

Poly(1,6-heptadiyne)-Based Materials by Metathesis Polymerization

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I. Introduction

π -Conjugated polymers such as polyacetylene,^{1–3} polyacetylene derivatives,^{4–10} poly(aromatic vinyl- enes),^{11–16} polyaromatics,^{17–24} polyazines,^{25–30} and polyazomethine,^{31–33} etc., have been extensively studied for the past 4 decades. Polyacetylene and its derivatives may be conceptually defined as the linear polymers having a π -conjugated system in the main chain. Polymers having a conjugated system in the main chain are expected to show unique properties such as electrical conductivity,^{34–39} paramagnetic susceptibility,^{40–42} optical nonlinearity,^{43–50} photocon- ductivity,^{51–55} gas and liquid mixture separation,^{56–62} and radiation degradation^{63–65} peculiar to their own structure.

Polyacetylene has a simple chemical structure, and the addition of small amounts of various dopants (both acceptors and donors) dramatically changes its electrical, optical, and magnetic behavior. The acety- lene was first polymerized to a linear π -conjugated polymer by Natta et al. using a $\text{Ti}(\text{O}-\text{Pr})_4/\text{Et}_3\text{Al}$ in 1958.⁶⁶

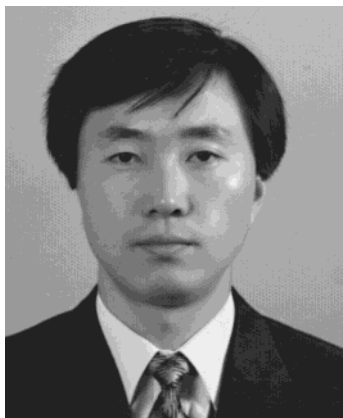
Watson et al. studied the polymerization of acety- lene with various Ziegler-type catalysts and gave the first report for the preparation of *cis*-polyacetylene.⁶⁷ Since Shirakawa et al. reported that the electrical conductivity of polyacetylene films formed at the liquid–gas interface of the $\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{Et}_3\text{Al}$ catalyst system increases many orders of magnitude when exposed to vapors of halogens,^{68,69} great efforts have been made out to produce similar highly conducting polymers.^{70–72} Another technique for the preparation of polyacetylene film, uses a catalyst developed by

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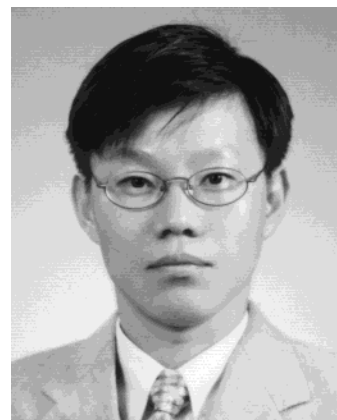


Sam-Kwon Choi was born in Taegu, Korea, in 1928. He received his B.S. degree in applied chemistry from Yeungnam University in 1953. His M.S. degree was earned in the Department of Chemical Technology at Seoul National University. From 1956 to 1965, he was an associate professor at Yeungnam University. He received his Ph.D. degree with the major of fluorine & polymer chemistry in the Department of Chemistry at Colorado State University under the superadvisor of Prof. D. J. Park in 1969. From 1969 to 1970, he was a senior researcher at Alrac Corp. He became professor in the Department of Chemistry at Korea Advanced Institute of Science and Technology (KAIST) in 1972. From 1985 to 1986, he was a visiting professor at University of Iowa and University of Clemson. He is now an emeritus professor at KAIST. Professor Choi was the recipient of a Moranjang Award of Korea government (1985) and the Excellent Scientist Award of the National Academy of Sciences, Korea (1995). His main interests include fluorine chemistry, anion polymerization of 2-pyrrolidone, synthesis of substituted polyacetylenes, multifunctional conjugated polymers, and group-transfer polymerization, etc. He has published more than 250 communications, papers, review articles, a number of chapters in books, and 9 patents.



Yeong-Soon Gal was born in Kyungsangnam-Do, Korea, in 1961. After receiving a B.S. degree from Kyungpook National University, Taegu, in 1983, he obtained M.S. (1985) and Ph.D. (1988) degrees in chemistry (major: polymer chemistry) from the Korea Advanced Institute of Science and Technology (KAIST) under the direction of Prof. Sam-Kwon Choi. From 1988 to 1995, he was a senior research scientist at the Agency for Defense Development (ADD), and he received Outstanding Technical Achievement Awards in 1990 and 1993 in ADD. In 1995, he became an assistant professor in the Chemistry Division of Kyungil University. He was a technical consultant of Hankook Fiber-glass Co. Ltd. and Iwha Chemical Co. from 1995 to now. His research interests center on design and synthesis of substituted acetylenes, modification of transition metal catalysts, conductive polymer and composites, advanced composite structure, applications and modification of thermoset matrix, and high-temperature adhesives, etc. He has published more than 108 communications, papers, and review articles.

Luttinger.⁷³ The main advantage of this technique is that the requirement for rigorous exclusion of moisture normally associated with the Ziegler catalyst is circumvented. A new type of polyacetylene film



Sung-Ho Jin was born in Pusan, Korea, in 1964. He received his B.S. degree in Chemistry from Pusan National University in 1988 and his Ph.D. in Chemistry from the Korea Advanced Institute of Science and Technology (KAIST) in 1993. In the same year he joined the Samsung Advanced Institute of Technology (SAIT) as a Senior Researcher where he worked in the field of Display Division. He joined the faculty of Pusan National University in 1999. His main research interests are (1) synthesis of new functional polymers (conducting polymers, photorefractive polymers), (2) side chain (anti)ferroelectric liquid crystal polymers, (3) polymer light emitting diodes, (4) (photo)alignment materials for liquid crystal display, (5) solid polymer electrolytes for lithium-polymer batteries, (6) photoresists and low-dielectric constant materials for semiconductors. He is the author or coauthor of over 40 publications and 21 patents.



Hwan Kyu Kim is an Associate Professor in the Department of Polymer Science & Engineering at Hannam University in Korea. Professor Kim's research and teaching interests have been focused on developing new optoelectronic polymeric materials for data communication and information technology for the past 9 years, particularly, in the research areas of NLO, LED, photorefractive polymers, optical waveguide polymers, and lanthanide-cored dendrimer complexes for optical amplification, between polymer science and photonics. He was born in Ulsan, Korea, in 1957. He graduated from the University of Ulsan where he received his B.Sc. degree in applied chemistry with summa cum laude in 1980. His M.Sc. (1982) was earned in the department of chemistry at the Korea Advanced Institute of Science and Technology (KAIST) under the direction of Professor Sam-Kwon Choi. From 1982 to 1986, he was a researcher at the Korea Research Institute of Chemical Technology (KRICT). He received a Ph.D. degree with the major of polymer chemistry in the Department of Chemistry at Carnegie Mellon University under the superadvisor of Prof. K. Matyjaszewski in 1990. After he joined Prof. C. K. Ober's research group in the Department of Materials Science & Engineering at Cornell University as a postdoctoral associate for 2 years, working with the development and applications of optoelectronic polymers, he returned to Korea in 1993 and worked to develop polymeric photonic devices as a Project Leader at the Photonic Switching Section at the Electronics & Telecommunications Research Institute (ETRI) for 1½ years. He became an Assistant Professor in the Department of Polymer Science & Engineering at Hannam University. Professor Kim was the recipient of the Excellent Scientist Award of the Korean Chemical Society for Polymer Chemistry in 1998. He has published more than 95 communications, papers, and review articles, a number of chapters in books, and 13 patents.

was prepared with an aged mixture of $\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{Al}(\text{C}_2\text{H}_5)_3$ in a viscous silicon oil medium by Naermann et al.^{74,75} This reaction medium yielded a homogeneous and defect-free polyacetylene film that can be mechanically stretched up to 600%. On being doped with iodine, the film displays metal-like electrical conductivities of higher than 100 000 S/cm.

A number of publications dealing with chemical, physical, and electrical properties of polyacetylene have appeared in the past 4 decades,^{1-3,76-82} But, the characterization of polyacetylene has not been fully investigated owing to its insolubility and infusibility, and the applications of polyacetylene have been restricted due to poor functionality peculiar to its simple chemical structure.

To increase the processability and provide various functionalities of polyacetylene, a study on the synthesis and characterization of substituted polyacetylenes has been extensively investigated.⁴⁻¹⁰ The introduction of functional substituents into polyacetylene causes a drastic change in various properties of the polymers, because of their solubility, fusibility, and interesting chemical, optical, and other properties.

Polymerization of substituted acetylenes has been carried out by a wide range of catalysts and conditions.^{6,8,9} Polymerization conditions include a homogeneous and heterogeneous Ziegler–Natta catalyst, transition metal complexes (Pd, Pt, Ru, W, Mo, Ni, etc.), free radical initiators such as 2,2'-azobis(isobutyronitrile) (AIBN), benzoyl peroxide (BPO), and di-*tert*-butylperoxide (DTBP), thermal polymerization, γ -irradiation, cationic initiation with BF_3 , and anionic initiation by butyllithium, triethylamine, and sodium amide.^{6,83}

The monosubstituted acetylene that has most often been employed to study polymerization is probably phenylacetylene.⁶ Conventional radical, cationic, or anionic initiation methods give only a low yield of phenylacetylene oligomers with a number-average molecular weight (M_n) of a few thousand.⁸⁴ Ziegler catalysts provide relatively high molecular weight oligomers ($M_n \approx 7000$) having a large insoluble fraction.^{85,86} In 1974, Masuda et al. found that phenylacetylene is effectively polymerized by WCl_6 and MoCl_5 catalyst,⁸⁷ which had been used for the olefin metathesis reactions and the metathesis polymerization of cycloolefins.⁸⁸⁻⁹⁰ Since then, there have been many studies on the polymerization of phenylacetylene and related acetylene compounds using W- and Mo-based catalyst systems.^{9,91-95} The M_n of polyphenylacetylene obtained by WCl_6 was about 15 000. Aromatics, halogenated hydrocarbons, and ethers are useful for polymerization solvents.

The polymerization with WCl_6 is significantly accelerated in the presence of tetraphenyltin (Ph_4Sn) as a cocatalyst.⁹⁶ And also the poly(phenylacetylenes) having high molecular weight ($M_n \approx 100\,000$) were prepared by two polymerization methods. One is to use solvents containing active hydrogens such as 1,4-dioxane, cyclohexenes, and tetralin in the polymerization by the WCl_6 – Ph_4Sn catalyst system.⁹⁷ The active hydrogen of solvents seems to prevent the polymer degradation reaction by a radical mechanism and/or modify the nature of the active species. An-

other method of enhancing the molecular weight is to use the catalyst system obtained by UV-irradiation of $\text{W}(\text{CO})_6$ in carbon tetrachloride.⁹⁸ This polymerization does not proceed without UV-irradiation or in a hydrocarbon solvent instead of carbon tetrachloride.

A trimethylsilyl or trifluoromethyl group containing poly(phenylacetylenes) for oxygen and ethanol permselective membranes had been prepared by WCl_6 and a Rh complex $[\text{Rh}(\text{cyclooctadiene})(\text{triphenylphosphine})_2]\text{PF}_6(\text{RhP})$.⁹⁹⁻¹⁰⁴

The polymerization of monosubstituted acetylenes having aromatic heterocycles such as thienyl, furyl, and pyridyl substituents has been also carried out by W- and Mo-based catalysts.¹⁰⁵⁻¹⁰⁷ The polymerization was generally activated by using organotin compounds such as Ph_4Sn , *n*- Bu_4Sn , and Me_4Sn . Especially, in the polymerization of 2-ethynylpyridine, the organoaluminum compounds such as Et_2AlCl and EtAlCl_2 were found to be very effective cocatalysts for the polymerization by WCl_6 and MoCl_5 . On the other hand, the organotin compounds showed only a low cocatalytic activity. The TiCl_4 – EtAlCl_2 catalyst system was also found to be effective for the polymerization.

Also, the polymerization of propargyl bromide and chloride was carried out by the catalyst systems such as PdCl_2 ,¹⁰⁸ γ -rays,¹⁰⁹ $\text{NiI}_2(\text{Ph}_3\text{P})_2$,¹¹⁰ $\text{W}(\text{CO})_6$ – CCl_4 – $h\nu$,¹¹¹ MoCl_5 ,¹¹² and MoCl_5 –polymer.¹¹³ However, these catalysts generally give only insoluble and intractable polymers. Soluble polymers from propargyl halides were firstly prepared by using WCl_6 - and MoCl_5 -based catalysts.¹¹⁴⁻¹¹⁶ EtAlCl_2 was found to be an effective cocatalyst in the polymerization of propargyl halides when used with WCl_6 and MoCl_5 . The resulting products were partially soluble in organic solvents. Especially, TiCl_4 – EtAlCl_2 gave a completely soluble polymer, although the polymer yield was low (about 50%).¹¹⁵

Recently, living polymerization of substituted acetylenes have also been carried out by using Schrock carbenes,¹¹⁷⁻¹¹⁹ tantalum catalysts,¹²⁰ rhodium complexes,¹²¹ and MoCl_4 -based catalysts.¹²²⁻¹²⁴ Living polymerizations are polymerizations in which propagating centers do not undergo either termination or transfer. Living polymerizations offer the potential for producing structures with defined end groups by deliberate termination of a living system with appropriate reagents and block copolymers by sequential addition of two or more different monomers.¹²⁵⁻¹²⁷

Potentially important advantages of controlled living polymerization reactions of acetylene derivatives are greater tolerance of functionalities, control over the nature of the capping groups, and the ability to prepare block or random copolymers that contain other monomers that can be polymerized by the well-defined alkylidene complexes.¹²⁸

1,6-Heptadiyne and its homologues of substituted acetylenes are very interesting examples of substituted acetylenes, which can be susceptible to the ring-forming polymerization to give a new type of conjugated polymer backbone system. The present review deals with the comprehensive research results in the field of poly(1,6-heptadiyne)-based conjugated polymer chemistry.

II. Poly(1,6-heptadiyne) Derivatives by Metathesis Cyclopolymerization

A. Poly(1,6-heptadiyne) and Its Homologues

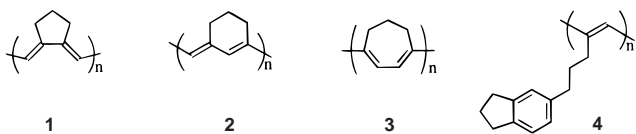
Cyclopolymerization (ring-forming polymerization) is any type of chain-growth polymerization that leads to the introduction of cyclic structure into the polymer main chain via an alternating intramolecular–intermolecular chain propagation. During the past 4 decades, studies on the cyclopolymerization of non-conjugated dienes have been extensively made.^{129–133} In 1951, Butler and Ingley found that diallyl quaternary ammonium salts polymerized with free-radical initiators to give water-soluble, non-cross-linked polymers.¹³⁴ The cyclopolymers obtained from nonconjugated dienes having various functionalities have potential applications such as photoresponsive coating,^{135,136} antistatic agents,¹³⁷ positively charged electrophotographic toners,¹³⁸ basic anion exchangers,¹³⁹ demineralization agents,¹⁴⁰ and an interferon inducer,¹⁴¹ etc.

This concept on cyclopolymerization was effectively applied to the nonconjugated diacetylene more than 35 years ago, which was the current enthusiasm for investigating the electrical,^{34–39,142} electrooptical,¹⁴³ and optical properties^{43–50,144,145} of unsaturated polymers existed at the earlier stage. More recently, since various substituted acetylenes have been polymerized to give the π -conjugated polymers,^{9,146–148} the cyclopolymerization of nonconjugated diynes were extensively investigated in an attempt to prepare the polymer that would contain alternating double and single bonds along the polymer main chain with a cyclic recurring unit.^{128,149–152}

In contrast to simple mono- and disubstituted polyacetylenes, in which the coplanarity is generally hindered by the bulky substituents adjacent to the polymer backbone, the presence of a cyclic ring in the cyclopolymer of nonconjugated diynes tends to make the conjugated polymer backbone more coplanar.¹⁵³

1,6-Heptadiyne was first chosen for polymerization since this monomer could be expected to give the most facile polymerization reaction via an internal head-to-tail propagation which would lead to a six-membered carbocyclic recurring unit.¹⁵⁴ Stille and Frey first reported the study on the polymerization of nonconjugated diynes, especially 1,6-heptadiyne with Ziegler type catalysts.¹⁵⁵

Poly(1,6-heptadiyne)s obtained were dark red or black, which indicates a high order of conjugation in the polymer. Even though a head-to-tail internal propagation would be expected, there are three possible cyclic recurring units (**1–3**) and structure **4**



which can be written to account for a soluble non-acetylenic polymer with alternating double and single bonds along the polymer backbone.

o-Diethynylbenzene was also polymerized by Ziegler-type catalysts $[\text{AlR}_n\text{Cl}_{(3-n)}\text{-TiCl}_4, \text{AlR}_n\text{Cl}_{(3-n)}\text{-Ti}$

Table 1. Effect of Catalyst Composition $\text{Ti}(\text{OR})_4$ Plus $\text{Al}(\text{C}_2\text{H}_5)_3$ for the Polymerization of 1,6-Heptadiyne^a

R	result	yield, %
<i>n</i> -C ₄ H ₉	golden-green lustrous somewhat flexible film	69
<i>i</i> -C ₃ H ₇ ^b	golden-green lustrous film (small amount) plus dull black thick film in bottom of reactor	~5 + ~85
<i>n</i> -C ₉ H ₁₉	golden-green lustrous somewhat flexible film	60

^a 4.0/1.0 $\text{Al}(\text{C}_2\text{H}_5)_3/\text{Ti}(\text{OR})_4$; $[\text{Ti}(\text{OR})_4] = 0.18$ M in toluene; reactor 20 °C; monomer 50 °C; catalyst prepared and aged 1 h at 25 °C; degassed $6 \times$ to $P \approx 4 \times 10^{-4}$ Torr at –78 °C; wash solvent = toluene. ^b Catalyst had low viscosity.

Table 2. Effect of Catalyst Composition $\text{Ti}(\text{OC}_4\text{H}_9\text{-}n)_4$ Plus AlR_3 for the Polymerization of 1,6-Heptadiyne^a

R	solvent	[Ti], M	reactor temp, °C	result
C ₂ H ₅	toluene	0.43	20	golden-green "metallic" film
C ₂ H ₅	hexane	0.32	20	very little film (thin)
CH ₃	hexane	0.47	5	no film
<i>i</i> -C ₄ H ₉	toluene	0.25	19	no film

^a Al/Ti = 4.0. Monomer 48 ± 3 °C; catalyst prepared and aged 1 h at 25 °C; degassed 6×10^{-4} Torr at –78 °C; wash solvent = toluene.

(*acac*)₃ (*n* = 1, 2, 3)],¹⁵⁶ and WCl_6 - and MoCl_5 -based catalysts¹⁵⁷ to give a high polymer yield. Colthup and Meriwether obtained oligomers and polymers from the alkadiynes of $\text{HC}\equiv\text{C}(\text{CH}_2)_n\text{C}\equiv\text{CH}$ on dicarbonylbis(triphenylphosphine) nickel $[\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2]$,¹⁵⁸ and the polycyclotrimerized structure (**4**) deduced by them was in agreement with the results on Ziegler catalysts ($\text{AlEt}_3/\text{TiCl}_4$) by Hubert and Dale.¹⁵⁹

Gibson et al. reported the insoluble, free-standing films with metallic luster by the polymerization of 1,6-heptadiyne on the surfaces of concentrated solutions of Ziegler-type homogeneous catalyst derived from $\text{Ti}(\text{OC}_4\text{H}_9\text{-}n)_4$ and $\text{Al}(\text{C}_2\text{H}_5)_3$, using a specifically designed reactor.^{149,160} The titanium(IV) *n*-butoxide, isopropoxide, and *n*-nonylate were used. The *n*-alkoxides gave a golden-green lustrous film in a comparable yield, but the branched alkoxide yielded primarily a black residue as a polymerization result in the catalyst pool rather than on the reaction walls, which may have resulted from the low viscosity of the catalyst solution (Table 1). As listed in Table 2, only triethylaluminum in toluene yielded the lustrous polymer films. However, when the hexane was used as a polymerization solvent, which is probably originated by hexane vapor pressure, the polymer films were not obtained. The effective Al/Ti ratios were in the range of 1 and 4, giving the polymer yield of 60–70%. Hexane vapor pressure is probably a factor in the failure of both $\text{Al}(\text{C}_2\text{H}_5)_3/\text{hexane}$ and $\text{Al}(\text{CH}_3)_3/\text{hexane}$ to bring about polymerization in a film form.

The attempted polymerization of 1,6-heptadiyne with NbCl_5 and TaCl_5 yielded a mixture of cyclotrimer (15%) and polymer (25% for NbCl_5 , 20% for TaCl_5), having a relatively low conversion (40% for NbCl_5 , 35% for TaCl_5). In most cases, the resulting poly(1,6-heptadiyne)s, besides a low molecular weight of oligomers, were insoluble in any organic solvents

Table 3. Cyclopolymerization of 1,6-Heptadiynes by Mo-Based Catalysts








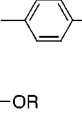








monomer	cat. syst	yield, %	M_n	ref
	MoCl ₅ -EtAlCl ₂	56	insoluble	162
	MoCl ₅	100	84 000	162
	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn	95	127 000	163
	Mo(CHCMe ₂ Ph)(<i>N</i> -2,6-C ₆ H ₃ - <i>i</i> -Pr ₂)(OCMe(CF ₃) ₂) ₂	97	30 500	128, 164
	MoCl ₅	98	20 000 - 30 000	165, 166
(R = H,  , ) 	MoCl ₅	92	95 000	167
(R = CH ₂ CF ₃ , CH(CF ₃) ₂) 	MoCl ₅	95	8 000	168
	MoCl ₅	98	46 000	169
	MoCl ₅ -EtAlCl ₂	78	54 000	169
R = CO ₂ Et, PO(OEt) ₂ 	MoCl ₅	88	8 070	170
	MoCl ₅	99	72 000	171
	MoCl ₅	97	42 000	172
	MoCl ₅	94	22 000	173
	MoCl ₅	95	156 000	174

Table 4. Polymerization of Diphenyldipropargylmethane (DPDPM) by Various Catalyst Systems^a

exp no.	cat. syst. ^b (mole ratio)	polym yield, %	M_n	color ^e
1	MoCl ₅	100	84 000	d-v
2	MoCl ₅ -EtAlCl ₂ (1:2)	76	43 000	d-v
3	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:2)	53	nd ^d	d-v
4	WCl ₆	23	nd ^d	d-b
5	WCl ₆ -EtAlCl ₂ (1:4)	84	20 000	d-b
6	PdCl ₂ ^c	57	11 000	r-b

^a Polymerization was carried out for 24 h at 60 °C in chlorobenzene. The initial monomer concentration ($[M]_0$) was 0.25 M, and the monomer to catalyst mole ratio was 100. ^b The mixture of catalyst and cocatalyst in chlorobenzene was aged at 30 °C for 15 min before use as a catalyst. ^c Polymerization was carried out for 24 h at 90 °C in *N,N*-dimethylformamide. ^d Nondetermined. ^e Color: d-v, dark violet; d-b, dark brown; r-b, red-brown.

and very susceptible to air oxidation, regardless of the catalysts used and the polymerization conditions.¹⁶¹

Introduction of substituent to the methylene carbon at the 4-position of 1,6-heptadiyne solved the pre-described problems of poly(1,6-heptadiyne) and expanded the research areas of π -conjugated polymers. The polymerization of various 1,6-heptadiynes having substituents using Mo-based catalysts has been studied as shown in Table 3. All monomers listed in Table 3 produce methanol-insoluble polymers in high yields. The firstly selected monomer, diphenyldipropargylmethane (DPDPM) was easily polymerized to give a high molecular weight polymer. The typical polymerization results are listed in Table 4. MoCl₅ alone polymerized DPDPM very effectively to give a quantitative yield of a polymer. In general, it was found that the MoCl₅-based catalysts are more effective than that of WCl₆-based catalysts. When 1,6-heptadiyne was polymerized (in the conditions $[M]_0 = 0.5$, monomer to catalyst mole ratio = 30, 24 h, 60 °C) by using MoCl₅-EtAlCl₂, the polymer yield was only 56% and insoluble in organic solvents.¹⁶² On the other hand, the resultant polymer from DPDPM was completely soluble and the yields were generally high. This result was explained by the substituent effect, which is the probability of cyclopolymerization enhanced by bulky substituents at the 4-position of 1,6-heptadiyne.¹⁷⁵⁻¹⁷⁹ This polymer has excellent oxidative stability in air relative to polyacetylene and poly(1,6-heptadiyne).

