{abs} , $\chi^{(3)}$ and γ for Ni-Polyynene Polymers^a

Polymer ^b	λ_{abs} (nm)	$\chi^{(3)} \times 10^{12b}$ (esu)	$\gamma \times 10^{32}$ (esu)	$\bar{M}_w \times 10^{-4}$ (GPC)
N1	389.5	4.06	85.7	0.79
N2	401.0	1.60	29.8	1.48
N3	389.5	0.76	48.6	0.72
N4	402.0	5.17	230	1.13
N5	388.5	1.37	23.5	0.49
N6	370.0	< 0.47	< 7.4	1.29

^a In THF(N₁, N₂, N₃, and N₆, 2 mg/mL; N₅, 1 mg/mL; N₄, 0.67 mg/mL).^b Measurement at 532 nm.

enhancement in γ , but this effort actually brings about the insoluble polymers.

CONCLUSIONS

1. Both the prepared Ni-polyynes copolymers with PPh_3 and PBU_3 ligands and modified π -conjugated nickel containing copolymers are yellow powder having a \bar{M}_w of about 10^4 and a MWD of less than 3, and they are highly soluble in THF, chloroform, and toluene.
2. The synthesis of Ni-polyynes copolymers with PPh_3 and PBU_3 ligands offers new third-order NLO materials with improved solubility and NLO properties.
3. Hyperpolarizability (γ) of Ni-polyynes polymers is related to the nature of the ligands attached to the nickel atoms and the structure and length of π -conjugation between the 2 metal centers along the main chain. Inserting a thiophene ring or unit with PPh_3 ligands into the main chain of Ni-polyynes polymer leads to a larger enhancement in γ than a benzene ring or a unit with PBU_3 ligands does. The longer the π -conjugation length between the 2 metal centers in the main chain, the larger the γ value of Ni-polyynes polymer.

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REFERENCES

1. C. Sauteret, J. P. Hermann, R. Frey, F. Pradere, J. Ducuing, R. H. Baughman, and R. R. Chance, *Phys. Rev. Lett.*, **36**, 956 (1976).
2. C. C. Frazier, S. Guha, P. L. Porter, and P. M. Cockerham, *Proc. SPIE*, **971**, 186 (1988).
3. P. L. Porter, S. Guha, K. Kang, and C. C. Frazier, *Polymer*, **32**, 1756 (1991).
4. S. Takahashi, H. Morimoto, E. Murata, S. Kataoka, K. Sonogashira, and N. Hagihara, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 565 (1982).
5. S. Takahashi, E. Murata, K. Sonogashira, and N. Hagihara, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 661 (1980).
6. K. Sonogashira, K. Ohga, S. Takahashi, and N. Hagihara, *J. Organomet. Chem.*, **188**, 237 (1980).
7. M. J. Yang, L. J. Zhang, Z. G. Cai, P. Q. Yang, and Z. L. Xu, *J. Polym. Sci., Part A: Polym. Chem.*, **33**, 2203 (1995).
8. A. S. Hay, *J. Org. Chem.*, **25**, 637 (1960).
9. J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964).
10. H. A. Tayim, A. Bouldoukian, and F. Awad, *J. Inorg. Nucl. Chem.*, **32**, 3799 (1970).
11. J. M. Barker, P. R. Huddleston, and M. L. Wood, *Synth. Commun.*, **5**, 59 (1975).
12. K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, 4467 (1975).
13. K. Takahashi, M. Kariya, T. Yatake, K. Sonogashira, and N. Hagihara, *Macromol.*, **11**, 1063 (1978).
14. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1954, p. 59.
15. J. Zhao, Y. G. Wang, J. H. Si, P. X. Ye, S. J. Li, L. J. Zhang, Z. F. Wu, and M. J. Yang, *J. Nonlin. Opt. Phys. Mater.*, **6**, 109 (1997).
16. A. P. Davey, D. J. Cardin, H. J. Byrne, and W. Blau, *Organic Molecular for Nonlinear Optics and Photonics*, J. Messier et al., Eds., 1991, p. 391.
17. S. A. Jenekhe, W. C. Chen, S. Lo, and S. R. Flom, *Appl. Phys. Lett.*, **57**, 126 (1990).
18. S. De Silvestri, M. Nisoli, V. Pruneri, S. Destri, W. Porzio, and R. Tubino, *Chem. Phys. Lett.*, **234**, 348 (1995).
19. Z. Vardeny, E. Ehrenfreund, O. Brafman, M. Nowak, H. Schaffer, A. J. Heeger, and F. Wudl, *Phys. Rev. Lett.*, **56**, 671 (1986).
20. J. L. Bredas and G. B. Street, *Acc. Chem. Res.*, **18**, 309 (1985).
21. Z. Vardeny, H. T. Grahn, A. J. Heeger, and F. Wudl, *Synth. Met.*, **28**, C299 (1989).