Another interesting monomer is diethyldipropargylmalonate (DEDPM), **5**. The polymerization of **5** was carried out by various catalyst systems. Table 5 shows the typical results for the polymerization of **5** by Mo- and W-based catalysts. The polymerization by MoCl₅-based catalysts was well-proceeded to give a high yield of a polymer which can be easily casted into a uniform thin film.¹⁶² In the polymerization of **5**, the MoCl₅-based catalyst systems [especially MoCl₅-(*n*-Bu)₄Sn] were very effective, whereas the WCl₆-based catalyst systems showed a low catalytic activity (Table 5). In the polymerization of monosubstituted acetylenes containing oxygen atom, high catalytic activity of MoCl₅-based catalysts were generally known, which is originated from the self-

Table 5. Polymerization of Diethyl Dipropargylmalonate (5**) by Transition Metal Catalysts^a**

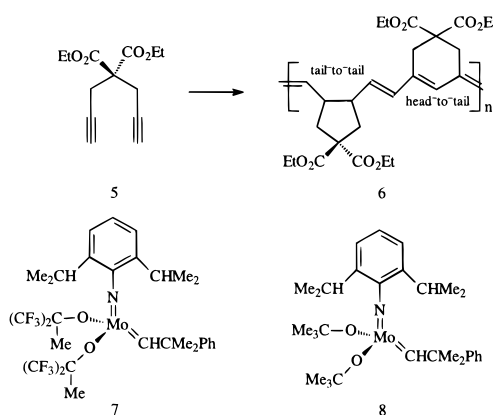
no.	cat. syst. ^b	polym yield, % ^c	$M_n, \times 10^4$
1	MoCl ₅	91	9.7
2	MoCl ₅ -EtAlCl ₂	75	6.1
3	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn	95	12.7
4	WCl ₆	12	
5	WCl ₆ -EtAlCl ₂	10	
6	WCl ₆ -(<i>n</i> -Bu) ₄ Sn	15	

^a Polymerization in 1,4-dioxane at 60 °C for 24 h; $[M]_0 = 0.25$, $[cat.] = [Cocat.] = 5mM$. ^b Mixture of catalyst and cocatalyst was aged at 30 °C for 15 min before used as catalyst. ^c Yields of methanol-insoluble polymers. ^d Determined by GPC with polystyrene standards.

activation of MoCl₅ catalyst by the oxygen atom of monomer.¹⁸⁰⁻¹⁸⁵

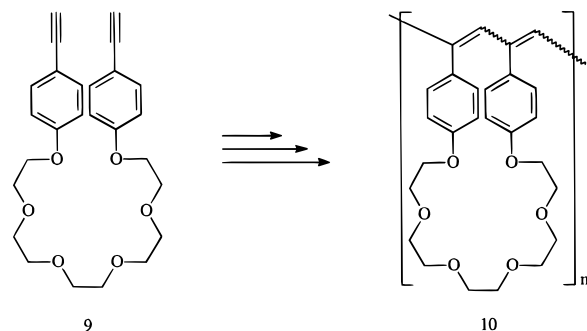
High oxidation state alkylidene molybdenum complexes such as Mo(CHCMe₂R)(*N*-2,6-C₆H₃-*i*-Pr₂)(OCMe₂CF₃)₂ (**7**) and Mo(CHCMe₂R)(*N*-2,6-C₆H₃-*i*-Pr)₂(*O*-*t*-Bu)₂ (**8**), which were frequently used for the ring-opening metathesis polymerization of 2,3-difunctionalized-7-oxanorbornenes and 7-oxanorborn dienes¹⁸⁶⁻¹⁸⁹ to give a polymer with narrow molecular distributions ($M_w/M_n \leq 1.17$), were also found to be effective for the cyclopolymerization of **5**. Monomer **5** was polymerized with Mo(CHCMe₂Ph)(*N*-2,6-*i*-Pr₂C₆H₃)-[OCMe(CF₃)₂] in 1,2-dimethoxyethane in a living manner to give a low polydispersity ($M_w/M_n \leq 1.25$), soluble polyene of a known type that contains a mixture of five- and six-membered moieties (Scheme 1).^{128,151,164}

Scheme 1



Various classes of crown ethers attached to polymers have been of interest due to their selective ionic binding of complexes with metal cations.¹⁹⁰⁻¹⁹⁴ π -Conjugated polymers such as polypyrroles^{192,195} and polythiophenes^{196,197} functionalized with crown ether were extensively investigated to explore the ion-selective electrodes and sensory materials. The polymerization of 4',4'-ethynylbenzo-1,5-crown-5 was carried out using the rhodium complex catalyst (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer, $[Rh(bhd)Cl_2]$,^{197,198} to give a maximum 55% yield of a polymer. α,ω -Diacetylene, 1,4-bis(4-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane (**9**), was polymerized with rhodium, tungsten, and molybdenum catalysts into poly(phenylacetylene) (**10**) having a crown cavity (Scheme 2).¹⁹⁹

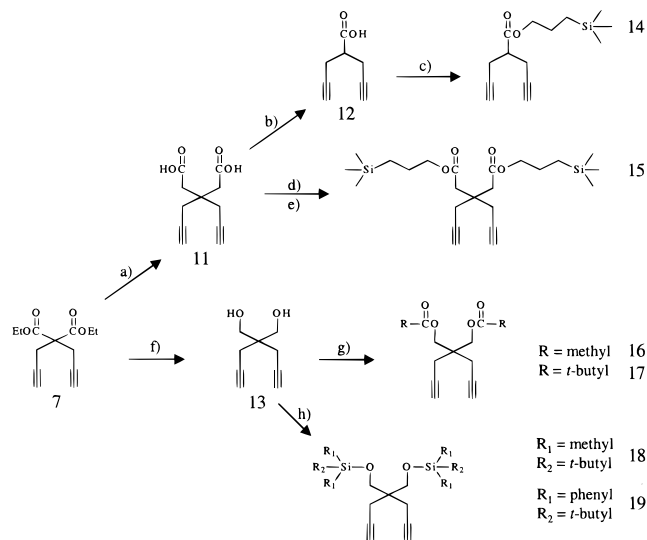
Scheme 2



The attempted cyclopolymerizations of 2,6-bis[7'-(4''-ethynylphenoxy)-2',5'-dioxahептыл]pyridine and 2,6-bis[10'-(4''-ethynylphenoxy)-2',5',8'-trioxadecyl]pyridine were also carried out using the bicyclo[2.2.1]-hepta-2,5-diene(rhodium(I) chloride dimer to give yellowish powdery polymers.²⁰⁰ The resulting polymers exhibited cation-binding ability for alkaline earth metal, heavy metal, and transition metal ions, in particular, for Ag⁺.

A polyacetylene derivative containing crown ether moiety, poly(dipropargyl-1,6-crown-5) was obtained from the cyclopolymerization of the corresponding monomer with MoCl₅-based catalysts.¹⁷³ The polymerization proceeded well, in spite of a high concentration of oxygen, to give soluble high molecular weight polymers. On the other hand, WCl₆-based catalysts failed to polymerize these acetylene derivatives having a crown-ether moiety.¹⁷³

Various substituents can be introduced at the 4-position of 1,6-heptadiyne, as shown in Scheme 3.

Scheme 3^a

^a (a) KOH/EtOH (90%); (b) H₂O/reflux (68%); (c) 3-(chloropropyl)trimethylsilane/K₂CO₃/DMF (71%); (d) SOCl₂/pyridine/ether (52%); (e) 3-(trimethylsilyl)-1-propanol/TEA/ether (83%); (f) LiAlH₄/ether (82%); (g) RCO-CITEA/ether, R = methyl (92%), R = *tert*-butyl (87%); (h) ClSi(R₁)₂R₂/imidazole/DMF [R₁ = methyl, R₂ = *tert*-butyl (76%); R₁ = phenyl, R₂ = *tert*-butyl (54%)].

Cyclopolymerization of 1,6-heptadiyne having bulky substituents was effectively carried out by the MoCl₅-based catalysts, and their optimized polymerization results are summarized in Table 6.²⁰¹ In most cases, the polymer yields were quantitative. And the result-

Table 6. Polymerization Conditions^a and Data for the Resulting Polymers

exp no.	monomer	cat. syst (mole ratio)	yield, ^b %	<i>M_n</i> /10 ^c	<i>M_w</i> / <i>M_n</i> ^c
1	14	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:4)	98	56.5	1.74
2	14	MoCl ₅	94	27.4	2.73
3	15	MoCl ₅	97	112.6	4.23
4	15	MoCl ₅ -EtAlCl ₂ (1:4)	98	102.2	2.87
5	16	MoCl ₅	97	73.0	2.86
6	16	MoCl ₅ -EtAlCl ₂ (1:2)	96	47.4	3.01
7	17	MoCl ₅	96	121.5	2.56
8	18	MoCl ₅ -EtAlCl ₂ (1:4)	98	118.4	2.15
9	18	MoCl ₅	94	88.8	2.49
10	19	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:4)	99	331.9	2.86
11	19	MoCl ₅	99	236.1	3.35

^a Polymerization was carried out in 1,4-dioxane at 60 °C for 24 h. [M]₀ = 0.25, mole ratio of monomer to catalyst = 50 °C. ^b Methanol-insoluble polymer. ^c Values were obtained by GPC analysis with polystyrene standards calibration.

ing polymers were highly soluble in common organic solvents such as CHCl₃, CH₂Cl₂, tetrahydrofuran (THF), and chlorobenzene.

B. Poly(1,6-heptadiyne) Derivatives Containing Heteroatoms

1. Symmetrical 1,6-Heptadiyne Homologues Carrying Heteroatoms

Various dipropargyl derivatives carrying heteroatoms at the 4-position of 1,6-heptadiyne has been synthesized and polymerized by transition metal catalysts (Table 7). The polymerization of dipropargyl ether (DPE) by MoCl₅ alone proceeded well to give a quantitative yield of a polymer.^{182,202} WCl₆-based catalysts, which had been known to be very effective for the polymerization of some monosubstituted acetylenes such as phenylacetylene,^{90,96} 2-ethynylthiophene,¹⁰⁵ and 2-ethynylpyridine,¹⁰⁶ were found to be less effective for this polymerization (yield ≤ 52%). Poly(dipropargyl sulfide) was prepared in a yield of 91% using the WCl₆-EtAlCl₂ catalyst system. The above two polymers were mostly insoluble in organic solvents and also unstable with air oxidation. To increase the polymerizability and the oxidation stability of poly(dipropargyl sulfide), two similar dipropargyl derivatives having different oxidation states of the sulfur atom were tested for the polymerization (Table 8). The polymer yield by MoCl₅ was increased as the oxidation state of sulfur was increased due to the increased cyclopolymerization probability.²⁰⁴

Dipropargylamine and its derivatives were polymerized by PdCl₂ to give a π-conjugated polymer,²⁰⁶ which is easily dopable with electron acceptor dopants such as Br₂, I₂, AsF₅, NO₂, etc. In the polymerization of these monomers using WCl₆, the polymer yield was below 10%. More interesting polymers were prepared by the cyclopolymerization of dipropargylsilanes having bulky substituents using WCl₆- and MoCl₅-based catalysts.²⁰⁸ These polymers were mostly soluble in organic solvents, film-castable, and relatively stable

Table 7. Polymerization of 1,6-Heptadiyne Derivatives Carrying Heteroatoms at the 4-Position of 1,6-Heptadiyne

X of (HC≡CCH ₂) ₂ X	cat. syst	yield, ^b %	M _n	ref
O	PdCl ₂	70	insoluble	202
O	MoCl ₅	100	insoluble	182
S	WCl ₆ -EtAlCl ₂	91	insoluble	203
SO	MoCl ₅	63	0.20 (η _{inh})	204
SO ₂	MoCl ₅	95	insoluble	205
	PdCl ₂	99	0.27 (η _{inh})	205
NR (R = H, Et, Me ₃ C, MeCO, Pr, Bu, Ph, α-naphthyl)	PdCl ₂	40–100		206
	WCl ₆	10		206
	PdCl ₂	84–91		207
SiR ₁ R ₂ (R ₁ , R ₂ : CH ₃ , CH ₃ ; CH ₃ , Ph; Ph, Ph)	MoCl ₅ , WCl ₆ , EtAlCl ₂	38–100	10 000–16 500	208
GeR ₁ R ₂ (R ₁ , R ₂ : CH ₃ , CH ₃ ; Ph, Ph)	MoCl ₅ -EtAlCl ₂	22–98	6000	209

Table 8. Polymerization of Dipropargyl Sulfur Derivatives by MoCl₅^a

exp no.	X of (HC≡CCH ₂) ₂ X	polym yield ^b (%)	color
1	S	56	brown
2	O=S	63	yellow
3	O=S=O	95	orange

^a Polymerization was carried out at 90 °C for 24 h in chlorobenzene. Initial monomer concentration ([M]₀) and monomer to MoCl₅ mole ratio were 1.5 M and 50, respectively.
^b Methanol-insoluble polymer.

Table 9. Substituent Effect in the Polymerization of Dipropargylsilane Derivatives^a

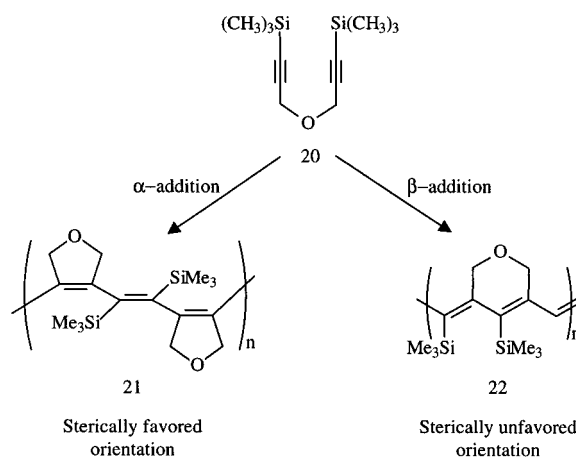
exp no	cat. syst (mole ratio)	polym yield, %		
		R ₁ = CH ₃ ; R ₂ = CH ₃	R ₁ = CH ₃ ; R ₂ = C ₆ H ₅	R ₁ = C ₆ H ₅ ; R ₂ = C ₆ H ₅
1	MoCl ₅	48	55	100
2	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:4)	43	47	95
3	WCl ₆ -EtAlCl ₂ (1:4)	38	42	47
4	WCl ₆ -Et ₂ AlCl (1:4)	7	27	87
5	TiCl ₄ -EtAlCl ₂ (1:4)	16	23	55

^a Polymerization was carried out at 60 °C for 24 h. Initial monomer concentration ([M]₀) was 2 M. Monomer to catalyst mole ratio was 50.

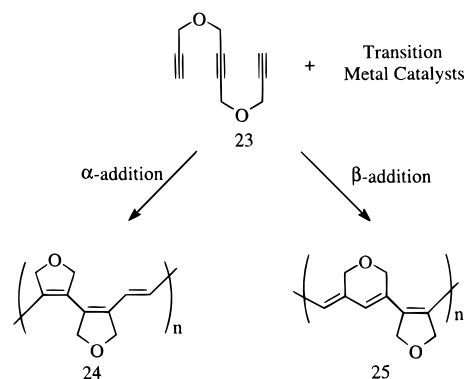
to air oxidation. The substituent effect in the polymerization of dipropargylsilane derivatives is listed in Table 9. Catalytic activity order was hardly affected by the bulkiness of substituents. Monomer reactivity was increased as the more bulky substituent is replaced. These results indicate that the substituent bulkiness considerably influences the cyclopolymerization of dipropargyl derivatives. It seems that the bulkier the substituent, the greater the probability of cyclopolymerization, similar to that with the cyclopolymerization of diallylsilane derivatives.^{210,211} Similar polymerization behaviors were also observed in the cyclopolymerization of dipropargylgermaniums by MoCl₅- and WCl₆-based catalysts.²⁰⁹

Another example is poly(propionic anhydride), which was easily synthesized from the corresponding diacetylene. Though this polymer is soluble and relatively stable to air oxidation, the polymer had a low molecular weight and underwent a side reaction with the solvent.^{212,213}

The cyclopolymerization of symmetrical disubstituted dipropargyl derivative bis(3-trimethylsilyl-2-propynyl) ether (**20**) was attempted as shown in Scheme 4. The polymer yields were generally very

Scheme 4

low (≤13%) and the polymer was a white powder and have a partially desilylated structure. A novel type of polyacetylene with double cyclic structures was synthesized by the double ring forming polymerization of 1,4-dipropargyl-2-butyne using transition metal catalysts as shown in Scheme 5.²¹⁵ When MoCl₅ was used as catalyst, the polymerization proceeded well to give a quantitative yield of a polymer, whereas WCl₆-based catalysts failed to polymerize. The polymers were insoluble in organic solvents and unstable to mostly air oxidation as like with that of poly(dipropargyl ether).²¹⁴

Scheme 5

2. Unsymmetrical 1,6-Heptadiyne Homologues Carrying Heteroatoms

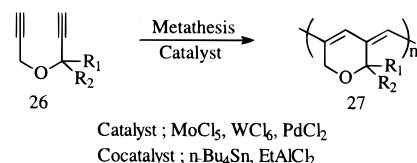
Unsymmetrically cyclized poly(dipropargyl ether) derivatives bearing α-substituents were also studied.

Table 10. Polymerization of 3-(Propargyloxy)-3-phenyl-1-butyne (POPB) by Various Transition Metal Catalysts^a

expt no.	cat. syst ^b (mole ratio)	polym yield, % ^c	M_w^d $\times 10^{-3}$	M_w/M_n^d
1	MoCl ₅	100	24	2.4
2	MoCl ₅ -EtAlCl ₂ (1:1)	82	15.6	2.1
3	MoCl ₅ -EtAlCl ₂ (1:4)	78	12.7	2.8
4	MoCl ₅ -(<i>n</i> -Bu ₄)Sn (1:4)	96	26.3	2.2
5	WCl ₆			
6	WCl ₆ -EtAlCl ₂ (1:4)	12		
7	WCl ₆ -(<i>n</i> -Bu ₄)Sn (1:4)	trace		
8	PdCl ₂ ^e	25	9.5	3.9

^a Polymerized in dioxane at 60 °C for 24 h. Mole ratio of monomer to catalyst was 50. Initial Monomer concentration was 1 M. ^b Mixture of catalyst and cocatalyst in chlorobenzene was aged for 15 min before use as catalyst. ^c The precipitated polymers in methanol were gravimetrically estimated. ^d Values were obtained by GPC analysis with polystyrene standards. ^e Polymerization was carried out at 90 °C for 24 h in DMF.

The monomers were propargyl α -substituted (methyl, pentyl, methyl phenyl, cyclohexyl) propargyl ethers. Polymerization was carried out with various transition metal catalysts, as shown in Scheme 6. The

Scheme 6

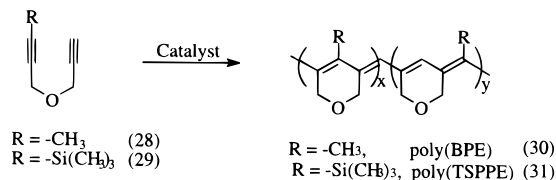
results are listed in Table 10. MoCl₅-based catalysts showed greater catalytic activity than WCl₆-based catalysts. And also (*n*-Bu)₄Sn exhibited excellent cocatalytic activity compared to EtAlCl₂ for the polymerization of 3-(propargyloxy)-3-phenyl-1-butyne by MoCl₅. These results are similar to those for the polymerization of other propargyl ether derivatives.^{182,215} The effect of α -substituents for the cyclo-polymerization of dipropargyl ether derivatives is listed in Table 11. In the case of unsubstituted dipropargyl ether, the polymerization proceeded well in high concentration, and the resulting polymer was a yellow-reddish insoluble powder. However, the presence of α -substituents yielded very interesting results in the cyclopolymerization of dipropargyl ether derivatives.²¹⁶ Polymerization proceeded well regardless of initial monomer concentration, and the resulting polymers were soluble in common organic solvents. The weight-average molecular weights (M_w) of poly(dipropargyl ether) derivatives were in the range of (24–73) $\times 10^3$.

Table 11. Polymerization of Dipropargyl Ethers with Various α -Substituent Groups by MoCl₅^a

exp no.	compd ^b	R ₁	R ₂	[M] ₀ ^c	polym time, h	polym yield, % ^d	M_w^e , $\times 10^{-3}$	M_w/M_n^e
1	DPE	H	H	1.5	24	100 ^f		
2	POB	H	CH ₃	0.5	2	84 ^g	29.4	3.1
3	POO	H	pentyl	0.25	24	92	73.0	4.0
4	POPB	CH ₃	phenyl	1	24	100	24.3	2.4
5	POECH		cyclohexyl	1	24	80	24.5	2.5

^a Polymerized in dioxane at 60 °C. Mole ratio of monomer to catalyst was 50. ^b Dipropargyl ether (DPE), 3-(propargyloxy)-1-butyne (POB), 3-(propargyloxy)-1-octyne (POO), 3-(propargyloxy)-3-phenyl-1-butyne (POPB), and 1-(propargyloxy)-1-ethynylcyclohexane (POECH). ^c Initial monomer concentration in moles per liter. ^d The precipitated polymers in methanol were gravimetrically estimated. ^e Values were obtained by GPC analysis with polystyrene standards. ^f Insoluble in any solvent. ^g Partially insoluble in THF.

Another example is the unsymmetrically substituted poly(diyne ether) derivatives. The cyclopolymerization of 2-butynyl propargyl ether (**28**) and 3-trimethylsilyl-2-propynyl propargyl ether (TSPPE, **29**) was also carried out by transition metal catalysts (Scheme 7).²¹⁷ In the polymerization of **28**, MoCl₅

Scheme 7

alone gives a good polymer yield (70%). And also EtAlCl₂ was found to be an effective cocatalyst for this polymerization by MoCl₅, WCl₆ alone and WCl₆-based catalysts were found to be less effective, giving only a low yield of polymer ($\leq 15\%$). The polymerization of **29** was also carried out by MoCl₅- and WCl₆-based catalysts. The polymerization behaviors were similar with those of **28**. EtAlCl₂ was also found to be a very effective cocatalyst for the polymerization of **29** (a maximum polymer yield of 94%).

C. Ionic Poly(1,6-heptadiyne)s

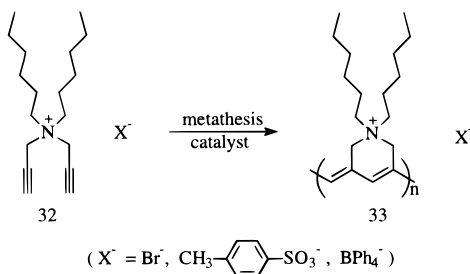
The π -conjugated polymers having an ionic nature were scarce and restricted to some cases as follows: the solid-state polymerization of propiolic salts by γ -irradiation,^{218,219} water-soluble polyene polymers by quaterization of poly(6-bromo-1-hexyne),²²⁰ and the synthesis of mono- and disubstituted ionic polyacetylene by the activation of the acetylene bond in ethynylpyridines by introduction of strong electron withdrawing substituents in conjugation with it.^{221–224} In recent years, monopropargyl derivatives carrying phosphonium, sulfonium, and ammonium salts had been polymerized to corresponding π -conjugated ionic polymers in high yields.^{225–229} Due to their extensive conjugation and ionic nature, these polymers have potential as materials for mixed ionic and electronic conductivity, energy storage devices, and permselective membranes.²³⁰

The cyclopolymerization of dipropargyl monomers carrying an ionic nature is a facile synthesis method for self-doped conjugated ionic polymers. Various dipropargyl quaternary ammonium salts were polymerized to yield the unusual conjugated polymers. The potential counterions are ionically bound to the polymer, as shown in Table 12. Dihexyldipropargyl-

Table 12. Ionic Poly(1,6-heptadiyne) Homologues

monomer	cat.	yield, %	η_{inh} , dL/g	ref
	MoCl ₅ -EtAlCl ₂	99	insoluble	231
	Pd(OAc) ₂	78	0.11	232
	MoCl ₅ -EtAlCl ₂	94	0.30	233, 234
X = Br ⁻ , CH ₃ -, BPh ₄ ⁻	Mo(CH- <i>t</i> -Bu)(NAr)[OCMe(CF ₃) ₂] ₂	92	nd	235
	MoCl ₅	78	0.18	236
	PdCl ₂	90	0.30	236
(R = Ethyl, <i>n</i> -Butyl <i>n</i> -Hexyl, <i>n</i> -Octyl)				

ammonium salts (**32**, counterion = Br⁻, *p*-CH₃C₆H₄SO₃⁻) were first polymerized to give the corresponding conjugated polymers (**33**) in high yields (Scheme 8). Typical polymerization results are listed

Scheme 8

in Table 13. MoCl₅ alone and MoCl₅-EtAlCl₂ catalyst systems showed generally high catalytic activities in spite of the ionic character of the monomers. The catalytic activity of MoCl₅-based catalysts was greater than that of WCl₆-based catalysts. In both cases, EtAlCl₂ exhibited excellent cocatalytic activity for this polymerization by MoCl₅ or WCl₆. A similar water-soluble conjugated polymer from the polymeric reaction of poly(*N*-hexyldipropargylamine) and methyl trifluoromethanesulfonate was reported at the same time, as shown in Scheme 9. The precursor polymer, poly(dipropargylhexylamine) (**35**), was ob-

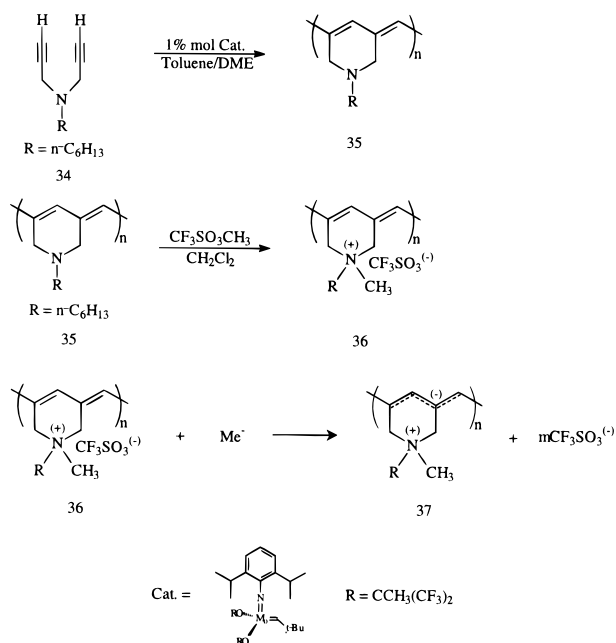
Table 13. Polymerization of Dihexyldipropargylammonium Bromide (DHDPA) by Transition Metal Catalysts^a

exp no.	cat. syst (mole ratio)	polym yield, ^b %	η_{inh} , ^c dL/g	λ_{max} , ^e nm
1	MoCl ₅	64	0.10	380
2	MoCl ₅ (M/C = 25)	78	0.12	385
3	MoCl ₅ -EtAlCl ₂ (1:4)	93	0.30	480
4	MoCl ₅ -EtAlCl ₂ (1:2)	85	0.25	460
5	MoCl ₅ -SnCl ₄ (1:4)	30	0.07	
6	WCl ₆	0		
7	WCl ₆ -EtAlCl ₂ (1:4)	53	0.08	
8	PdCl ₂	62	0.09	

^a Polymerization was carried out in chlorobenzene at 70 °C for 24 h; [M]₀ = 0.5. ^b Hexane-insoluble polymer. ^c Inherent viscosity at 30 °C in methanol. Concentration C = 0.1 g/(100 mL). ^d Polymerized in DMF at 90 °C for 24 h. ^e λ_{max} in a methanol solution.

tained in a good yield via a cyclopolymerization of the corresponding monomer using a Schrock catalyst, Mo(CH-*t*-Bu)(NAr)[OCMe(CF₃)₂]₂.²³⁵ Treatment of this polymer with methyl trifluoromethanesulfonate in methylene chloride affords the poly(dipropargyl-*N*-hexyl-*N*-methylammonium triflate) (**36**) in 92% yield. The UV-visible spectrum of a final polymer showed the characteristic broad band of a conjugated polyene $\pi \rightarrow \pi^*$ transition in the visible region (400–650 nm) similar to those of poly(dihexyldipropargylammonium salts).^{233,234}

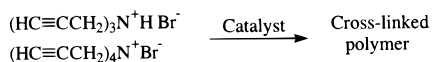
Scheme 9



The bromide ion of dihexyldipropargylammonium salts can be easily replaced by another anion such as BPh_4^- , ClO_4^- , and N_3^- . The dihexyldipropargylammonium tetraphenylborate was also easily polymerized to give the corresponding polymer in a high yield, having quite different solubility behaviors compared to those of poly(dihexyldipropargylammonium bromide).²³⁴ This polymer was insoluble in hydroxylic solvents such as methanol and ethanol despite its ionic nature, but soluble in polar solvents such as chloroform, THF, methylene chloride, acetone, and dimethylformamide (DMF), etc. This polymer was found to be less hygroscopic than those containing bromide or tosylate as a counterion.

The cyclopolymerization of multipropargylammonium bromides was also carried out to yield highly conjugated and cross-linked polymers (Scheme 10).^{237,238} The polymerization proceeded well to give

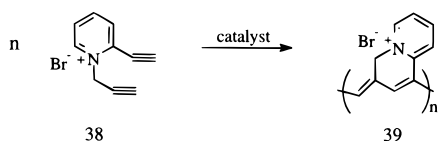
Scheme 10



a high yield when the transition metal catalysts such as PdCl_2 , PtCl_2 , $\text{MoCl}_5\text{-EtAlCl}_2$, and $\text{WCl}_6\text{-EtAlCl}_2$ were used. However, the resulting polymers were mostly insoluble in common organic solvents.

The cyclopolymerization of 2-ethynyl-*N*-propargylpyridinium bromide (**38**) having two different acetylene functionalities (acetylenic and proargyl), yielded an interesting conjugated polymer (**39**), having a pyridyl moiety (Scheme 11).²³⁹ This polymerization proceeded well with the catalysts PdCl_2 , PtCl_2 , and RuCl_3 to give a quantitative yield of a polymer.

Scheme 11



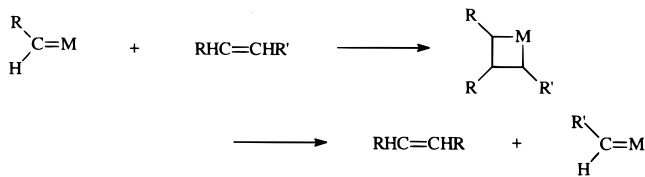
III. Mechanism and Conformational Structures

A. Mechanism

1. Polymerization Mechanism of Acetylene Derivatives

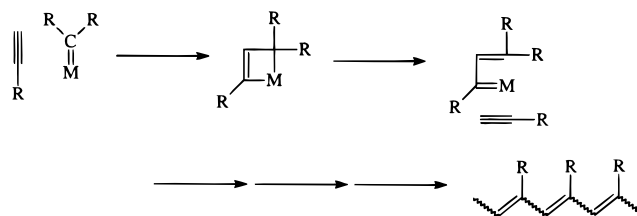
A corollary of the hypothesis that metal carbenes combine with olefins, as in Scheme 12, to propagate

Scheme 12



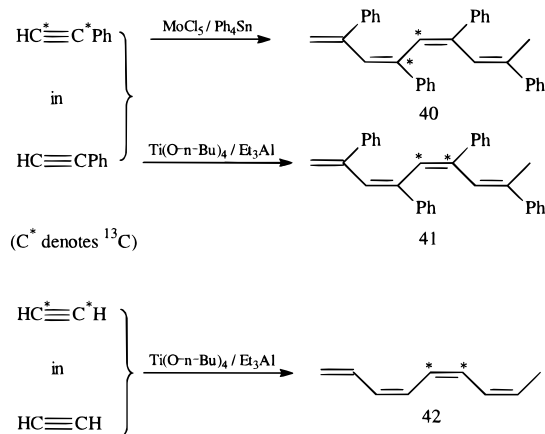
the metal-catalyzed metatheses of olefins²⁴⁰⁻²⁴² is the hypothesis of a similar combination with acetylenes, as in Scheme 13,^{94,95,243} to propagate the metal-

Scheme 13



catalyzed polymerization of acetylenes. In 1975, Masuda et al. inferred a metal carbene mechanism for the present polymerization of substituted acetylenes.²⁴³ The propagation mechanism can be depicted by Scheme 13. Katz has demonstrated the validity of the metal carbene mechanism by another method (Scheme 14).²⁴⁴ When a mixture of ^{13}C -labeled and ^{13}C -unlabeled phenylacetylenes is polymerized by $\text{MoCl}_5\text{-Ph}_4\text{Sn}$, the labeled carbons in the polymer are separated by single bonds according to ^{13}C -nutation NMR (Scheme 14).²⁴⁴

Scheme 14



This observation means the cleavage of two π -bonds in the acetylene monomer during polymerization. In contrast, only one bond of phenylacetylene or acetylene cleaves in the case of polymerization by $\text{Ti}(\text{O-}n\text{-Bu})_4/\text{Et}_3\text{Al}$.^{244,245} These findings clearly show that polymerization of acetylenes by the Mo catalyst

proceeds via the metal carbene mechanism, whereas that by the Ziegler catalyst occurs via the metal alkyl (insertion) mechanism.⁹⁵

2. Cyclopolymerization Mechanism of 1,6-Heptadiyne Derivatives

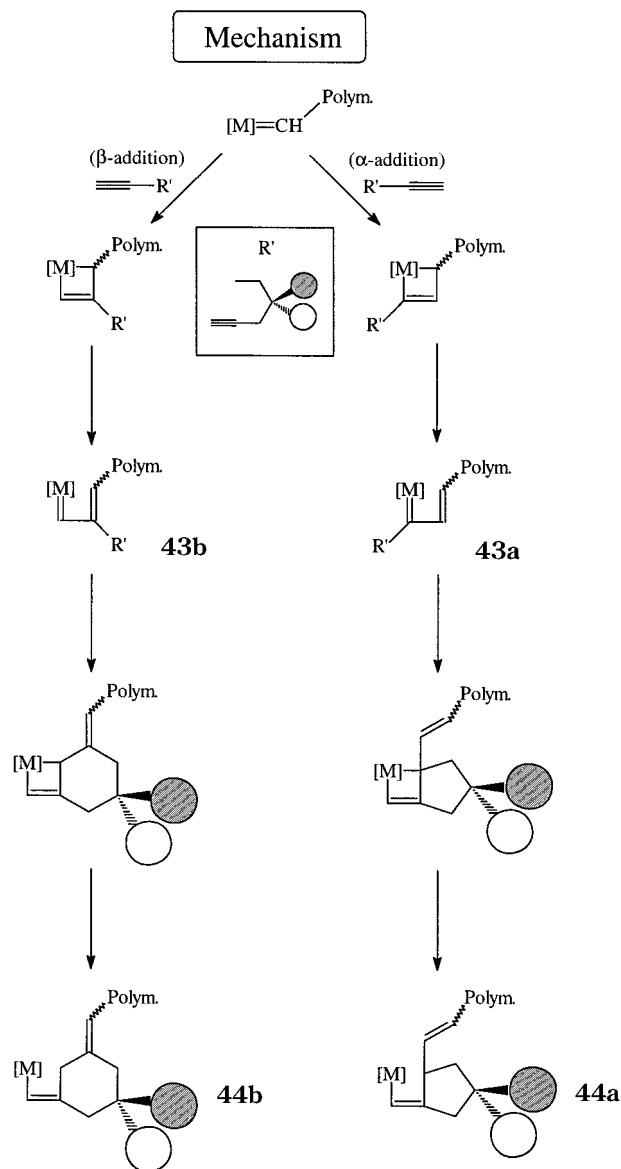
The mechanism for the cyclopolymerization of 1,6-heptadiyne derivatives was not clearly elucidated, although the polymerization using transition metal catalysts has been investigated over the past 4 decades. There is abundant indirect evidence in the literature, suggesting that Mo or W initiators cyclopolymerize 1,6-heptadiyne derivatives via an "alkylidene mechanism", i.e., a mechanism in which the triple bond reacts with a $M=C$ bond to give a metallacyclobutene intermediate, followed by the ring-opening reaction to give a vinyl alkylidene complex.^{45,128,246,247} It was reported that the "alkylidene mechanism" for the living polymerization of 2-butyne²⁴⁸ and acetylene itself²⁴⁹ was operative in two systems that contained well-defined alkylidene complexes, although controlled living acetylene polymerization by well-defined initiators is still relatively rare.

Since the mechanism of polymerization by the well-defined initiators reported unfortunately is not clear, it is not yet possible to control the cyclopolymerization to the extent that some ROMP reactions of some norbornenes and norboradienes can be controlled.^{128,250–252} It is a very important task to prepare cyclopolymers that have only one size ring and cis/trans and head/tail regularity (when applicable). It was thought that the ring size is controlled by the extent of α -addition versus β -addition of the acetylene to the alkylidene, the two modes that presumably give rise to five- and six-membered rings, respectively.¹²⁸ Recently, Schrock et al. reported the cyclopolymerization mechanism of **5** by $Mo(CHCMe_2Ph)(NAr)(OR_{F6})_2$ ($Ar = 2,6-iPr_2C_6H_3$, $OR_{F6} = OMe(CF_3)_2$) in 1,2-dimethoxyethane (DME) (Scheme 15).¹²⁸

If the acetylene adds with the substitution on the α -carbon of the new alkylidene (α -addition), a sterically hindered disubstituted alkylidene obtained, which will react at a slower rate with intramolecular formation of a five-membered ring in **43a**, may be fast enough to yield another terminal alkylidene (**44a**) on the time scale of the polymerization scale.

On the other hand, the other direction of addition (β -addition) produces a monosubstituted alkylidene that is sterically comparable to the initiating alkylidene, making this the desired direction of addition. Formation of a six-membered ring in a reaction involving a more reactive terminal alkylidene would transform **43b** into **44b**. The ¹³C NMR spectrum of poly-**6** reveals two carbonyl carbon resonances. Therefore it was speculated that poly-**6** consist of a random distribution of five- and six-membered rings formed through what is nominally tail-to-tail and head-to-head cyclopolymerization of the two acetylenic bonds in the same monomer (Scheme 1). Other uncertainties in catalyst systems of the type are the rate at which alkylidene rotamers interconvert, the extent to which the reactivities of the two alkylidene rotamers differ, and the degree of selective formation of one rotamer when a triple bond reacts with a $Mo=C$ bond.¹²⁸

Scheme 15



From a practical perspective an important feature of the cyclopolymerization to give soluble conjugated polymers is to limit the number of "ordinary" or "monoinsertions" of a triple bond; such "dangling" triple bonds eventually serve to cross-link chains. Therefore intramolecular cyclization must be fast relative to ordinary intermolecular (linear) polymerization through one triple bond per monomer. Cyclization appears to be encouraged by the presence of at least one bulky group in the 4-position, and preferably two, but it was not certain to what extent this preference is linked to any given aspect of the polymerization mechanism. In any case the combination of DME as a coordinating solvent and an electrophilic metal catalyst appears to encourage cyclization.

The formation of a high percentage of five-membered rings by tail-to-tail cyclopolymerizations via α -substituted metallacyclobutene intermediates, in the classical systems as well as the well-defined systems, is further evidence that the disubstituted alkylidene intermediate is, in fact, surprisingly reac-

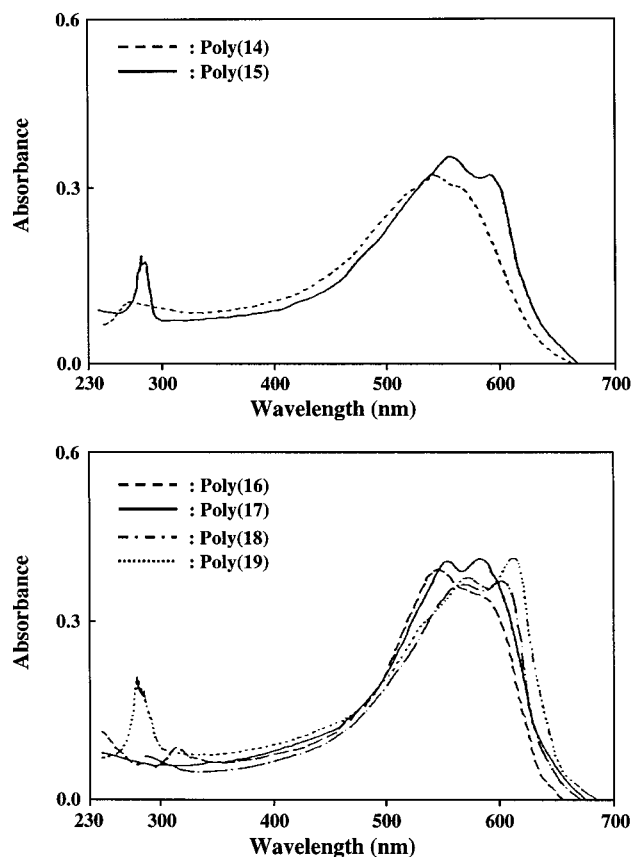


Figure 1. UV-visible spectra of the polymers 14–19 in chloroform.

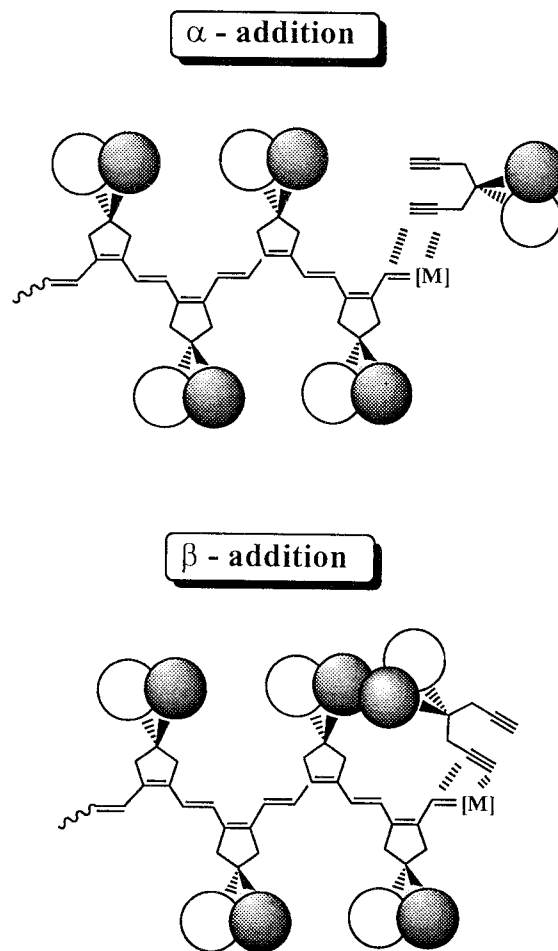
tive. The reason for the high reactivity of disubstituted alkylidene complexes could be ascribed simply to a greater lability (for steric reasons) of coordinating solvents or functionalities; it is too early to say with any certainty.¹²⁸

B. Conformational Structures

It has been also reported that these cyclic polymers obtained by both a classical metathesis catalyst and a well-defined alkylidene initiator produced five- and six-membered rings of a certain ratio, which depended on the polymerization conditions and kinds of catalyst used.^{128,164} The effect of size and type of substituents upon the fine and conformational structure for this potentially interesting class of cyclic polyenes was systematically performed.²⁰¹ FT-IR spectra of the polymers did not show a $\equiv\text{CH}$ stretching band around 3300 cm^{-1} and $\text{C}\equiv\text{C}$ stretching bands around 2100 cm^{-1} , while these two stretching bands were present in monomers. Infrared spectra results and an excellent solubility of the polymers suggest that the intramolecular cyclization is fast relative to the intermolecular linear polymerization, through one triple bond per diyne monomer, and so lead to a complete cyclopolymerization. From a recent series of studies on the cyclopolymerization of 1,6-heptadiyne derivatives using metathesis catalysts based on MoCl_5 and WCl_6 . It was found that the soluble linear cyclic polymers can be obtained by introducing at least one substituent in the 3- or 4-position of 1,6-heptadiyne.^{162,174,208,209} From a series

of λ_{max} values, it was found that incorporating a bulkier substituent in the 4-position of 1,6-heptadiyne forces the conjugated polyene into a more planar structure, as indicated by the bathochromatic shift of maximum absorption bands from the $\pi-\pi^*$ transition of the conjugated polymer backbone (see Figure 1). These results provide remarkable contrast to mono- and disubstituted polyacetylenes and mono-substituted polycyclooctatetraenes by the ring-opening metathesis polymerization (ROMP), in which the steric bulk at the point of attachment to the polymer chain increases: the effective conjugation length decreases because of twisting around the single bonds on polyacetylene, as a result of steric repulsions between the side groups. These unusual optical absorption behaviors could not be explained by the planar transoidal conformation of unsubstituted poly(1,6-heptadiyne) proposed by Gibson et al.¹⁶⁰ Also, Schrock et al. reported an authentic polymerization mechanism of **5** using well-defined alkylidene initiators.¹²⁸ They proposed that five- and six-membered rings are produced by attaching the α - and β -additions of the first triple bond to the $\text{Mo}=\text{C}$ bond followed by cyclization and ring opening (Scheme 15). It is believed that the well-defined alkylidene complexes behave differently from the classical metathesis catalysts based on MoCl_5 and WCl_6 in such a way that their steric bulkiness should cause an important effect on the direction of the first triple bond addition. As shown in Chart 1, the classical

Chart 1



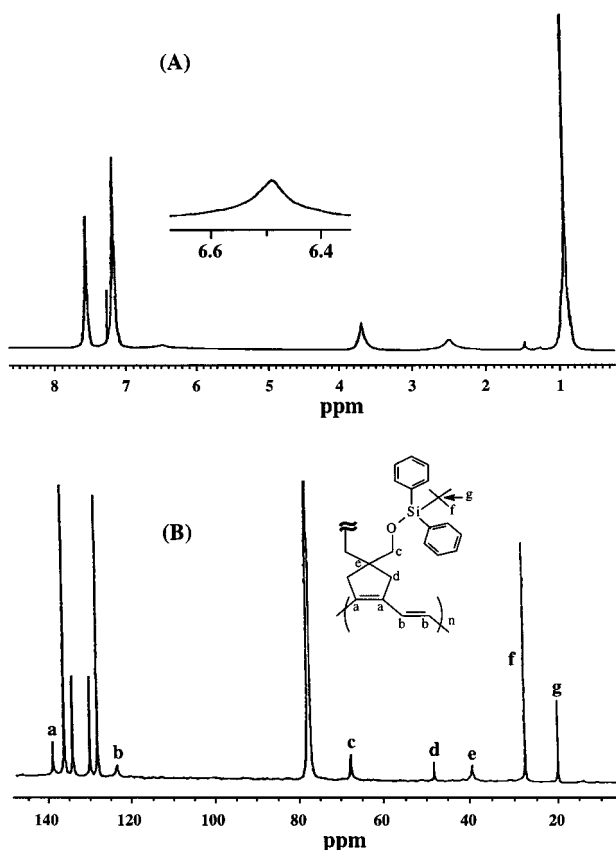


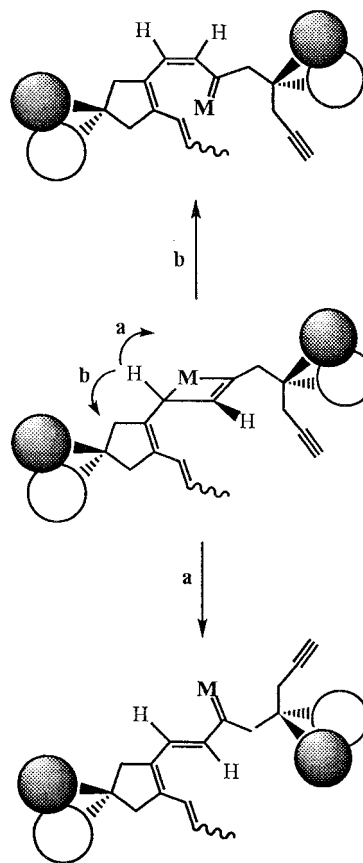
Figure 2. ¹H NMR (A) and ¹³C NMR spectra (B) of poly-**19** in CDCl₃.

catalyst is sterically very small compared to well-defined alkylidene complexes, the α -addition (**45**) of the first triple bond leading to a five-membered ring. The structures of the polymers were almost independent of the type of classical catalysts used: the polymers prepared only with MoCl₅ were almost identical to the corresponding polymers with MoCl₅-cocatalyst systems. The ratio between five-membered and six-membered rings increased with the size and number of substituents at the 4-position. In particular, when an extremely bulky substituent such as the *tert*-buyldiphenylsiloxymethyl group was introduced at the 4-position of 1,6-heptadiyne, the ¹H-NMR spectrum (see Figure 2) shows a broad single peak at 6.5 ppm due to newly forming vinylic protons, while poly(1,6-heptadiyne)s with five- and six-membered-ring repeat units exhibited broad multiple peaks.^{163,167} In addition, the ¹³C-NMR spectrum of the polymer **19** (as well as the polymers with other bulky substituents such as polymer **17**) also shows two sharp peaks at 138 and 123 ppm. These peaks can be attributed the presence of a quaternary olefinic carbon and a vinylene carbon of the π -conjugated system, respectively, as well as one sharp quaternary carbon on the ring around 46 ppm (see Figure 2). On the other hand, polymers **14**–**16** and poly-**6** were determined to have both five- and a six-membered ring structures. They showed numerous olefinic resonances in the range between 120 and 140 ppm and two clusters of peaks for the quaternary carbon atoms and many resonances for the allylic methylene groups. Such a difference in NMR spectra and two

sharp olefinic carbon peaks suggest that polymer **19**, containing extremely bulky substituents, has predominantly a symmetric single repeat unit with a five-membered ring and a vinylene structure as shown below.

The ratio of *trans* and *cis* vinylene groups is believed to be governed by the relative ease of ring opening of the metallacyclobutene, as shown in Scheme 16. The formation of *trans* double bond

Scheme 16



through rotation *a* should lead to a lower-energy transition state than the rotation *b*. This is because less steric interaction between the substituents attached to the newly forming vinylene group and hence *trans* double bond should predominate. From the spectroscopic results of polymers and considering the mechanism forming the vinyl group of the polymer backbone, the *trans*–*cis* structure as the main structures of poly(1,6-heptadiyne)s containing bulky substituents at the 4-position was proposed. With such a *trans*–*cis* structure, the longer distance among the substituents reduces the steric hindrance between the substituents, and thus a more planar π -conjugated polyene is retained. On the basis of unusual optical behavior with a bulkier substituent at the 4-position, and the polymer structures proposed here, it appears that chain twisting of the substituted poly(1,6-heptadiyne)s may be limited primarily by the bulk of the substituent group at the 4-position (*b* interaction) rather than by the point of attachment to the polymer chain (*a* interaction), which usually decreases the effective conjugation length of the polymer π -system.

IV. Properties of Poly(1,6-heptadiyne)s

A. Physical Properties

Poly(1,6-heptadiyne) itself was insoluble in any organic solvents. The soluble products were the oligomeric products of 5-(4-pentynyl)indane (**4**) from the cyclotrimerization of two 1,6-heptadiynes and the indane ring system from a novel type of catalytic cyclization reaction in which two triple bonds from one diacetylene monomer reacted with one triple bond of a second monomer molecule.^{154,155} The introduction of a substituent at poly(1,6-heptadiyne) made the polymers be soluble in organic solvents and provide the oxidative stability. Poly(diphenyldipropargylmethane) (DPDPM) was completely soluble in aromatic hydrocarbons (benzene, toluene, xylene) and halogenated hydrocarbons (CCl₄, CHCl₃, CH₂Cl₂, chlorobenzene), but insoluble in ethyl ether, aliphatic hydrocarbons, and alcohols. Poly(dipropargyl ether) and poly(dipropargyl sulfide), which are very similar to poly(1,6-heptadiyne), were also insoluble in any organic solvents.^{202,203} However, similar homologues, poly(dipropargyl sulfoxide) and poly(dipropargyl sulfone), were soluble in DMF and DMSO.^{204,205} It was assumed that the ideal linear conjugated polymers were mainly obtained by the increased cyclopolymerization probability as the oxidation state of sulfur is increased.²⁵³ In most cases, the poly(1,6-heptadiyne)s having substituents were soluble and easily solution castable.¹⁵⁰

Poly(1,6-heptadiyne)s having substituents were found to be generally stable to air oxidation. It was known that poly(1,6-heptadiyne) is very susceptible to air oxidation similar to polyacetylene, reducing the π -conjugation. However, poly(DPDPM) exhibited some excellent oxidative stability in air. Figure 3 is a typical example of oxidative stability comparison of poly(1,6-heptadiyne) and poly(DPDPM).¹⁶² The IR spectrum of poly(1,6-heptadiyne), which had been standing at room temperature with exposure to air for 3 days, showed a new strong carbonyl absorption band at about 1650 cm⁻¹. However, in the case of poly(diphenyldipropargylmethane), it was not until it had stood for 6 months that a band of the carbonyl group appeared at 1650 cm⁻¹.

Although thermal and oxidative stabilities of poly(1,6-heptadiyne)s reported previously had been enhanced over those of analogous unsubstituted polyenes, decomposition of a long, π -conjugated polyene framework could not be avoided completely especially in the case of polymers having a sterically small substituent at the 4-position.^{128,162,163} However, polymer **19** ($\lambda_{\max} = 606$ nm) with an extremely bulky substituent such as *tert*-butyldiphenylsilyloxymethyl group is environmentally more stable than other polymers currently available.²⁰¹ This stability of the conjugated polymer backbone to air oxidation is originated from the effective shielding of the highly conjugated backbone by the bulky substituents. These findings are particularly important in synthetic polyene chemistry, since they can offer the possibility of obtaining polyacetylenes processing stability and processibility.^{254,255}

A differential scanning calorimetry (DSC) thermogram of poly(1,6-heptadiyne) showed two irreversible

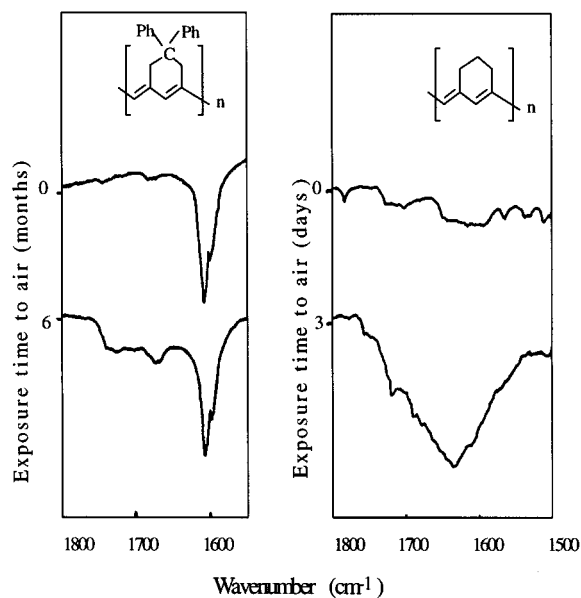


Figure 3. IR spectra for oxidation stability to air at room temperature of poly(diphenyldipropargylmethane) and poly(1,6-heptadiyne).

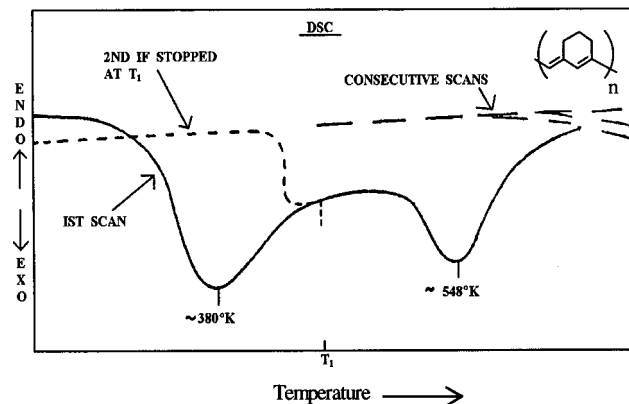


Figure 4. Differential scanning calorimetric (DSC) traces for poly(1,6-heptadiyne).

exothermic processes, one peaking at 107 °C and the other at 275 °C (Figure 4).¹⁶⁰ The lower process is originated from the rearrangement of the exo double bond of ideal poly(1,6-heptadiyne) structure to convert to the polymer from a helical structure to a nearly planar polyene backbone configuration (Scheme 17).

Scheme 17

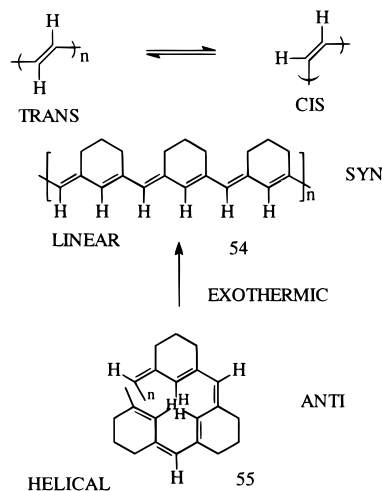


Table 14. Comparison of the Exothermic Peak Temperature of Poly(1,6-heptadiyne) and Its Homologues

X of (HC≡CCH ₂) ₂ X	exothermic peak temp, °C		ref
	first	second	
CH ₂	107	275	160
S	160	267	203
CPh ₂	160	240	162
GePh ₂	112	260	209
C(CO ₂ Et) ₂	138	280	163

The isomerization temperature of linear polyacetylene is reported as 155 °C.²⁵⁶ The higher temperature process is assumed to be due to the exo to endo rearrangement and/or the thermal decomposition reaction. Poly(1,6-heptadiyne) homologues also showed similar two exothermic peaks in the DSC thermogram, as shown in Table 14.

Some poly(1,6-heptadiyne) homologues having a relatively high molecular weight ($M_n > 100\,000$) were easily solution-casted into homogeneous polymer films. The mechanical properties of poly-6 with tensile measurement are summarized as follows:¹⁶³ Young's modulus (E), 4800 MPa; tensile strength (γ_B), 104 MPa; ultimate elongation (γ_B), 3.4%. The polymer from 1,6-heptadiyne with fluorinated alkyl esters, bis(2,2,2-trifluoroethyl) and bis(1,1,1,3,3,3-hexafluoro-2-propyl) dipropargylmalonate, generally showed lower Young's moduli (1160, 750 MPa, respectively) and tensile strengths (28, 18 MPa, respectively).¹⁶⁷ The relatively poor mechanical properties of poly(1,6-heptadiyne) having fluorinated alkyl esters is due to the weak intermolecular interaction.

Poly(1,6-heptadiyne) is distinct from polyacetylene in its morphology. Polyacetylene is very porous, being comprised of fibrils of diameter 100–800 Å,^{257,258} and has an apparent density of about 0.4 g/cm³.²⁵⁹ On the other hand, poly(1,6-heptadiyne) has very little void content (density, 1.05 g/cm³) and exhibits a number of morphologies upon the polymerization conditions and the catalysts used.¹⁶⁰ Poly-6 presents a fibrillar morphology.¹⁶² The dull side of the film (facing toward the air) is very porous with identical fibrils. The shiny side of the film (facing the glass wall) is very smooth with the fibril matter. The fibrils range from 200 to 300 Å in diameter. The poly-6 morphology is similar to that of polyacetylene with the fibers, generally having diameters of 200–500 Å.^{260–262} On doping with iodine, an increase in fibrillar diameter to 400 Å is observed. Poly(1,6-heptadiyne) did not show any crystallinity to the X-ray diffraction, while polyacetylene prepared by Shirakawa catalysts is 80–90% crystalline. Poly(1,6-heptadiyne) homologues having substituents at 4-position of 1,6-heptadiyne mostly showed all broad peaks in X-ray diffractograms. It was found that the ratios of the half-height width to the diffraction angle ($\Delta 2\theta/2\theta$) are greater than 0.35. So, the polymers are mostly amorphous.^{233,234,236}

B. Electrical/Electronic Properties

π -Conjugated polymers dramatically change its electrical and electronic behavior by incorporation of small amounts of various dopants (both acceptors and donors).^{34,35,68,69} Poly(1,6-heptadiyne) films prepared

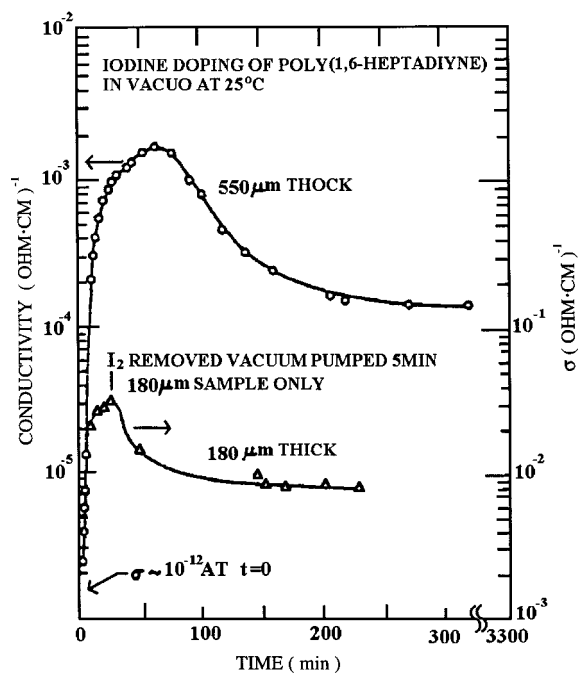


Figure 5. Electrical conductivity of poly(1,6-heptadiyne) films as a function of time after exposure to iodine at 25 °C in a vacuum.

by Gibson et al. were also easily doped with the electron acceptors such as iodine and arsenic pentafluoride.¹⁶⁰ The polymer films changed from initial green through purple-to-blue into blue-black colors with the exposure to iodine vapor. AsF₅ also changed the polymer film from green to blue to blue-black. A typical conductivity diagram of poly(1,6-heptadiyne) films as a function of exposure time to iodine under vacuum is shown in Figure 5. The electrical conductivity of poly(1,6-heptadiyne) changes by a factor of 10¹⁰ from 10⁻¹² Ω⁻¹ cm⁻¹ to 10⁻² Ω⁻¹ cm⁻¹ over a period of 60 min. However, the conductivity–time curve proceeded through this maximum value and then decreased by about a factor of 10 before plateauing. This phenomenon was found to be general one in the electrical conductivity experiment of poly(1,6-heptadiyne) homologues such as poly(dipropargyl ether),³⁵ poly(dipropargyl sulfide),³⁵ poly(dipropargylsilane)s,²⁶³ and poly(diphenyldipropargylmethane).¹⁶² This was hypothesized to be due to the iodine-catalyzed rearrangement of the double bonds in the conjugated polymer backbone, resulting in loss of conjugation.

The typical electrical conductivity of a poly(DP-DPM) pellet, a substituted poly(1,6-heptadiyne), is displayed as a function of exposing time in Figure 6.¹⁶² In 5 h, the polymer pellet exhibited a maximum in the conductivity and then began to decrease slowly. When film-type polymer was exposed to iodine vapor, it changed from dark violet to blue-black and the electrical conductivity increased from 10⁻¹⁰ Ω⁻¹ cm⁻¹ to 10⁻⁴ Ω⁻¹ cm⁻¹. The maximum electrical conductivity of iodine-doped poly(DPDPM) is smaller than that of iodine-doped poly(1,6-heptadiyne), which is reported to have a value of 10⁻¹–10⁻³ Ω⁻¹ cm⁻¹.¹⁶⁰ The activation energy for conduction was derived from the temperature, T , dependence of conductivity. For the undoped poly(DPDPM), the activation energies have

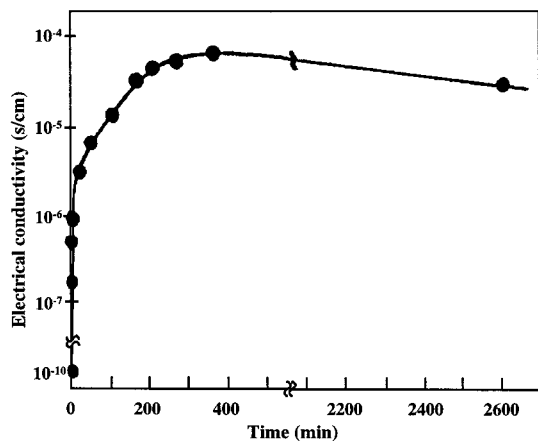


Figure 6. Electrical conductivity of poly(DPDPM) pellet as a function of exposure time to iodine at 25 °C under nitrogen.

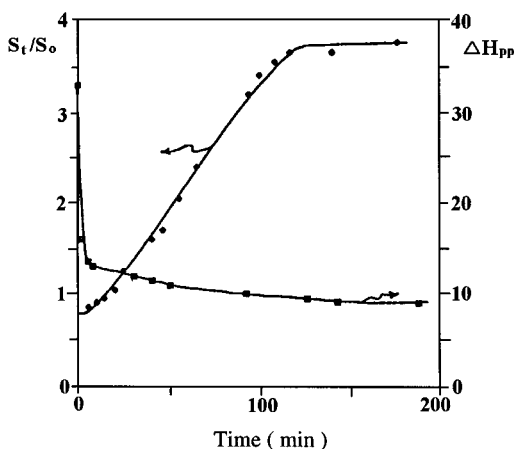


Figure 7. Line width (■) and free spin population (◆) of poly(DPDPM) as a function of exposure time to iodine at 25 °C in vacuo: S_0 , initial spin population; S_t , spin population at each time (t).

a value of 12–13 kcal/mol, which is comparable to those of polyacetylene (11 kcal/mol) and poly(1,6-heptadiyne) (12.2 kcal/mol).^{160,162} The iodine-doped poly(DPDPM) film has a value of only 3.5 kcal/mol. The spin density of undoped poly(DPDPM) was 10^{18} spins/g, and the line width (H_{pp}) was 33 G at $g = 2.0011$.¹⁶² Figure 7 represents the changes of the relative spin population and the line width of poly(DPDPM) as a function of iodine exposure time in situ.¹⁶⁴ The line width of 33G narrows to a sharp intense band of only 9 G upon doping. This polymer has a significantly larger H_{pp} than that of polyacetylene. It was explained by the following: the probability that the radicals are placed in the trapped state^{264,265} is increased because the polymer having a bulky substituent has a more twisted polymer backbone due to the substituents and the nonequivalent double bonds of the polymer backbone. The relative spin population increased, with first-order kinetics, as a function of exposure time to iodine, and it was saturated in 2 h. The increasing result is similar to that of poly(1,6-heptadiyne). Upon heating, the ESR spectrum changed as shown in Figure 8. As the poly(DPDPM) is transformed from helical to linear, the ESR signal sharpens (α). Moreover, as

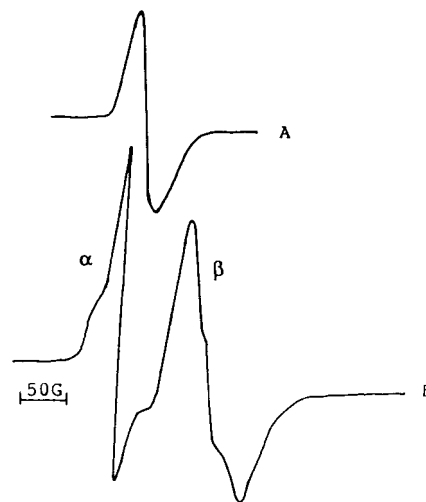


Figure 8. Electron spin resonance (ESR) spectra of poly(DPDPM) as a function of heating time at 230 °C under nitrogen gas: (A) zero time; (B) after 15 min.

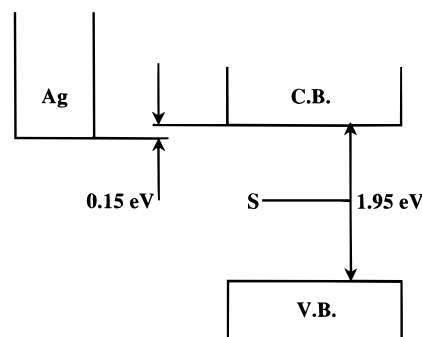
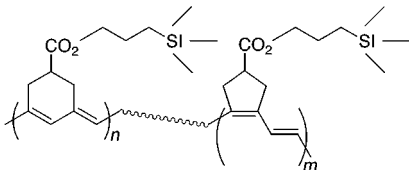
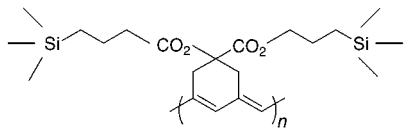
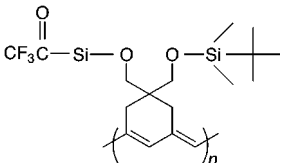
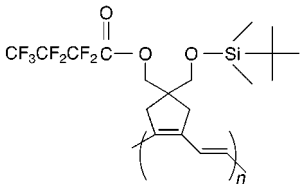
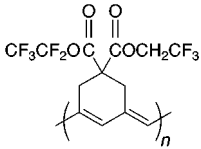
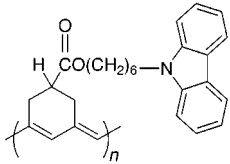
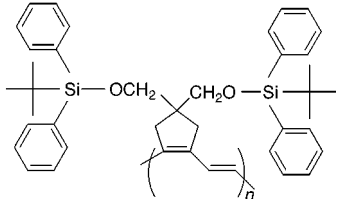


Figure 9. Electronic energy band scheme of polymer 33 ($X = \text{Br}$).

heating is continued for a long time, the configuration of backbone structure becomes ruptured, resulting in a new ESR signal (β).

From the absorption spectrum of poly-**33** film,²³³ the band gap energy of poly-**33** was evaluated to be 1.95 eV (Figure 9), which is larger than that of *trans*-polyacetylene but comparable to that of *cis*-polyacetylene.²⁶⁶ The electrical conductivity of the film was $10^{-8} \Omega^{-1} \text{cm}^{-1}$ at room temperature and increased with temperature with an activation energy of about 0.6 eV. This conductivity is much higher than those of nondoped *cis*- and *trans*-polyacetylene and other substituted polyacetylenes such as poly(phenylacetylene),³⁴ poly(*o*-trimethylsilylphenylacetylene),²⁶⁷ and poly(diethylpropargylmalonate).¹⁶³ This may be due to the existence of an ionic group in the side chain of poly-**33**. This polymer also exhibited a drastic change in the ESR spectrum upon iodine doping. That is, in PDHPAB, the spin density of as large as 1020 spins/g was evaluated from ESR spectrum in the nondoped state, but it decreased drastically with the increasing doping time of iodine. The ESR characteristics are similar to those of polyacetylene and can be interpreted in terms of a soliton model. The line width of the ESR also becomes narrower with the increasing doping time of iodine but does not become so narrow as the case of electrochemically BF_4 -doped polyacetylene.

Table 15. Linear and Nonlinear Optical Properties for Poly(1,6-heptadiyne)s

polym	λ_{\max} (UV), nm	$\chi^{(3)}$ $\times 10^{-11}$ esu	$\langle \gamma \rangle^{(3)}$ $\times 10^{-32}$ esu
	540	2.6	
	560 and 590	3.1	
	540 and 595	3.6	
	540 and 595	4.3	
	530 and 575	4.1	44
	540	0.99	2.9
	550 and 610	0.44	0.43

C. Linear and Nonlinear Optical Properties

Organic polymers with π -electron delocalization are recently of wide interest as third-order nonlinear optical materials with potential applications as all-optical switches and ultrafast optical devices.^{268,269} Many π -conjugated polymers, including polyacetylene, polydiacetylene, polythiophene, and poly(*p*-phenylenevinylene) have been reported to have very large third-order optical nonlinearity $\chi^{(3)}$, ranging from 10^{-12} to 10^{-9} esu.^{270–273} It has been observed that third-order optical nonlinearity $\chi^{(3)}$ increases with the extent of π -electron delocalization and the polarizability of the molecules.^{274,275} It has guided most of the current approaches to molecular design and optimization of polymers with potentially large third-order optical nonlinearity $\chi^{(3)}$ values. However, such an extended π -electron conjugation generally renders the polymer insoluble and infusible as well, which has seriously limited the fabrication of practical

applications. For these reasons, poly(1,6-heptadiyne) derivatives are promising candidates for the third-order nonlinear optical materials with practical applications, since these polymers were highly soluble in common organic solvents to afford the processability. Their third-order nonlinear optical susceptibility of poly(1,6-heptadiyne)s was measured by the degenerate four-wave mixing method (DFWM) at the wavelength of $1.06 \mu\text{m}$. Also, their structure–optical property relationship was investigated. Table 15 summarizes the linear and nonlinear properties for poly(1,6-heptadiyne)s. It was found that the incorporation of a bulkier substituent in the 4-position of 1,6-heptadiyne enforces the conjugated polyene into a more planar structure, as indicated by the bathochromic shift of the maximum absorption bands from the π - π^* transition of the π -conjugated polymer backbone. These results provide remarkable contrast to mono- and disubstituted polyacetylene and mono-

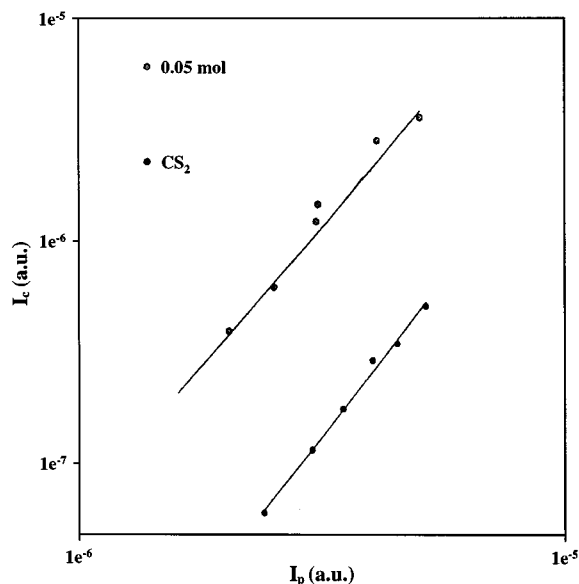


Figure 10. Intensity of phase conjugated beam (I_c) vs intensity of incident beam (I_p) of DFWM experiment on a reference and 0.05 M of poly(1,6-heptadiyne) (see poly-86 in Scheme 22) in THF.

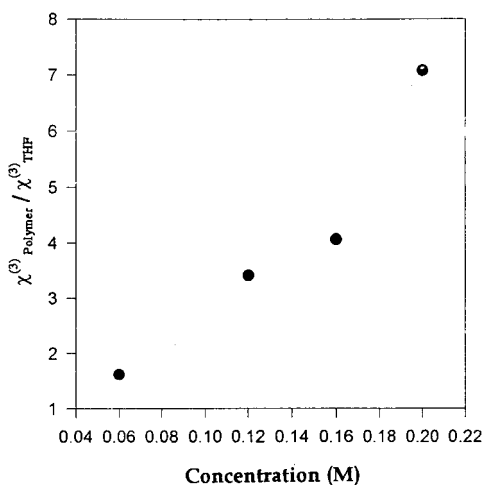


Figure 11. Concentration dependence of $\chi^{(3)}$ of poly(1,6-heptadiyne) (see poly-86 in Scheme 22) in THF.

substituted polycyclooctatetraenes by ROMP, in which the steric bulk at the point of attachment to the polymer chain increases.

The intensity of the DFWM signal for the poly(1,6-heptadiyne)s increased linearly with intensity of the incident beam, as shown in Figure 10. From the direct comparison between the intercepts of the Y axis of the polymers and the carbon disulfide reference, the $\chi^{(3)}$ values of the polymers were obtained. And also, as the concentration of the polymer solution was increased, the $\chi^{(3)}$ values of the polymers were increased (Figure 11). The third-order nonlinear optical properties were enhanced with an increase in the bulk of the substituents at the 4-position, which is in accord with the bathochromic shift of λ_{\max} in the UV-vis spectra. From these results, it was concluded that the incorporation of bulky substituents into the 4-position of 1,6-heptadiynes enforces the π -conjugated polyene into the more planar conformation, resulting in a red shift and the increment of the $\chi^{(3)}$ values of the polymers. Recently, Schrock

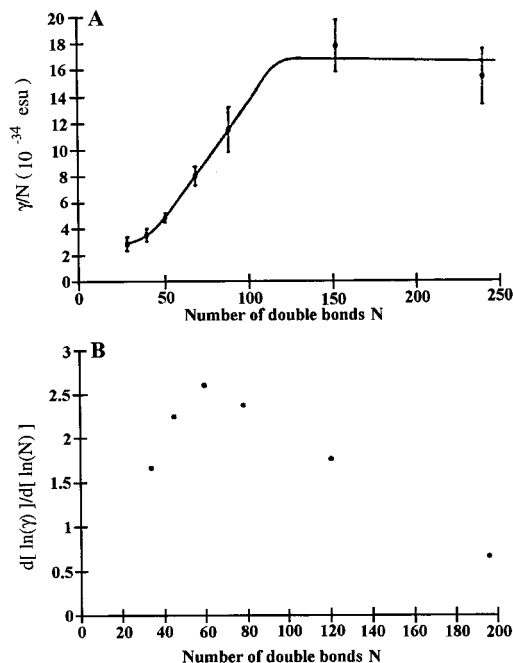


Figure 12. (A) Values of $\gamma(-3\omega; \omega, \omega, \omega)/N$ as a function of the number of double bonds N for the model oligomer **6** [poly(DEDPM)] as measured by third harmonic generation at 1.9 μm . The solid line is a guide for the eye. (B) Plot of $d[\ln(\gamma)]/d[\ln(N)]$ as a function of chain length for the data in A.

et al. synthesized long-chain conjugated oligomers from **5** by living polymerization techniques for the measurement of the hyperpolarizability γ as a function of a chain length n with up to 240 double bonds.⁴⁶ The results were shown in Figure 12. They observed a saturation of λ/N in these very long polyenic systems. In the case of poly(1,6-heptadiyne), the values of the hyperpolarizability γ were in the range of $(0.43\text{--}44) \times 10^{-32}$ esu, depending on the conformation of chain molecules and the substituents at the 4-position. And, also, Heeger et al. reported that poly(1,6-heptadiyne) rendered a 160-fs optical image processor with the diffraction efficiency of $\eta = 10^{-4}$, achieving peak processing rates of 3×10^{16} operations/s.⁴⁷

D. Electrochemical and Electrochromic Properties

Free-standing 0.1 mm *cis*-polyacetylene films have been most commonly used in the electrochemical and battery-type studies.^{276–278} The electrochemical properties of poly(1,6-heptadiyne)s have also been studied. The electrochemical measurements of poly(bis(*N*-carbazolyl)-*n*-hexyldipropargyl malonate) (PBCHDPM) films were performed in a 0.1 M tetrabutylammonium perchlorate ((TBA)ClO₄)/acetonitrile solution.²⁷⁸ The cyclic voltammograms of PBCHDPM with the consecutive scan are shown in Figure 13. As the cycling number increased at the potential range of -0.5 to $+1.5$ V, PBCHDPM showed the well-defined redox process and the increase of current density in cyclic voltammograms. On the other hand, the oxidation occurred only at 1.4 V in the first scan, where the pendant carbazole units were oxidized and coupled each other irreversibly to form the dicarbazoles. After the first scan, two oxidation peaks at 0.98

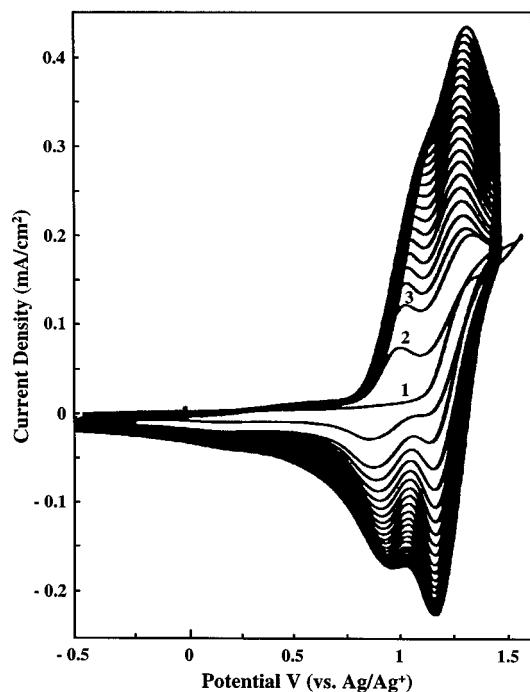


Figure 13. Cyclic voltammograms of poly-**86** with consecutive scans at 30 mV/s (0.1 M (TBA)ClO₄/acetonitrile).

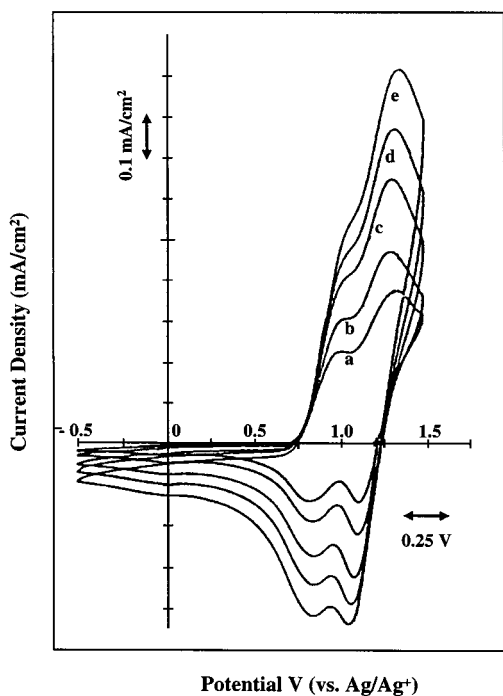


Figure 14. Cyclic voltammograms of poly-**86** with various scan rates (0.1 M (TBA)ClO₄/acetonitrile): (a) 20, (b) 30, (c) 50, (d) 70, and (e) 100.

and 1.32 V were observed, which might be attributed to the dicarbazoyls coupled. These electrochemical properties are similar to those of *N*-carbazole derivatives.^{279–281} Figure 14 shows the variation of the redox peak current density as the various scan rates to investigate electrochemical kinetic behavior. The peak potential shifts are almost independent of scan rate. Also, the redox current value increased as the scan rate increased. This indicates that the electrochemical process is reproducible in the potential range of 0.0–1.5 V vs Ag/Ag⁺. The relationship

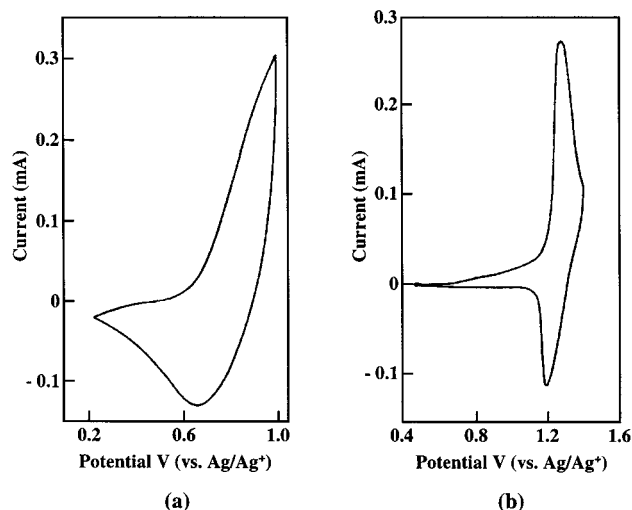


Figure 15. Cyclic voltammograms of PMHBDPM (poly-**59**) film in 0.1 M TBAFB/acetonitrile solution (a) between 0.2 and 1.0 V vs Ag (sweep rate = 20 mV/s) and (b) between 0.5 and 1.4 V vs Ag (sweep rate = 2 mV/s).

between redox peak current and the scan rate can be expressed as a power law type as follows:^{282,283}

$$i_{p,a} = kv^x$$

where $i_{p,a}$ = oxidation peak current density, v = scan rate, k = proportional constant, and x = exponent of scan rate.

The oxidation current density versus the scan rate is approximately linear in the range of 20–100 mV/s. The exponent of scan rate, x , value was found to be 0.6, indicating that the kinetics of the redox process is almost controlled by the diffusion process.²⁸⁴ This means that insertion/desertion of ClO₄⁻ ions is responsible for the charge electroneutrality during the redox process of PBCHDPM.

The conjugated polymeric liquid crystal, poly(bis(4-methoxy-4'-hexyloxybiphenyl)dipropargylmalonate) (PMHBDPM), can be reversibly doped by using electrochemical doping with the common three-electrode method utilizing acetonitrile solution containing tetrabutylammonium fluoroborate (TBAFB) as an electrolyte.²⁸⁵

Parts a and b of Figure 15 indicate cyclic voltammograms of the PMHBDPM film with two different sweep rates. Figure 15a is the cyclic voltammogram of PMHBDPM in TBAFB/AN solution with the scan rate of 20 mV s⁻¹ in the range of 0.2–1.0 V. In this figure, an oxidation wave was observed around 0.7 V vs Ag. On the other hand, as evident in Figure 15b in the cyclic voltammogram with a much slower sweep rate of 2 mV s⁻¹, an oxidation wave was observed around 1.2 V vs Ag, and the wave around 0.7 V was not as obvious as in Figure 15a. That is, there are two oxidation and reduction waves around 0.7 V vs Ag and 1.2 V vs Ag. The first oxidation and reduction waves at 0.7 V vs Ag are not clear in Figure 15b, but this is reasonable because this cyclic voltammogram was observed with a much slower sweep rate and a larger sweep range. These results mean that there are two different electrochemical reaction systems with different reaction kinetics and thermodynamical electrochemical potentials.

Table 16. Polymerization of 56, 58, 60 and 62 by Various Transition Metal Catalysts^a

monomer syst	cat. syst ^b (mole ratio)	M/C ^c	[M] ₀ ^d	polym yield, ^e %	GPC ^f	
					<i>M_n</i> /10 ⁴	<i>M_w</i> / <i>M_n</i>
56	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:1)	50	0.25	95	10.5	2.7
56	MoCl ₅	100	0.125	56	8.0	2.1
56	WCl ₆	50	0.25	trace		
58	MoCl ₅	50	0.25	100	11.0	3.5
58	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:1)	50	0.25	90	7.8	3.1
58	MoCl ₅ -EtAlCl ₂ (1:1)	50	0.25	80	6.49	2.4
58	WCl ₆ -(<i>n</i> -Bu) ₄ Sn (1:1)	50	0.25	trace		
58	WCl ₆ -EtAlCl ₂ (1:1)	50	0.25	15		
60	MoCl ₅	50	0.25	84	6.0	2.9
60	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:1)	50	0.25	42	3.8	2.1
60	MoCl ₅ -EtAlCl ₂ (1:1)	50	0.25	46	4.7	2.4
60	PdCl ₂ ^g	50	0.25	50	0.49	
62	MoCl ₅	50	0.125	trace		
62	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:1)	50	0.25	50	3.2	

^a Polymerization was carried out at 60 °C for 24 h in 1,4-dioxane. ^b Mixture of catalyst and cocatalyst was aged at 30 °C for 15 min before use. ^c Monomer to catalyst mole ratio. ^d Initial monomer concentration [mol/L]. ^e Methanol-insoluble polymer. ^f Values were obtained by GPC analysis with polystyrene standards calibration. ^g Polymerization was carried out at 90 °C for 24 h in 1,4-dioxane.

V. Multifunctional Poly(1,6-heptadiyne)-Based Materials

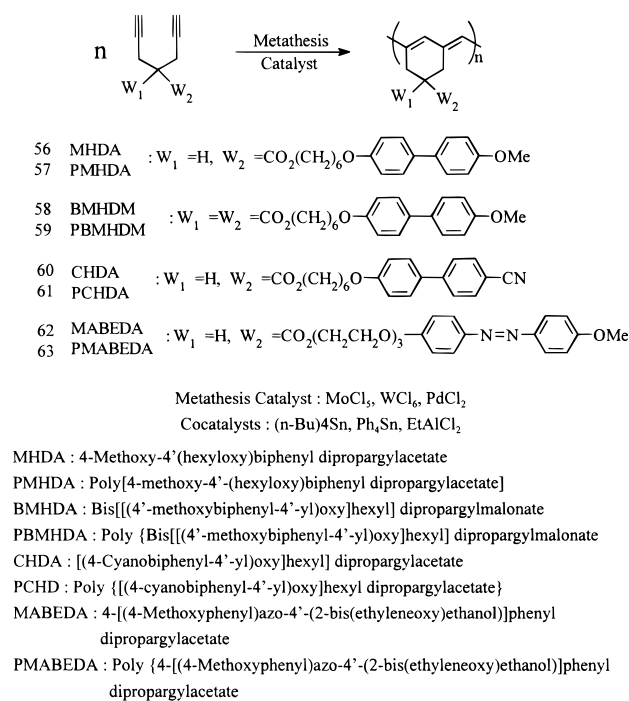
A. Side Chain Liquid Crystalline Poly(1,6-heptadiyne)s

Much attention has been paid recently to liquid crystalline polymers, especially those with side chain, because of their potential application for electronic devices.^{286,287} Most of the side chain liquid crystalline polymers (SCLCP) have been prepared to attach mesogenic groups onto various polymer backbones, like polysiloxane, polyacrylate, or polymethacrylate, etc. Very little work has been done on liquid crystalline monoacetylene derivatives.²⁸⁸ Such monomers are very interesting as sources of novel structures with a π -conjugated rigid backbone which can be generated by metathesis reaction. To obtain the thermotropic LC mesomorphism from such a rigid polymer backbone, substituted poly(1,6-heptadiyne) derivatives containing mesogenic groups with the flexible spacer was synthesized and characterized.^{289–294} Scheme 18 outlines the polymerization of various monomers with transition metal catalysts. Table 16 summarizes the polymerization results. The catalytic activity of MoCl₅ is greater than that of WCl₆. When the mole ratio of the monomer to the catalyst was relatively low, a high yield was obtained. Also, it was observed that (*n*-Bu)₄Sn is an excellent cocatalyst for the polymerization of **56**.

The number-average molecular weight (*M_n*) and polydispersity (*M_w*/*M_n*) of poly-**57** obtained were ca. 10.5×10^4 and 2.7, respectively. It shows that WCl₆ exhibits less effective catalytic activity by itself. However, WCl₆ and a cocatalyst were effective. Especially, EtAlCl₂ exhibited more cocatalytic activity. Also the effect of variation in the mole ratio of monomer to catalyst on the polymerization were also studied.²⁸⁹ The maximum yield was obtained, when the mole ratio of monomer to catalyst was 50.

As shown in Table 16, (*n*-Bu)₄Sn exhibited more cocatalytic activity compared with EtAlCl₂ for the polymerization of **58** by a MoCl₅-based catalytic system.²⁹⁰ However, EtAlCl₂ is especially effective

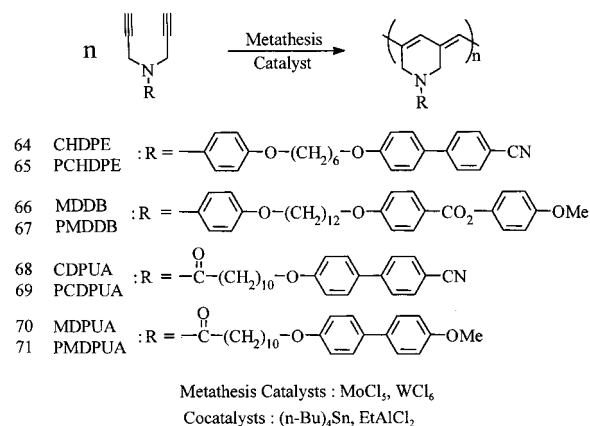
Scheme 18



for the polymerization of **58** by a WCl₆-based catalyst system. In contrast with **56**, MoCl₅ alone effectively catalyzes the polymerization of **58**. The highest number-average molecular weight (*M_n*) of poly-**59** obtained was ca. 11×10^4 (with MoCl₅ alone). MoCl₅ alone catalyzes the polymerization of **60** more effectively than MoCl₅-cocatalyst systems.²⁸⁸ The number-average molecular weight (*M_n*) and polydispersity (*M_w*/*M_n*) of poly-**61** were 6×10^4 and 2.9, respectively. In **62**, the polymer yield was relatively low. The low catalytic activity may be due to the interaction of a heteroatom (azo unit of the mesogenic group) with the catalyst, thus hindering triple bond coordination. The number average molecular weight (*M_n*) of poly-**63** was 5.0×10^4 .

Scheme 19 outlines the cyclopolymerization of dipropargylamine monomers having liquid-crystalline moiety with transition metal catalyst systems.^{291–295}

Scheme 19



CHDPE : [[4'-Cyano-(1,1'-biphenyl)-4-yl]oxy]hexyl-4-(dipropargylamino)phenyl ether
 PCHDPE : Poly {[[4'-Cyano-(1,1'-biphenyl)-4-yl]oxy]hexyl-4-(dipropargylamino)phenyl ether}

MDDB : 4-Methoxyphenyl[(((4-dipropargylamino)phenyl)oxy)dodecanyl]oxy benzoate
 PMDDB : Poly {4-Methoxyphenyl[(((4-dipropargylamino)phenyl)oxy)dodecanyl]oxy benzoate}

CDPUA : 11-(4-Cyanobiphenyl)oxy-N,N-dipropargylundecaneamide
 PCDPUA : Poly {11-(4-Cyanobiphenyl)oxy-N,N-dipropargylundecaneamide}

MDPUA : 11-(4-Methoxybiphenyl)oxy-N,N-dipropargylundecaneamide
 PMDPUA : Poly {11-(4-Methoxybiphenyl)oxy-N,N-dipropargylundecaneamide}

The polymerizations of the dipropargylamine monomers were carried out with MoCl₅- and WCl₆-based catalysts and their results are summarized in Table 17. The catalytic activity of MoCl₅ was greater than that of WCl₆. EtAlCl₂ exhibited excellent cocatalyst activity compared with (*n*-Bu)₄Sn for the polymerization of **64**. When the polymerization was carried out with MoCl₅-EtAlCl₂, a quantitative polymer yield was obtained. The polymerization results of **66**, **68**, and **70** are similar to those for the polymerization of **64**.

The resulting polymers are completely soluble in various organic solvents such as chloroform, methylene chloride, THF, 1,4-dioxane, and pyridine and can be easily casted on glass plates to give a black, shiny thin film. But poly-**65** and poly-**71** are partially soluble in various organic solvents as those mentioned. It is, however, insoluble in *n*-hexane, acetone,

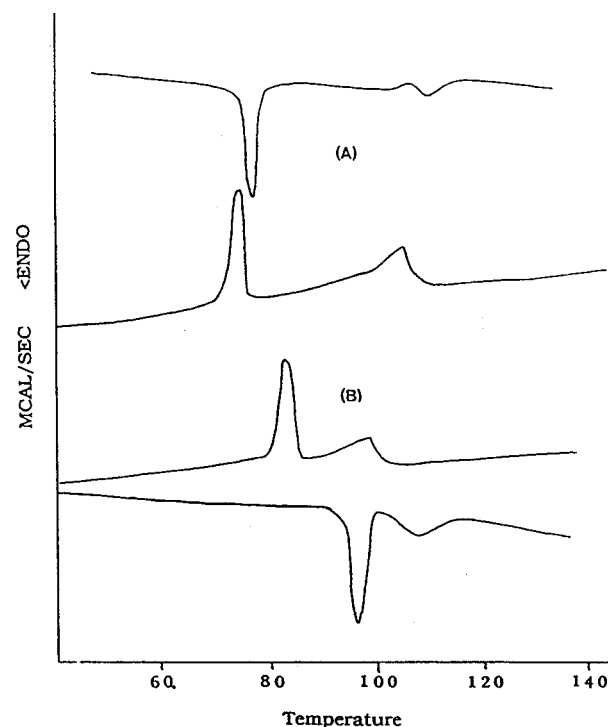


Figure 16. DSC thermograms of **56** (A) and poly-**57** (B) (scan rate: 10 °C/min.).

diethyl ether, and ethyl acetate. One minor difference is found in that poly-**57** and poly-**59** dissolved in toluene or DMF, but not poly-**61** and poly-**63**. On the other hand, the solubility of the polymers obtained increases with the spacer chain length, which is more consistent with the greater solvation of the mesogens attached to longer spacer. Such a good solubility of the present cyclopolymers supports the hypothesis that these polymers incorporated into the polyene backbone contain both five- and six-membered rings. It was confirmed by typical analytic techniques.

Figure 16A shows the DSC curves obtained for consecutive heating and cooling cycles on **56**. In the second heating, two prominent endotherms are observed at $T_m = 75$ °C and $T_i = 106$ °C. There is a

Table 17. Polymerization of 64, 66, 68, and 70 by Various Transition Metal Catalysts^a

monomer syst	cat. syst ^b (mole ratio)	M/C ^c	[M] ₀ ^d	polym yield, ^e %	GPC ^f	
					$M_n/10^4$	M_w/M_n
64	MoCl ₅	50	0.25	95	0.8	2.7
64	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:4)	50	0.25	80	0.7	3.0
64	MoCl ₆ -EtAlCl ₂ (1:4)	50	0.25	100	0.7	2.4
64	WCl ₆	50	0.25	trace		
64	WCl ₆ -(<i>n</i> -Bu) ₄ Sn (1:1)	50	0.25	trace		
66	MoCl ₅	50	0.25	88	1.8	2.0
66	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:4)	50	0.25	80	1.5	1.8
66	MoCl ₆ -EtAlCl ₂ (1:4)	50	0.25	100	1.3	2.1
68	MoCl ₅	50	0.25	91	1.4	2.7
68	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:4)	50	0.25	60	1.6	2.1
68	MoCl ₆ -EtAlCl ₂ (1:4)	50	0.25	100	1.8	2.4
68	WCl ₆	50	0.25	trace		
70	MoCl ₅	50	0.25	85	1.0	2.7
70	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:4)	50	0.25	72	1.1	2.3
70	MoCl ₆ -EtAlCl ₂ (1:4)	50	0.25	100	1.4	2.2
70	WCl ₆	50	0.25	trace		

^a Polymerization was carried out at 60 °C for 24 h in 1,4-dioxane. ^b Mixture of catalyst and cocatalyst was aged at 30 °C for 15 min before use. ^c Monomer to catalyst mole ratio. ^d Initial monomer concentration [mol/L]. ^e Methanol-insoluble polymer. ^f Values were obtained by GPC analysis with polystyrene standards calibration.

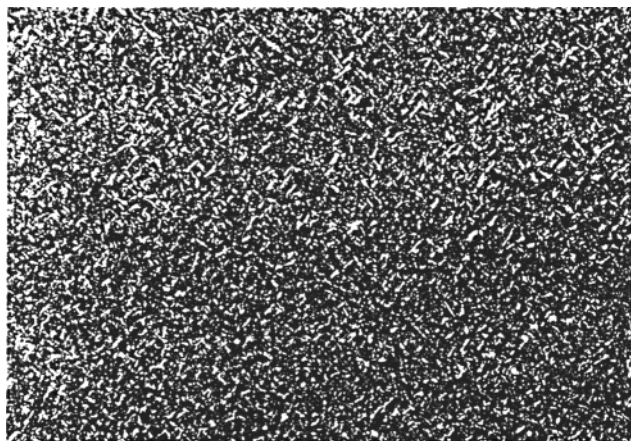


Figure 17. Microphotograph of **56** taken at 80 °C.

slight shoulder on the isotropization peak between 103 and 105 °C. In the first cooling scan, the transition temperatures were lower than that of second heating scan. Figure 17 shows the photomicrographic property of the liquid-crystalline state of **56**. The mesophase found for **56** in the region of 75–106 °C (69–96 °C on cooling cycles) was characterized by the following observation through the polarizing optical microscope. The mesophase found for poly-**57** has probably a smectic texture. Figure 16B, which presents the second heating and the cooling DSC scans of poly-**57**, indicated two well-separated transition regions in the polymer. The liquid crystal to isotropic transition occurs at temperatures well above 100 °C and is very broad. This is probably due to the high viscosity and polydispersity of the polymeric product.²⁹³ On the cooling cycle, the mesophase region is broadened with exotherms at 101 and 85 °C. The typical texture for poly-**57** is presented in Figure 18. Upon cooling the temperature of the isotropic liquid, a mesophase begins to form at 105 °C, in the form of “spherulites” (Figure 18A) which, after further cooling to 103 °C within 30 min (Figure 18B), grow, coalesce, and reorganize their shape until a final texture is established at ca. 101 °C (Figure 18C), suggesting the existence of a smectic mesophase. The enthalpies of isotropization (ΔH_i) of poly-**57** are relatively small according with those of the melting transition and with those of the isotropization for conventional smectic liquid crystals. Due to the rigid backbone of the sample, it was thought that enthalpies of isotropization were relatively small, compared with the conventional smectic mesophase. In addition, it was observed experimentally by optical polarized microscopy that the flow properties of poly-**57** were poor, so it may be thought that the resulting polymer had a mainly smectic mesophase. Due to the paired mesogens, phase transition temperatures of poly-**59** are higher than that of the single mesogenic unit (poly-**57**). Another interesting observation is that the temperature range, even in which the mesophase existed, is consistently broader for the bimesogenic cyclopolymer, compared with a single mesogenic cyclopolymer as shown in Scheme 18. These results can be attributed to the increase in anisotropic molecular polarizability. The bimesogenic compound has four polarizing aromatic rings.²⁹⁶ Figure 19

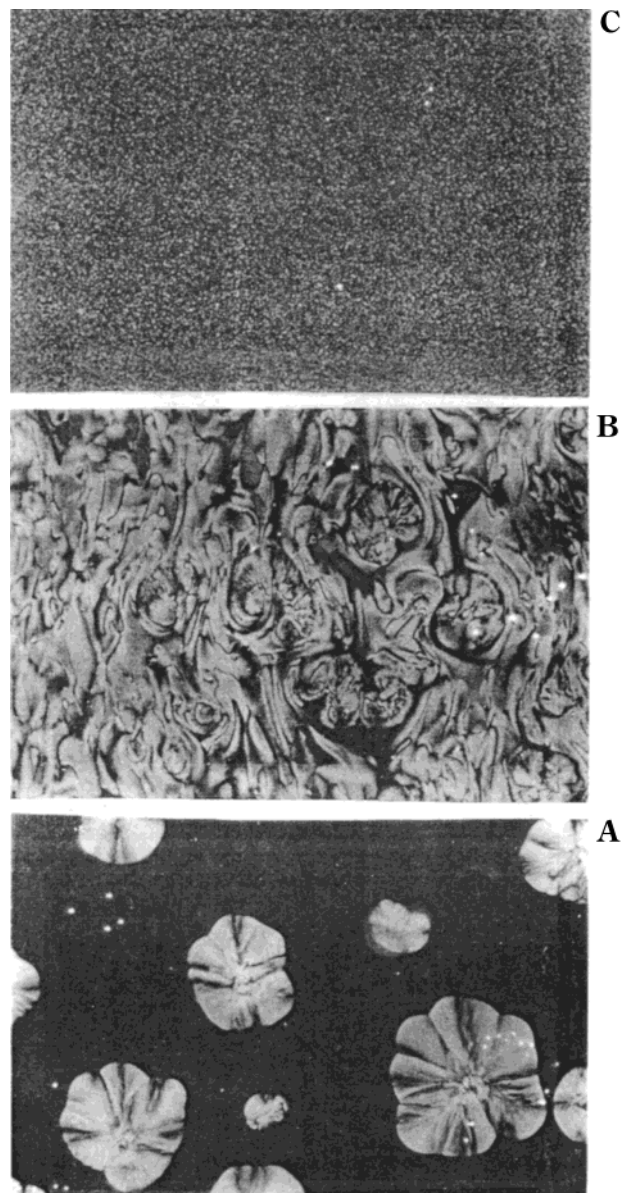


Figure 18. Effect of temperature on the microscopic morphology of poly-**57**: (A) annealing time, $t_a = 1$ h, taken at 105 °C; (B) $t_a = 1$ h, taken at 103 °C; (C) $t_a = 1$ h, taken at 101 °C.

presents the second heating and the cooling DSC curves of Figure 19A for monomer-**58** and Figure 19B for poly-**59**, which indicated two well-separated transition regions of the samples. And the liquid crystal to isotropic transition was relatively broad. This is probably due to the high polydispersity and rigid backbone of the polymeric product. It was shown that the mesophase of **58** and poly-**59** were in the range of 78–110 and 95–107 °C on the heating cycles (71–94 °C and 85–103 °C on the cooling cycles), respectively. A texture of **58** corresponds to a smectic phase at 90 °C in Figure 20A.⁹⁵ In poly-**59**, a highly ordered smectic texture was observed at 101 °C on cooling from the isotropic state as seen in Figure 20B. Its result was confirmed by X-ray diffraction (see Figure 23). The texture of poly-**59** shows a typical undeveloped smectic phase, which is due to the molecular weights and rigidity of poly-**59**. Furthermore, it was found that the flow property of poly-**59** was poor.

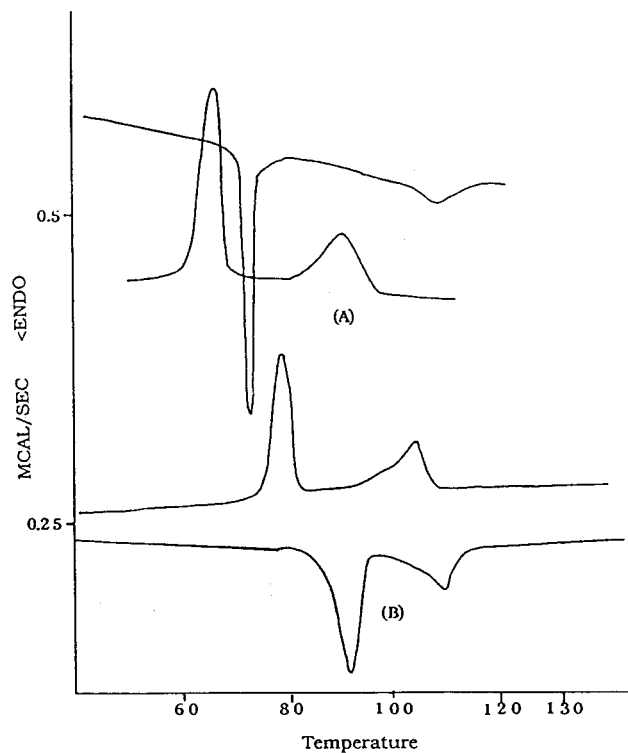
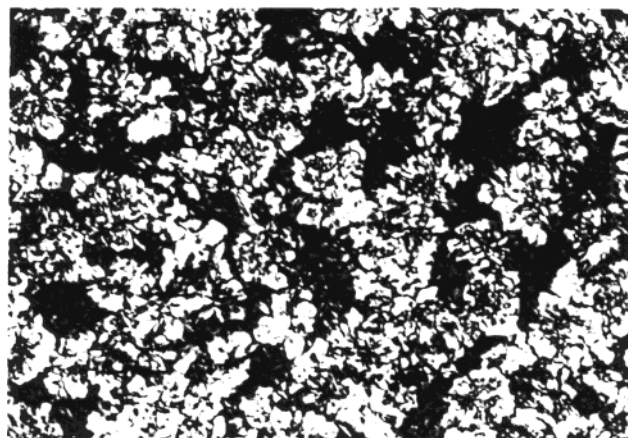
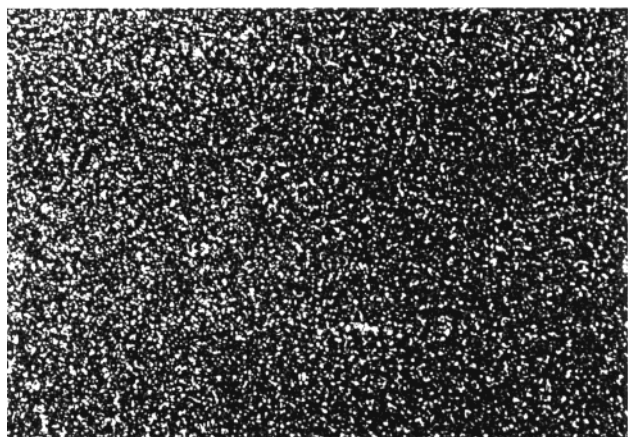


Figure 19. DSC thermograms of **58** (A) and poly-**59** (B) (scan rate: 10 °C/min.).



(A)



(B)

Figure 20. Microphotograph of **58** (A), taken at 90 °C, and poly-**59** (B), taken at 101 °C: annealing time, $t_a = 2$ days.

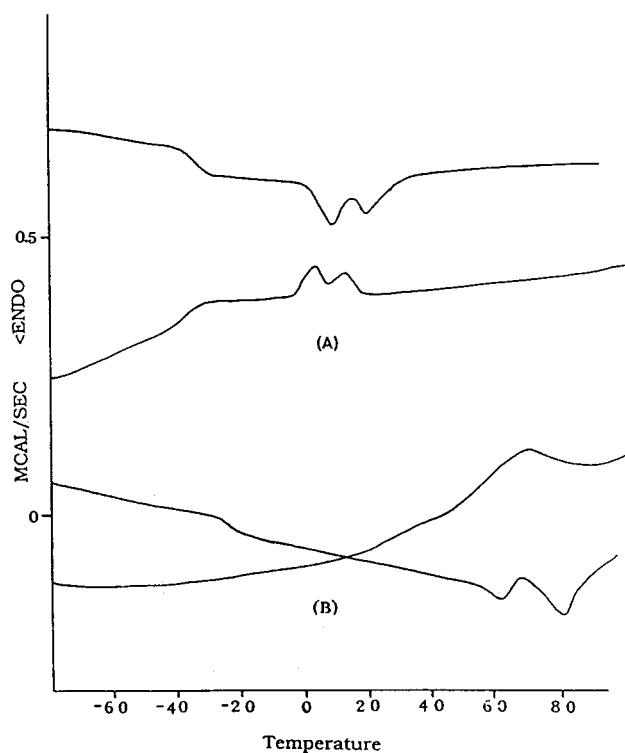
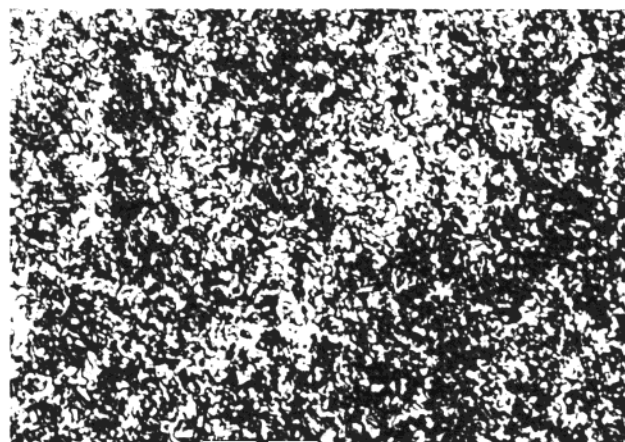
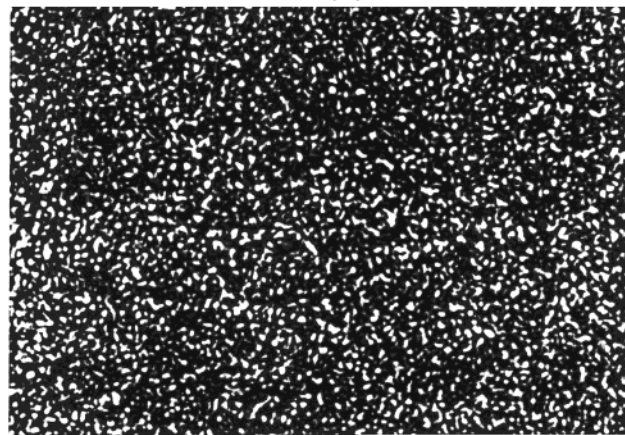


Figure 21. DSC thermograms of **60** (A) and **61** (B) (scan rate: 40 °C/min.).



(A)



(B)

Figure 22. Microphotographs of **60** (A), taken at 11.2 °C, and **61** (B), taken at 75 °C: annealing time, $t_a = 2$ days.

Figure 21 shows the DSC curves obtained from the heating and cooling cycles in Figure 21A for monomer

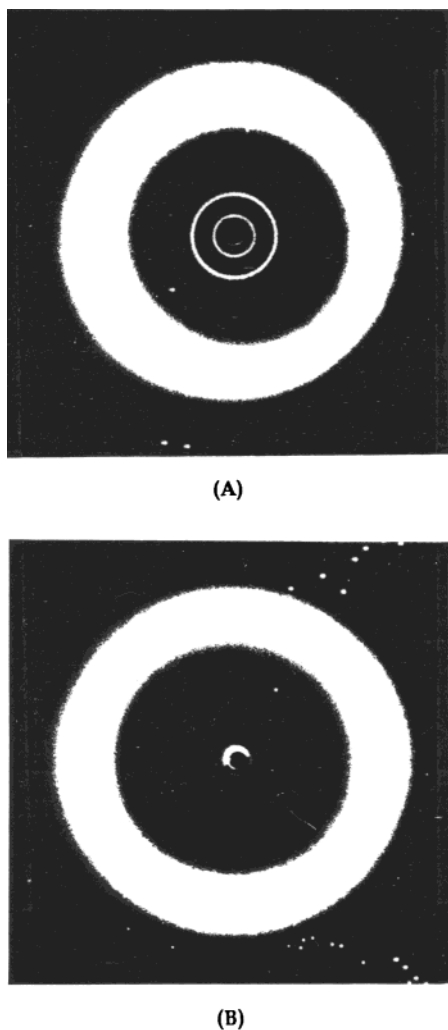


Figure 23. Wide-angle X-ray diffraction diagrams of **59** (A) and poly-**61** (B).

60 and Figure B for poly-**61**. Both **60** and poly-**61** exhibit glass transitions (-33 °C for **60** and -20 °C for **61**) and enantiotropic mesomorphic transitions. The mesophase is found to be in the range of -33 to $+20$ °C for **60** (A) and -20 to $+70$ °C for poly-**61** (B) on heating cycles. In the first cooling curve of poly-**61**, only one broad exotherm is shown at $T = 67$ °C. The peak shown at higher temperature in the DSC thermogram of the poly-**61** could be a first-order melting process with a semirigid backbone. Figure 22 shows the photomicrographs of the liquid crystalline mesophase in poly-**60** (A) and poly-**61** (B), respectively. Figure 22A for poly-**60** which was obtained after cooling from isotropic to 11.2 °C might be a nematic mesophase in **60**.

Figure 22 (B) shows a nematic mesophase in poly-**61**, which was identified in the X-ray analysis as described later. On the other hand, in the case of **62** and poly-**63**, on cooling scan, **62** exhibits glass transition at -30 °C and isotropization temperature at 43 °C. And, on cooling from the isotropic state to the glass transition state, spherulite textures were observed at 40 °C for **62** and at 32 °C for poly-**63**, respectively.

Also, X-ray diffraction studies were carried out to provide detailed morphological information, especially for the structure of liquid crystal polymers and

the layer spacing.²⁹⁰ X-ray diffraction patterns of poly-**59** at 100 °C and poly-**61** at 75 °C are shown in Figure 23. Figure 23A shows the presence of the discrete sharp inner ring, indicating that poly-**59** has the smectic structure. On the other hand, Figure 23B does not show any sharp inner ring, indicating that poly-**61** has the nematic structure. The small-angle diffraction (inner ring) corresponds to the Bragg maximum of $d = 30.7$ Å for poly-**59**. The wide-angle diffraction (outer ring) corresponds to an intermolecular spacing (or the diffuse diffraction) in the layer. These results suggest that the layer spacings correspond to a single-layer packing, on a single side of the main chain. The calculated spacing of a single-layer packing was determined by assuming the extended structure, associated with the planar backbone geometry shown in Figure 24. The difference between the calculated and observed layer spacing is about 28.8 ± 2.1 Å. In addition, the wide halo at wide angle corresponds to an intermolecular spacing (or diffuse diffraction) of 4.52 Å.

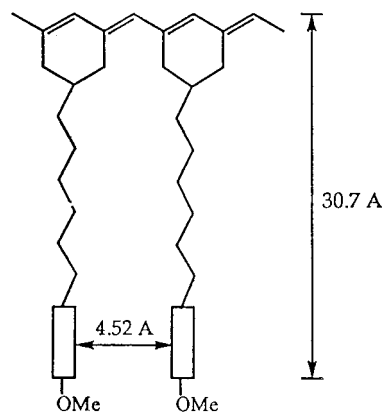


Figure 24. Single-layer packing structure of liquid-crystalline poly-**57** derived from X-ray diffraction.

Figure 25 shows the temperature dependence of electrical conductivity and molecular structure of poly-**59**.²⁸⁵ As evident in this figure, conductivity increases with temperature just as for other conventional nondoped conducting polymers. Above about 70 °C, in particular, the conductivity exhibits a drastic increase with temperature. However, two inflection points are observed at about 90 °C and 110

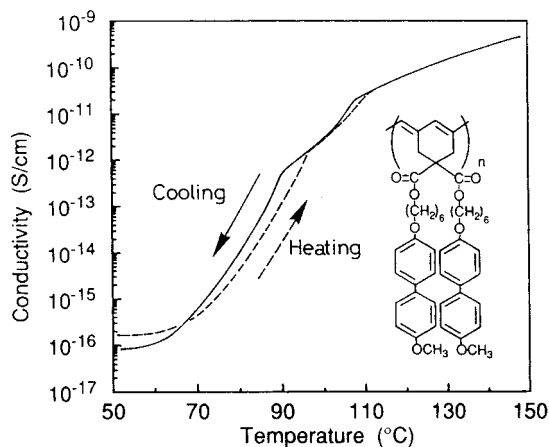


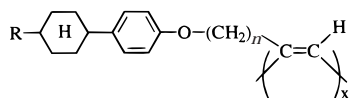
Figure 25. Molecular structure and temperature dependence on conductivity of PMHBDPM (poly-**59**).

°C in the curve of the heating stage. In the decreasing cycle of temperature, the inflections appear at slightly lower temperature, indicating hysteresis in the heating and cooling cycles. These inflection points at about 90 and 110 °C correspond to the phase transition points of poly-59 between solid and isotropic liquid states and also between liquid crystal and isotropic liquid states, which is consistent with the optical microscopic observation. And also, in X-ray diffraction, it was found that diffraction peaks at 20.5 and 24.3° around 90 °C disappeared, which may correspond to the transition between the solid and liquid crystal phases.

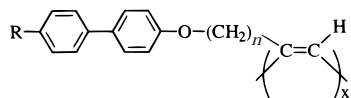
The absorption spectrum of poly-59 film did not change markedly as a function of temperature, contrary to the case of poly(3-alkylthiophene) in which a drastic spectral change with temperature was observed due to the change of effective conjugation length.²⁷⁴ This characteristic indicates that the conformation of the main chain, and therefore effective conjugation length, does not change in poly-59 with temperature. The side chain of this conducting polymeric liquid crystal may not undergo a large conformation change with temperature, or for the twisting of bonds in the main chain, high energy may be necessary, just as in the cases of poly(3-alkylfuran) and poly(9,9-dialkylfluorene).²⁹⁷ On the other hand, in poly(3-alkylthiophene), the trans-gauche conformation change was observed in the side alkyl chain resulting, in the change of the steric hindrance, leading to the twisting of bonds in the main chain and considerable spectral shift. It should also be mentioned that solvatochromism was not observed in poly-59, unlike that in poly(3-alkylthiophene).

Recently, Shirakawa et al. also synthesized mono-substituted acetylenes with liquid crystallinemoieties by Ziegler–Natta and metathesis catalysts (see Chart 2).^{298–301} The polymer prepared were abbreviated as PPCHmOnA, where P = polymer, PCH = phenylcyclohexyl, m = carbon number of alkyl group attached to the cyclohexyl group, O = ether-type oxygen, n = carbon number of methylene unit as a flexible spacer, A = acetylene unit. And in the case of PBP503A, BP means biphenyl.

Chart 2



PPCH001A : R = H, n = 1
 PPCH003A : R = H, n = 3
 PPCH004A : R = H, n = 4
 PPCH303A : R = n-propyl, n = 3
 PPCH503A : R = n-pentyl, n = 3
 PPCH803A : R = n-octyl, n = 3



PBP503A : R = n-pentyl, n = 3

The results of the polymerization for a series of PPCHmOnA by Ziegler–Natta catalysts ($\text{Fe}(\text{acac})_3\text{-AlEt}_3$) are summarized in Table 18. The polymer

Table 18. Polymerization of the Substituted Acetylene by $\text{MoCl}_5\text{-Ph}_4\text{Sn}$ Catalyst^a

polym	yield, ^b %	$M_n/10^4$	$M_w/10^4$	M_w/M_n
PPCH001A	90	1.3	3.1	2.4
PPCH003A	59	1.3	3.0	2.3
PPCH004A	21	1.2	3.0	2.5
PPCH303A	61	1.5	3.4	2.3
PPCH503A	67	1.4	3.3	2.4
PPCH803A	73	1.2	2.7	2.3
PBP503A	85	0.75	6.8	9.1

^a Polymerization was carried out at room temperature for 21 h in toluene: $[\text{Monomer}] = 3 \text{ mmol/L}$; $[\text{MoCl}_5] = 0.01 \text{ mol/L}$; $[\text{Ph}_4\text{Sn}]/[\text{MoCl}_5] = 0.5$. ^b Methanol-insoluble polymer.

yield increases with the length of methylene units as a spacer between acetylene and cyclohexylphenoxy groups in the monomer series of PPCHmOnA ($n = 1, 3, \text{ and } 4$). Also, Table 18 summarizes the results of the polymerization for a series of PPCHmOnA by $\text{MoCl}_5\text{-Ph}_4\text{Sn}$ catalyst. The polymer yield depends upon the number of methylene group in the spacer. The yield decreased with the increasing number of methylene groups, in contrast to the result of polymerization with the $\text{Fe}(\text{acac})_3\text{-AlEt}_3$ catalyst. No methanol-soluble polymer was obtained from the $\text{WCl}_6\text{-Ph}_4\text{Sn}$ catalyst. In the case of 4-phenyl-1-butyne, the $\text{WCl}_6\text{-Ph}_4\text{Sn}$ catalyst gave a polymer with higher molecular weight and a higher yield compared to the $\text{MoCl}_5\text{-Ph}_4\text{Sn}$ catalyst.³⁰² It is noted that the relative activity of polymerization between $\text{WCl}_6\text{-Ph}_4\text{Sn}$ and $\text{MoCl}_5\text{-Ph}_4\text{Sn}$ toward the present monomers is opposite to the case of 4-phenyl-1-butyne monomer. The number-average molecular weight of the present polymers was evaluated to be $(1.2\text{--}1.5) \times 10^4$, independent of both the number of the methylene groups as a spacer and the alkyl groups attached to the cyclohexyl group. The solubility of these polymers is higher (more than 10 vol %) than that of polymers prepared by $\text{Fe}(\text{acac})_3\text{-AlEt}_3$ catalyst, probably due to the lower molecular weights compared to the polymers obtained by Ziegler–Natta catalysts.

The mesomorphic properties of PPCHm03As prepared by $\text{Fe}(\text{acac})_3$ -based and MoCl_5 -based catalysts were examined by differential scanning calorimetry and cross-polarized optical microscopy. In the first heating, the DSC thermograms of PPCH503A and PPCH803A prepared by the $\text{Fe}(\text{acac})_3\text{-AlEt}_3$ catalyst showed large exothermic peaks, corresponding to enthalpy changes of 3.5–3.6 kcal/mol, due to cis to trans thermal isomerization at 167 and 175 °C. And the clearing point of these polymers were found to be around 175–195 °C through the observation of a polarizing microscope. In the second heating, two endothermic peaks corresponding to the crystal–mesophase transition and the clearing point were observed, and the exothermic isomerization peak detected in the first heating disappeared. Upon the first cooling from the isotropic phase of the PPCH503A, two exothermic peaks were observed at 146 °C due to isotropic phase–mesophase transition and at 98 °C due to mesophase–crystal transition (in the case of PPCH803A at 151 and 81 °C, respectively).

Table 19 also summarizes the thermal transition temperature and enthalpies for PPCHm03As prepared by Fe-based and Mo-based catalysts. The

Table 19. Thermal Transition Temperatures and Enthalpies for PPCHm03 As Prepared by Fe(acac)₃-AlCl₃ and MoCl₅-Ph₄Sn Catalysts

cat.	polym	phase transitions (°C) and corresponding enthalpy change, ^a J/g	
		first cooling	second heating
Fe	PPCH303A	i 107 (4.5) S _A 60 (0.7) K	K 70 (0.7) S _A 102 (3.3) i
	PPCH503A	i 146 (6.3) S _A 98 (1.1) K	K 100 (1.3) S _A 128 (6.2) i
	PPCH803A	i 151 (8.2) S _A 81 (3.2) K	K 83 (3.3) S _A 142 (5.8) i
Mo	PPCH303A ^b	i 133 (4.2) S _A	S _A 134 (3.7) i
	PPCH503A ^b	i 160 (6.2) S _A	S _A 160 (4.5) i
	PPCH803A	i 171 (6.7) S _A 86 (3.4) K	K 91 (3.7) S _A 166 (6.4) i

^a Abbreviations: K, crystal; S_A, smectic A; i, isotropic. ^b No distinct DSC peaks associated with the phase transition between the crystalline phase and smectic A phase was observed.

enthalpies and temperatures corresponding to isotropic phase–mesophase transitions increased with the length of the alkyl groups (R), which is due to more stability of Mo-based polymers having trans-rich configurations than Fe-based polymers in the first heating process. In the case of PPCH503A prepared by Fe-based catalyst, upon cooling from the clearing point of 181–188 °C, a smectic A phase with a fan-shaped texture was observed at 130–145 °C and no dramatic change of the texture was visible until room temperature. On reheating the polymer, a mixed phase of mesophase and isotropic phases was observed at 140–174 °C. In the first heating process of PPCH503A prepared by Mo-based catalyst, a smectic A phase appeared at 150–159 °C and changed to an isotropic phase at 163–185 °C. Upon cooling from the clearing point, a smectic A phase with a fan-shaped texture was observed at 165–169 °C. Its domain size is larger than that of the Fe-based PPCH503A. Additionally, both PPCH303As and PPCH803As also showed the fan-shaped texture similar to those of the PPCH503As. Interestingly, it was found that an enantiotropic process for the smectic liquid crystalline phase appearance of the MoCl₅-based polymers contrast to a monotropic process in the Fe(acac)₃-based polymers.

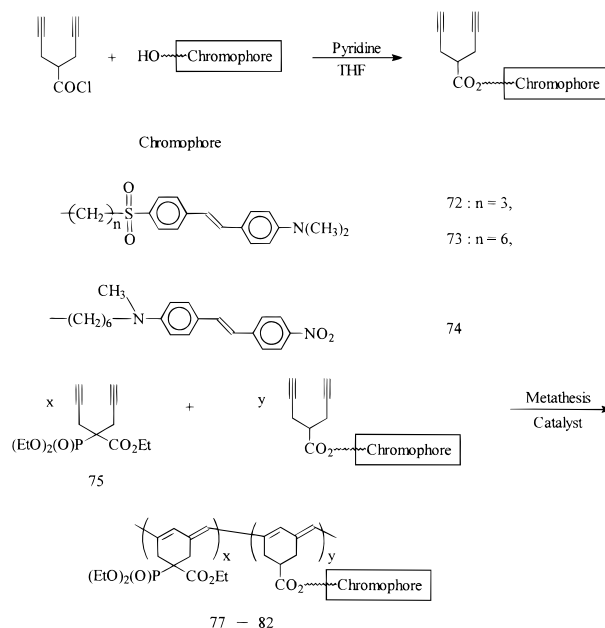
B. Side Chain NLO Poly(1,6-heptadiyne) Derivatives

Nonlinear optical (NLO) materials have been actively studied for such potential optoelectronics application as second harmonic generation (SHG) and third harmonic generation (THG), holography, frequency up and down conversion, electrooptic modulation, and switching.^{303–305} Recently, organic poled polymer systems containing chromophores with large second-order nonlinear susceptibilities have emerged as a promising class of electrooptic materials, because of their fast response time, modification capability, and ease of processing for integrated assembly.³⁰⁶ These polymer materials include doping NLO dyes into amorphous polymer matrices (guest–host systems),³⁰⁷ attaching NLO moieties covalently onto polymer backbone as pendants (side chain systems),^{308,309} incorporating NLO chromophores as part of a polymer main chain (main chain systems),^{300,311} and utilization of sequential synthesis methods (cross-linked systems).³¹²

A number of side-chain NLO polymers have been prepared by various polymerization meth-

ods.^{308,309,313–316} Recently, in our laboratory, a metathesis polymerization technique to synthesize second-order NLO polymers was investigated by the metathesis polymerization of the 1,6-heptadiyne derivatives bearing NLO chromophores. It yielded a type of multifunctional polymers that contain a conjugated backbone and a pedant NLO chromophore for both third- and second-order nonlinear optical materials, respectively. It was the first example of polymers containing second- and third-order susceptibilities.³¹⁷ The monomers were synthesized by reacting the chromophore with dipropargyl acetic acid chloride in the presence of pyridine using THF as a solvent (see Scheme 20).³¹⁸ The chromophore monomers of **72**, **73**, and **74** were homopolymerized or copolymerized with triethyl dipropargyl phosphonate (**75**) to produce NLO-active polymers.³¹⁷ Scheme 20 also outlines the cyclopolymerization of the chromophore monomers by transition metal catalysts such as MoCl₅, WCl₆, and PdCl₂-based catalysts.

Scheme 20

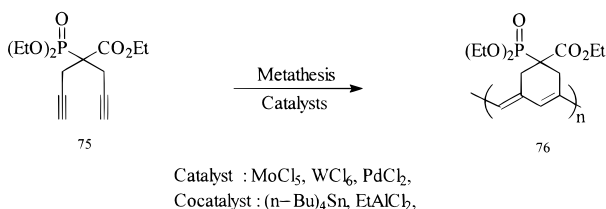


In Table 20, the results for the homopolymerization of the chromophore monomers by various catalyst systems are listed.³¹⁸ Triethyl dipropargyl phosphonate (**75**) was easily polymerized by MoCl₅-based catalysts to give poly-**76** (Scheme 21). Poly-**76** containing a phosphonate group was completely

Table 20. Polymerization of the Chromophore-Containing Monomers with Various Transition Metal Catalysts^a

exp no.	monomer	cat. syst ^b (mole ratio)	M/C ^c	[M] ₀ ^d	polym yield, % ^e
1	72	MoCl ₅	50	0.25	trace
2	72	MoCl ₅ -EtAlCl ₂ (1:4)	50	0.25	40
3	72	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn (1:4)	25	0.25	15
4	72	WCl ₆ -EtAlCl ₂ (1:4)	25	0.25	
5	72	PdCl ₂ ^f	25	0.25	97
6	73	MoCl ₅ -EtAlCl ₂ (1:4)	20	0.125	45
7	73	PdCl ₂ ^f	50	0.25	93
8	74	MoCl ₅ -EtAlCl ₂ (1:4)	20	0.125	
9	74	PdCl ₂ ^f	50	0.25	96

^a Polymerization was carried out at 60 °C for 24 h in dioxane. ^b The mixture of catalyst and cocatalyst in chlorobenzene was aged for 15 min before use as catalyst. ^c Mole ratio of monomer to catalyst. ^d Initial monomer concentration. ^e The precipitated polymers in methanol were gravimetrically estimated. ^f Polymerization was carried out at 90 °C in DMF.

Scheme 21

soluble in common organic solvents and rendered an excellent quality thin film.³¹⁹ Among various catalyst systems, PdCl₂ was found to be a very effective catalyst for the polymerization of chromophore monomers. This result was similarly observed for the polymerization of dipropargyl derivatives having a highly polar functional group reported previously.²⁰⁴ Polymerizations by PdCl₂ gave high polymer yields and soluble polymers in chloroform, but relatively low molecular weight polymers were obtained. The polymerization reaction of chromophore monomers using MoCl₅-based catalyst, however, produced insoluble, and intractable materials. To yield soluble NLO-active polymers, the cyclocopolymerization of the dye bearing monomer **75** was achieved. Synthetic and characterization data for the copolymers are summarized in Table 21. The polymerization of

Table 21. Copolymerization of the Chromophore-Containing Monomers with TDPA **75 by MoCl₅^a**

polym	monomer	<i>m</i> _{feed} ^b	<i>M</i> _{polymer} ^c	polym yield ^d	GPC ^e	
					<i>M</i> _n /10 ⁴	<i>M</i> _w / <i>M</i> _n
76 ^f	75	1/0	1/0	96	4.6	3.2
77	72	70/30	71/29	79	3.6	1.9
78	72	60/40	57/43	78	2.3	2.4
79	73	70/30	62/28	93	2.6	1.8
80	73	50/50	51/49	94	2.8	1.7
81	74	70/30	80/20	74	2.8	1.8
82	74	50/50	62/38	59	1.6	1.7

^a Polymerization was carried out at 60 °C for 24 h in dioxane. The mole ratio of monomer to catalyst was 25. The initial monomer concentration was 0.2 M. ^b The mole ratio of TDPA/monomer. ^c Mole fraction (%) of chromophoric monomer in copolymer by ¹H NMR. ^d The precipitated copolymers in hexane were gravimetrically estimated. ^e Values were obtained by GPC analysis with polystyrene standards. ^f Homopolymer of TDPA.

chromophore monomers having a sulfone group by metathesis catalyst led to the formation of higher polymer yields than those of a nitro group as an electron acceptor. The composition of the copolymers **79–80** closely matched the composition of the monomer feed mixture except for the copolymers **81, 82**, which were lower in the polymers than in the monomer feed composition for the NLO chromophore monomer.

When the concentration chromophore monomer was high, the resulting polymers were partially insoluble. The practical concentration of chromophore monomer was limited up to approximately 50 mol % for the yield of soluble copolymers. The number-average molecular weights (*M*_n) and polymer dispersity values of the resulting polymers were estimated to be in the ranges of (1.6–4.3) × 10⁴ and 1.7–3.2, respectively. All of the stilbene compounds were isolated as pure trans isomers, judged from the values of ¹H NMR coupling constants of the vinyl protons (~16 Hz). Figure 26 shows the ¹H-NMR spectra of poly-**76**, and a copolymers from the monomers of **73** and **75**. As the polymerization proceeded, an acetylenic proton peak at 2.0 ppm disappeared, and new vinylic proton peaks appeared at the region of 6.8–7.2 ppm together with aromatic stilbene peaks. For copolymers, the NLO chromophore ratios were estimated by a comparison of the integration of the phenyl resonance at 7.8 ppm with the methyleneoxy resonance at 4.0 ppm (see in Table 21).

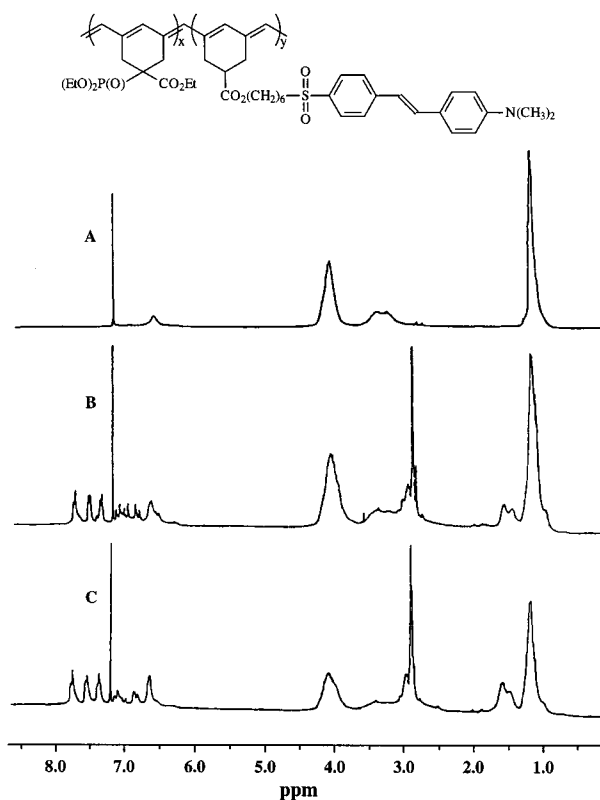
**Figure 26.** ¹H NMR spectra of **76** (A), **79** (B), and **80** (C) in CDCl₃.

Figure 27 shows the FT-IR spectra of monomer **72** and the corresponding polymers. Infrared spectroscopy for all of the polymers shows no absorption at 3285 and 2140 cm⁻¹ which is expected to be present

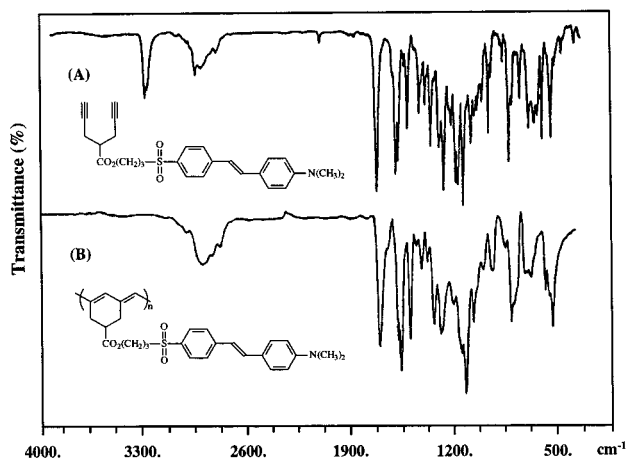


Figure 27. FT-IR spectra of **72** (A) and poly-**77** (B) in KBr pellet.

for the acetylenic carbon–hydrogen stretching and carbon–carbon triple bond stretching of the monomer. The absorbance for the SO_2 unit around 1378 cm^{-1} and the $\text{P}=\text{O}$ unit around 1297 cm^{-1} were detected at the copolymers.

Figure 28 shows the UV–visible spectra of monomer **72**, poly-**76**, and copolymers **77–80**. The monomer spectrum was taken in CHCl_3 , and the polymer spectra were taken in spin-coated films on a quartz substrate. Compound **75** shows the characteristic broad band at 540 nm due to the $\pi-\pi^*$ electronic transition of the conjugated cyclic polyene backbone. Copolymers **77–82** containing a chromophore show two maximum absorption values around 390 and 550 nm due to a pendant chromophore and conjugated cyclic polyene backbone, respectively.

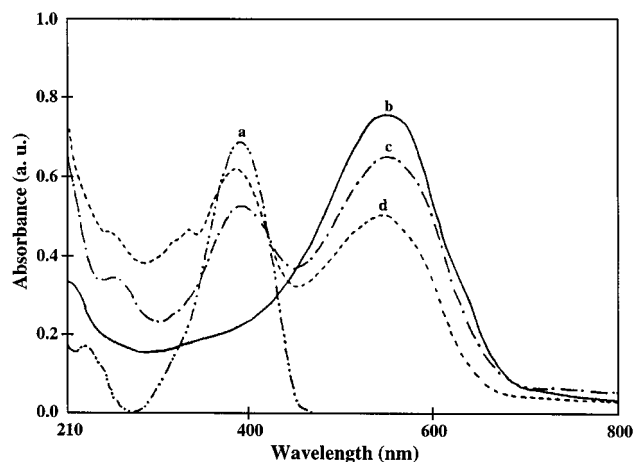


Figure 28. UV–visible spectra of **72** in CHCl_3 solution (a) and **76** (b), poly-**77** (c), and poly-**80** (d) coated films on quartz substrate.

From the above spectral data, the polymer structure is believed to be a linearly cyclized form as described in Scheme 20. Also, it has been known that the resulting cyclized polymers with conjugated double bonds have both five- and six-membered ring structures with a certain ratio, which should depend on the polymerization conditions, monomer structures, and the kinds of catalysts used.^{128,160}

The thermogravimetric analysis (TGA) data of the copolymer exhibits the initial decomposition temper-

Table 22. Linear and Nonlinear Optical Data for Polymers

polym ^a	λ_{max} , nm		n^b ($1.3\ \mu\text{m}$)	V_p^c V/ μm	r_{33}^d , pm/V ($1.3\ \mu\text{m}$)
	NLO-phore	backbone			
76		548	1.584		
77	390	547	1.618	87	1.7
78	389	548	1.633	92	5.2
79	391	549	1.656	120	4.6
80	392	550	1.664	161	10.1
81	461	553	1.665	115	3.2

^a See Table 23. ^b Indices of refraction were determined from waveguiding experiments. ^c Electric field during poling. ^d Electrooptic coefficient.

ature above $250\text{ }^\circ\text{C}$. Copolymer **79** exhibits the most thermal stability among the three, and it started its weight loss at about $300\text{ }^\circ\text{C}$. Unfortunately, the glass transition temperature of the poly(1,6-heptadiyne)s bearing NLO chromophores by the DSC thermogram was not observed clearly. So, it failed to determine the poling temperature. Instead, it was observed that UV–visible spectra of the copolymers did not change upon heating to $100\text{ }^\circ\text{C}$. But, at an elevated temperature of $130\text{ }^\circ\text{C}$, they resulted in a small blue shift and hyperchromic shift of the $\lambda_{\text{max}} = 550\text{ nm}$ due to conformational deformation or air oxidation promoted by heat to the conjugated backbone. These results suggest that these copolymers exhibit conformational stability of at least $100\text{ }^\circ\text{C}$, so the poling process was applied at this temperature on the basis of the UV–visible study. In addition, all of these side chain NLO polymers appeared to be amorphous when examined by polarized optical microscopy and by X-ray diffraction analysis.

The linear and nonlinear optical behaviors of poly(1,6-heptadiyne)s containing NLO chromophores was summarized in Table 22. It was found that n of the copolymers gave higher values than that of poly-**76** not bearing any chromophore while the values of λ_{max} were similar to each other. This result clearly shows the effects of incorporation of chromophore into the polymer backbone. The values of electrooptic coefficients, r_{33} , for poled film samples of poly-**77** to poly-**81** by using a simple reflection technique reported by Teng et al. was measured.³¹⁹ Table 22 shows the measured electrooptic coefficients of polymer films at $1.3\ \mu\text{m}$ at different poling conditions. It was observed that the highest value of r_{33} in them was 10.1 pm/V for poly-**80** poled at $161\text{ V}/\mu\text{m}$. This result also indicates that the orientation of the NLO chromophores in poly-**78** shows no significant relaxation at ambient conditions within 60 days after poling.

The polymers having delocalized π -electron in the main chain have been expected to possess extremely large third-order optical susceptibility.^{320–323} However, such an extended π -electron conjugation generally rendered the polymers insoluble and infusible as well, which has seriously limited the fabrication of practical NLO devices. Recently, it was reported that the third-order nonlinear optical properties of poly(1,6-heptadiyne)s which were environmentally stable, soluble, and processable.³²⁴ The third-order optical nonlinearities of poly(1,6-heptadiyne)s bearing NLO active chromophores were evaluated for the first time. The third-order nonlinear susceptibility ($\chi^{(3)}$)

Table 23. Third-Order Nonlinear Optical Susceptibilities of the Polymers^a

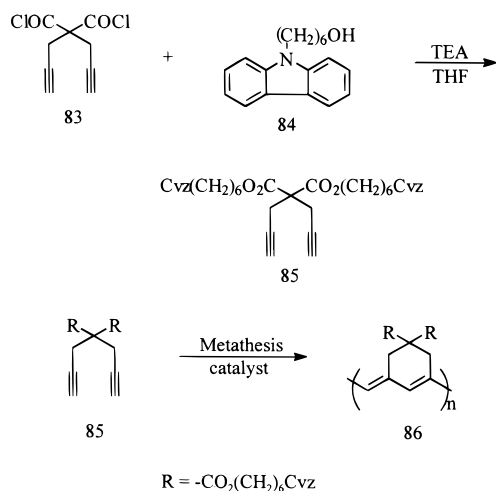
sample	chromophore concn, mol %	$10^{11}\chi^{(3)}$, esu
76	0	3.4
78	45	2.6
79	28	2.1
80	49	2.7
81	20	3.3

^a The third harmonic generation (TGH) measurement was performed using the Maker fringe technique at 1.907 μm .

values of chromophore polymers were measured using the Maker fringe technique at 1.907 μm . The $\chi^{(3)}$ value of the polymer films were calculated by comparing the measured THG peak intensity of the films with that of the standard fused silica substrate according to the equation reported elsewhere.²⁸⁸ It is clear that the $\chi^{(3)}$ values of the poly(1,6-heptadiyne)s bearing chromophore pendant group are in the range of $(2.1\text{--}3.3) \times 10^{-11}$ esu, depending on the chromophore concentration, as shown in Table 23. It indicates that the $\chi^{(3)}$ values are a little affected by incorporating the pendant NLO chromophores, compared with $\chi^{(3)}$ values of poly(1,6-heptadiyne) parents.^{317,319,322}

C. Photoconductive Poly(1,6-heptadiyne)s

Photoconductive polymers containing a carbazole (Cvz) and related groups, e.g. poly(vinyl carbazole)–TNF complex systems, have been of great interest because of their useful applications, especially in the field of photocopiers, laser printers, and electrophotography.^{325,326} In recent years, several attempts^{327,328} have also been focused on the copolymer systems to develop intramolecular charge-transfer complexes, while it was not easy to obtain high molecular weight copolymers with good film qualities. Scheme 22 outlines the synthesis and the cyclopolymerization of the monomer of di[N-(*n*-hexyl)carbazoyldipropargyl malonate](**85**) with various transition metal catalyst systems for a kind of photoconductive polymers based on poly(1,6-heptadiyne)s.²⁷⁹ It was the first example of the homopolymer system with an intramolecular

Scheme 22

Catalyst : MoCl_5 , WCl_6

Cocatalyst : (*n*-Bu)₄Sn, EtAlCl_2

Table 24. Polymerization of Bis(*N*-carbazolyl)-*n*-hexyl Dipropargyl Malonate by MoCl_5 - and WCl_6 -Based Catalysts^a

exp no.	cat. syst (mole ratio)	M/C ^b	polym yield, ^c %	GPC ^d	
				$M_n/10^4$	M_w/M_n
1	MoCl_5	50	90	8.9	3.2
2	MoCl_5 –(<i>n</i> -Bu) ₄ Sn (1:1)	50	95	6.8	2.1
3	MoCl_5 – EtAlCl_2 (1:1)	50	60	3.2	2.5
4	WCl_6 – EtAlCl_2 (1:1)	50	trace	–	–

^a Polymerization was carried out at 60 °C for 24 h in chlorobenzene. $[M]_0$ (initial monomer concentration) = 0.25. ^b Monomer to catalyst mole ratio. ^c Methanol-insoluble polymer. ^d Values were obtained by GPC analysis with polystyrene standards calibration (Waters high-pressure GPC assembly Model M590 pump; μ -Styragel columns of 10^5 , 10^4 , 10^3 , 500, and 100 Å; refractive index detectors, solvent, THF).

charge transfer complex. The monomer of **85** was synthesized by the reaction of dipropargyl malonyl dichloride(**83**) with *N*-(6-hydroxy-*n*-hexyl)carbazole(**84**) in the presence of triethylamine using THF as a solvent.

The polymerizations of the monomer were carried out with MoCl_5 - and WCl_6 -based catalysts, and their results were summarized in Table 24.³²⁹ The catalytic activity of MoCl_5 was found to be greater than that of WCl_6 . (*n*-Bu)₄Sn exhibited better cocatalytic activity than EtAlCl_2 for the polymerization of the monomer. These results are similar to those reported for the polymerization of **5**. The resulting polymers exhibited good solubility in common organic solvents such as chloroform, tetrahydrofuran, and dimethylformamide, etc., and easily spin-coated on glass plates to give violet shiny thin films. In addition, these π -conjugated polymers had surprisingly good stability in air. The number-average molecular weight (M_n) values of the polymers obtained here were in the range of $(3.2\text{--}8.9) \times 10^4$.

Figure 29 exhibits the UV–visible spectra of poly-**86**, including poly-**6**,¹⁶³ and photocurrent values³³³ of

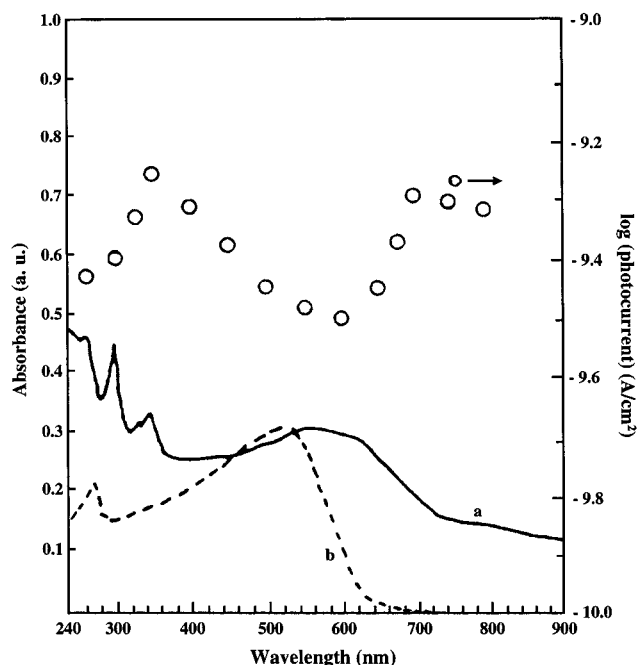


Figure 29. Absorbance and photoconductivity action spectra of the conjugated polymers: (a) poly-**86**, (b) poly-**6**, and (top) photocurrent with wavelength in poly-**86**.

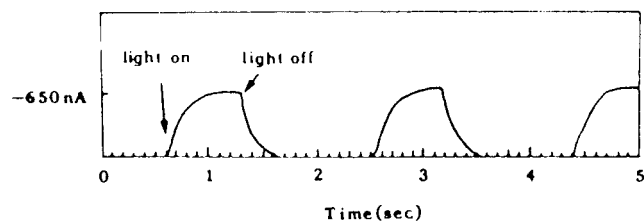


Figure 30. Time-dependent photocurrent response for a ITO/poly-86/Au cell with a Hg–Xe lamp (4.5 mW/cm^2 , OV-bias).

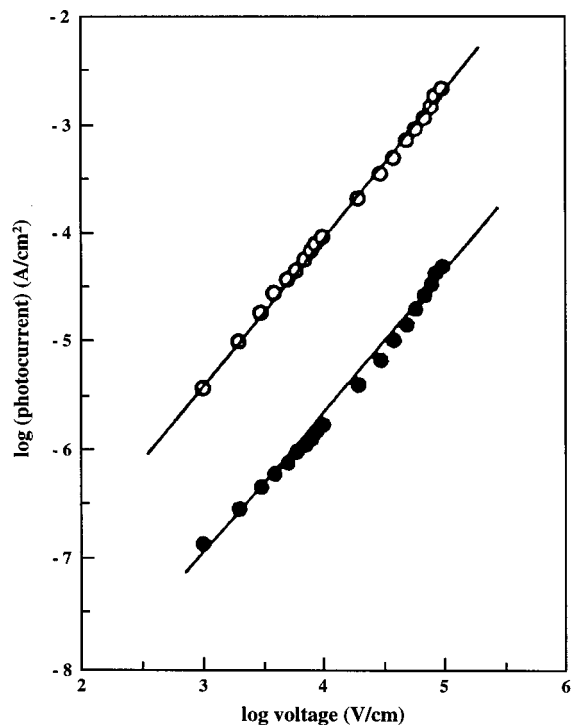


Figure 31. Photocurrent density vs electric field for poly-86.

poly-86 as a function of wavelength. These polymers have the characteristic broad peaks at the longer wavelength regions of above 350 nm, which should be due to the $\pi-\pi^*$ transition of the conjugated polyenes. As compared with poly-6, however, only poly-86 has a long tail band at above 700 nm, suggesting intramolecular charge-transfer complexes between the carbazole groups and the conjugated double bonds in the polymer backbone. Consequently, poly-86 shows two maximum values of photocurrent around 350 and 700 nm. The former value might be due to the carbazole groups. The latter one might be based on the phototrapping in shallow electron traps and charge carrier generation in the charge-transfer band.³³⁰ The photocurrent response curves depending on time by oscilloscope without applying electric field are shown in Figure 30. It was found that under the white light, the polymer had not only a curvature due to trapping and recombination process but also a photovoltaic response -640 nA .³³¹ Relations between the photocurrent density (J_{ph}) and the electric field (E) are shown in Figure 31. The photo- to dark conductivity ratio without a doping agent was found to be in the range of 30–50 at the whole electric field. And it is also shown that the photocurrent value increases in both dark and photo

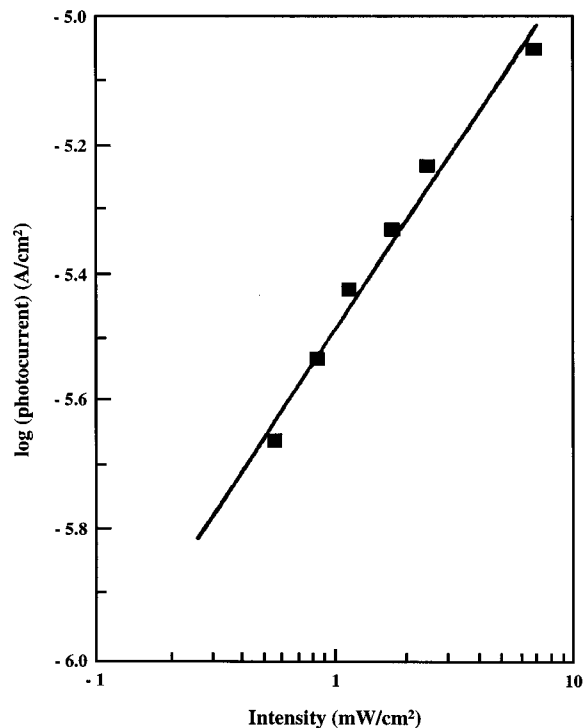


Figure 32. Photocurrent density vs light intensity for poly-86.

states as the electric field (E) increased, and their slopes are greater than 1. This indicates that the space charge perturbed photocurrents are associated with a large population of trapped charge.³³² Figure 32 shows the dependence of the photocurrent density on the light intensity (I). It is almost a linear relationship, and the slope was about 0.5, indicating an equilibrium between free carriers trapped on the charge-transfer complexes.³³³

D. Photorefractive Poly(1,6-heptadiyne)s

Materials exploring a photorefractive effect are main candidates for numerous applications, including high-density optical data storage, optical image processing, phase conjugated mirrors and laser, dynamic holography, optical computing, pattern recognition, etc.^{84,334,335} Photocharges generated in a medium by a spatially modulated light intensity migrate through drift and/or diffusion processes and eventually become trapped, establishing an internal space charge field which, in turn, modulates the material's refractive index via the linear electrooptic effect—the Pockels effects. To manifest the photorefractive effect, the polymer must possess a photocharge generator, a charge transporter, a charge trapping center, and a nonlinear optical chromophore. In an earlier period, most of the initially reported polymeric photorefractive materials fell into one of two following composite systems:³³⁵ (i) second-order nonlinear optical polymers doped with both charge transporters and charge generators, (ii) photoconductive polymers doped with both charge generators and second-order nonlinear optical chromophores. These polymeric composite systems have the merit of ease of preparation. However, they also have some problems such as phase separations and the instability of electrooptical

Table 25. Copolymerization of the Monomer 87 with 88 by MoCl₅

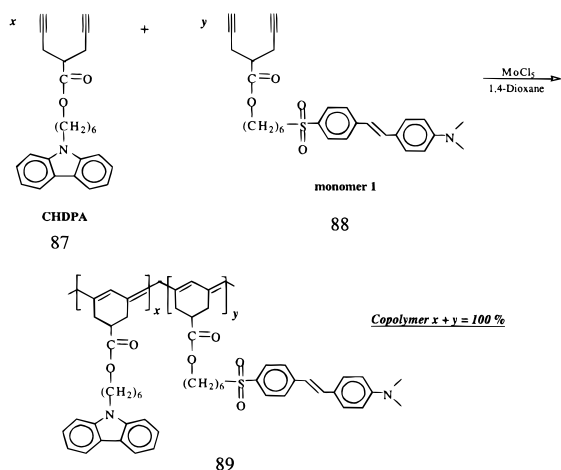
exp no.	mole ratio of 87/88	M/C ^a	[M] ₀ ^b	copolymer yield, %	M _n /10 ³	GPC M _w /M _n
1	100/0	50	0.25	93	45	2.1
2	90/10	30	0.125	90	32	2.5
3	70/30	35	0.125	89	29	2.3
4	50/50	35	0.125	90	23	3.1
5	0/100	25	0.125			

^a Mole ratio of monomer to catalyst. ^b Initial monomer concentration.

activities. To overcome these problems, multifunctional polymers with all of the four functionalities (NLO-chromophore, charge generator, charge transfer, trapping center) covalently attached to the polymer backbone were synthesized. Moreover, the synthetic approach to multifunctional polymers offers further opportunity to explore new structures rationally for the photorefractive effects, while it is difficult in composite systems.

Very recently, the first metathesis reaction was utilized to synthesize a new type of photorefractive polymers, based on poly(1,6-heptadiyne) derivatives, that contain both a carbazole moiety as a hole transporter and NLO chromophores, attached to π -conjugated backbones.³³⁶ Photorefractive polymers based on the previous works for the photoconductivity of poly(1,6-heptadiyne) derivatives containing a carbazole moiety³²⁹ and electrooptic activity of poly(1,6-heptadiyne) derivatives containing NLO chromophores were developed.^{318,319} Herein, all functional groups are covalently linked to the polymer backbone.

Scheme 23 outlines the copolymerization of chromophoric monomer 88 with (*N*-carbazoyl-*n*-hexyl) dipropargyl acetate (CHDPA, 87) by MoCl₅. The

Scheme 23

copolymerization of 87 with 88 by MoCl₅ catalyst gave the copolymer 89 in high yields. In Table 25, the results for the copolymerization are summarized. The molecular weights of the resulting polymers were estimated by gel-permeation chromatography (GPC) to be in the range $M_n = (2.3\text{--}4.5) \times 10^4$, and polydispersities of the resulting polymers were in the range of 2.1–3.1. The maximum content of monomer 88 having a NLO chromophore in copolymer was limited by the solubility of the resulting polymeric

Table 26. Copolymer Composition by ¹H-NMR

monomer feed (calcd) CHDPA 87 (phenyl protons, Ha, of carbazoles)	¹ H NMR data (found) ^a 88 (phenyl protons, H _a , of NLO chromophores)
copolymer I	90/10
copolymer II	70/30
copolymer III	50/50

^a Determined by integration of phenyl protons of carbazoles (H_a, 7.97 ppm) and phenyl protons of NLO chromophores (H_a, 7.67 ppm) (see Scheme 23).

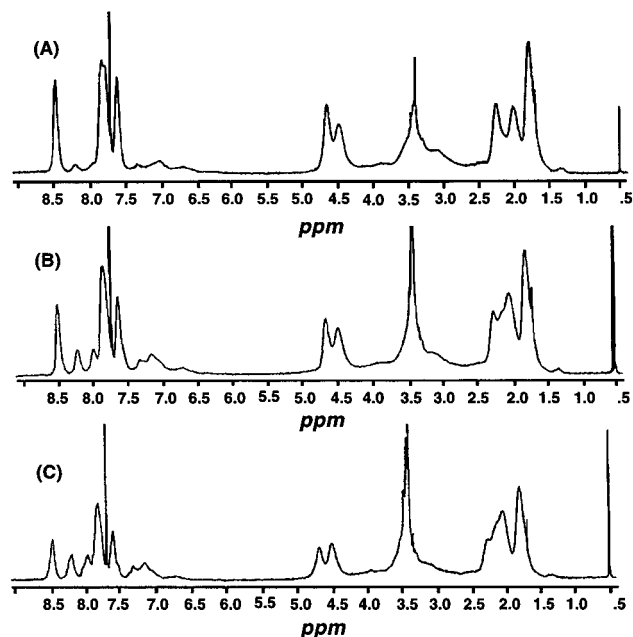


Figure 33. ¹H NMR spectra of 10 mol % copolymer I (A), 30 mol % copolymer II (B), and 50 mol % copolymer III (C) in CDCl₃ (see Table 26).

products. It was due to high polarity of the NLO chromophore, which could act as a deactivator for transition metal catalysts.

The analysis of the resulting copolymers were established by ¹H NMR, infrared and UV–visible spectroscopies. Table 26 shows the copolymerization results by metal catalysts. The ¹H-NMR spectra of both the monomer and the polymer are shown in Figure 33. As the polymerization proceeded, the acetylenic proton peak at around 1.96 ppm disappeared and a new vinylic proton peak appeared in the aromatic region. Also, the IR spectra of the polymer showed no absorption peaks at 3290 and 2140 cm⁻¹, which are expected to be present for the acetylenic carbon–hydrogen bond stretching and carbon–carbon triple bond stretching in the monomer, respectively.

Like homopolymerization of 87, copolymerization of 87 with 88 by using MoCl₅ catalyst proceeded well to give a high yield of a copolymer 89. As the polymerization proceeded, an acetylenic proton peak at 2.0 ppm disappeared and new vinylic proton peaks appeared at the region of 6.2–7.2 ppm together with aromatic stilbene peaks (see Figure 33). NLO-phore contents for copolymers were estimated by the comparison of the integration of the phenyl resonance of carbazole and stilbene, respectively (see Table 26).

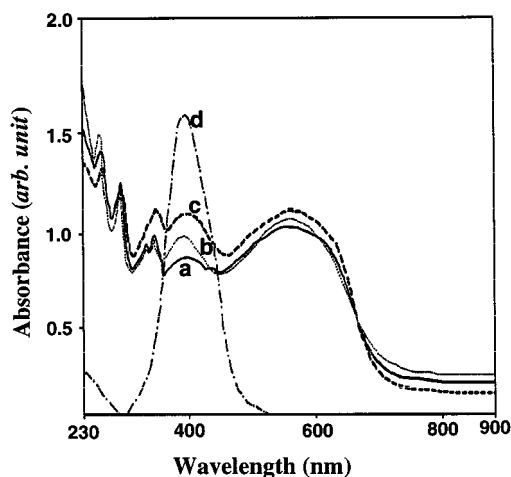


Figure 34. UV-visible spectra of 10 mol % copolymer I (a), 30 mol % copolymer II (b), 50 mol % copolymer III (c), and the monomer (d) in CHCl_3 (see Table 26).

Figure 34 shows the UV-visible spectra of monomer **88** and copolymers. These polymers have a long tail band at above 700 nm, indicating the formation of intramolecular charge-transfer complexes between the carbazole groups and the conjugated double bonds in the polymer backbone. Also, these polymers show two maximum values of photocurrent around 350 and 700 nm. The former one might be due to the carbazole groups and the latter might be based on the phototrapping in shallow electron traps and charge carrier generation in the charge-transfer band.

The thermal stability of the resulting polymers was evaluated by thermogravimetric analysis under a nitrogen atmosphere. The initial decomposition temperature of poly-**87** exhibited near 303 °C (scanning rate = 10 °C/min. in N_2), while one of the copolymers decreases according to the mole ratio increase of monomer **88**.

The intensity of DFWM (degenerate four-wave mixing) signal for the poly(CHDPA) increased linearly with the intensity of the incident beam. From the direct comparison between the intercepts of the Y axis of the poly(CHDPA) and the carbon disulfide reference, the $\chi^{(3)}$ values of the polymers were obtained. The hyperpolarizabilities, $\langle \gamma \rangle$, of the poly(CHDPA) were obtained at the incident wavelength of 1.907 μm . And, the electrooptic coefficient, r_{33} , of the poled polymer films measured by the simple reflection technique at the wavelength of 1.3 μm were in the range of 10.1 pm/V. In present, the photorefractive properties of the polymer are being studied by the four-wave mixing (FWM) and two-beam coupling (2BC) techniques.

VI. Conclusions and Perspectives

This review dealt with the recent studies on design, synthesis, characterization, and functionalization of poly(1,6-heptadiyne)-based materials as a new class of conjugated polymers. 1,6-Heptadiyne, a nonconjugated diyne, is a very simple monomer and very susceptible to cyclopolymerization via an intramolecular-intermolecular chain propagation to give conjugated polymers having cyclic recurring units.

However, poly(1,6-heptadiyne)s were insoluble in any organic solvents and unstable with air oxidation, regardless of the catalysts and polymerization conditions used. Introduction of substituent on the methylene carbon at the 4-position of 1,6-heptadiyne solved the predescribed problems of poly(1,6-heptadiyne) such as the insolubility and the facile oxidation to air.

In the cyclopolymerization of 1,6-heptadiynes carrying heteroatoms such as oxygen and nitrogen, the MoCl_5 -based catalyst systems were found to be more effective than those of WCl_6 -based catalyst systems. Especially, monomer **5** was polymerized by the MoCl_5 -(*n*-Bu) $_4$ Sn catalyst system to give high yield and high molecular weight. And high oxidation state alkylidene molybdenum complexes also effectively polymerize DEDPM in a living manner to give a low polydispersity. This polymer was found to be easily film-castable and considered a candidate for electronic materials. Various poly(1,6-heptadiyne)s having functionalities such as self-dopable ionic, side-chain liquid crystalline, nonlinear optical, photoconductive, and photorefractive functionalities were designed and synthesized.

Poly(1,6-heptadiyne)s having bulky substituents revealed excellent oxidative stability in air relative to polyacetylene and poly(1,6-heptadiyne). This stability of the conjugated polymer backbone to air oxidation is thought to be due to the effective shielding of the highly conjugated backbone by the bulky substituents. These findings are particularly important in synthetic polyene chemistry, since they can offer the possibility of obtaining polyacetylenes processing stability and processibility. The effect of size and type of substituents upon the fine and conformational structure and unusual optical absorption behavior for the poly(1,6-heptadiyne)s was found to be very important factor.

The preparation of π -conjugated cyclopolymers based on poly(1,6-heptadiyne)s is a challenging task as evidenced by the fact that the synthesis of the most famous member of this class of polymeric materials is possible by molecular design. And the number of polymer chemists and physicists and material scientists who are interested in poly(1,6-heptadiyne)-related materials is increasing. Some further challenges remain for the future: exploitation of more active catalysts, polymerization mechanism, and microstructure, functionalization showing special property, and applications.

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