



Review

Poly(1,6-heptadiyne)-based functional materials by metathesis polymerization

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Abstract

Poly(1,6-heptadiyne)-based polyacetylenes as a new class of π -conjugated polymer were designed and prepared. In general, the Mo-based catalysts were found to be very effective for the cyclopolymerization of 1,6-heptadiyne and its derivatives with various substituents, whereas the W-based catalysts gave only a low yield of polymers for the same polymerization. The chemical structures of the resulting poly(1,6-heptadiyne)s were characterized by various instrumental methods such as NMR, IR, UV-visible spectroscopies and elemental analysis to have the conjugated polymer backbone systems with functional substituents. The microstructures of poly(1,6-heptadiyne) homologues were found to be dependant on the catalysts, the polymerization conditions, the size of substituents, etc. Poly(1,6-heptadiyne) derivatives having bulky substituents revealed excellent oxidative stability in air relative to polyacetylene and poly(1,6-heptadiyne). The examples of poly(1,6-heptadiyne)s having such peculiar functionalities as side-chain liquid crystalline, nonlinear optical, photoconductive, photorefractive, and self-dopable ionic groups were presented.

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Keywords: Polyacetylene; Poly(1,6-heptadiyne); Cyclopolymerization; Conjugated polymers; Metathesis catalyst

1. Introduction

Acetylene triple bonds have rich π -electrons, which can be used to polymerize to yield the linear conjugated polymer systems. The conjugated polymers have been extensively studied because of their unique properties on the basis of the π -conjugation through alternating double bonds on the main chain [1–9].

Among the π -conjugated polymers, polyacetylene (PA) is the simplest conjugated polymer. However, it was difficult for application because PA is insoluble, infusible, and unstable to air oxidation [10,11]. In order to overcome these problems of PA itself, various substituents are introduced into the conjugated backbone [1–6]. 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 [2–5].

Polymerization of substituted acetylenes has been carried out by a wide range of catalysts and conditions [1,2,5]. The monosubstituted acetylene that has most often been employed to study polymerization is probably phenylacetylene. In 1974, Masuda et al. [12] found that phenylacetylene is effectively polymerized by WCl_6 and $MoCl_5$ catalyst, which had been used for the olefin metathesis reactions and the metathesis polymerization of cycloolefins [13,14]. Since then, there have been many studies on the polymerization of phenylacetylene and related acetylene compounds using W- and Mo-based catalyst systems [15].

We have also prepared various substituted polyacetylenes via the polymerization of the corresponding acetylenic monomers with the same catalysts [16–18]. The living polymerizations of substituted acetylenes have also been performed by using Schrock carbenes [19], tantalum catalysts [20], rhodium complexes [21], and $MoCl_4$ -based catalysts [22,23].

1,6-Heptadiyne and its homologues are very interesting examples of substituted acetylenes, which can be susceptible to the ring-forming polymerization (cyclopolymerization) to give a new type of conjugated polymer backbone system [24]. In contrast to simple mono- and

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di-substituted 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. Gibson et al. [25] reported a free-standing film with metallic luster by the polymerization of 1,6-heptadiyne on the surfaces of concentrated solutions of Ziegler-type homogeneous catalyst derived from $\text{Ti}(\text{OC}_4\text{H}_9-n)_4$ and $\text{Al}(\text{C}_2\text{H}_5)_3$, using a specifically designed reactor. However, the resulting poly(1,6-heptadiyne)s, besides low molecular weight of oligomers, were insoluble in organic solvents and very susceptible to air oxidation, regardless of the catalysts used and the polymerization conditions [26].

Introduction of substituent to the methylene carbon at the 4-position of 1,6-heptadiyne solved the predescribed problems of poly(1,6-heptadiyne) and expanded the research areas of π -conjugated polymers. The polymerizations of various 1,6-heptadiynes having substituents have been carried out by Mo- and W-based catalysts [3–5,27–29].

In the present article, we report the results on the preparation of various poly(1,6-heptadiyne)-based conjugated polymers and the properties of the resulting poly(1,6-heptadiyne)s.

2. Experimental

2.1. Materials

The synthesis of cyclopolymerizable diacetylenic monomers were prepared according to the literature procedures [4,5,30]. 1,6-Heptadiyne (Farchan Laboratories) was dried with CaH_2 and distilled. Some dipropargyl monomers such as diphenyldipropargylmethane, dipropargylsilanes, dipropargylgermaniums, etc. were prepared by the Grignard reaction of propargylmagnesium bromide and the corresponding dichloro compounds [30]. Diethyl dipropargylmalonate (DEDPM) was prepared by the reaction of propargyl bromide and the sodium ethoxide solution of diethyl malonate [31]. Some functional dipropargyl monomers were synthesized by reacting various alcoholic functional groups with dipropargylmalonyl chloride or dipropargylacetyl chloride in the presence of triethylamine or pyridine using THF as solvent [4]. Dialkyldipropargylammonium bromide was obtained from the reaction of dialkylpropargylamine and propargyl bromide [32]. MoCl_5 (Aldrich Chemicals, 99.99%+), Cp_2MoCl_2 (Aldrich Chemicals, 98%), WCl_6 (Aldrich Chemicals, 99.99%+), PdCl_2 (Aldrich Chemicals, 99.995%), PtCl_2 (Strem), RuCl_3 (Aldrich Chemicals), and EtAlCl_2 (Aldrich Chemicals, 25 wt.% solution in toluene) were used without further purification. $\text{Mo}(\text{CO})_6$ (Aldrich Chemicals) was sublimed prior to use. The solvents were analytical grade materials. They were dried with an appropriate drying agent and fractionally distilled.

2.2. Polymerization

All procedures for catalyst solution preparation and polymerization were carried out under nitrogen atmosphere. MoCl_5 , MoCl_4 , WCl_6 , and organoaluminium compounds were dissolved in the reaction solvent as 0.1 or 0.2 M solution before use. A typical polymerization procedure is as follows; solvent, catalyst solution, and cocatalyst solution (in case of need) are injected into a polymerization reactor equipped with a rubber septum in the order given. When a cocatalyst was used, these catalyst systems were aged at 30 °C for 15 min. Finally, monomer in each solvent was injected into the polymerization reactor. After the given polymerization time, the polymerization was terminated by adding a small amount of methanol. The resulting polymer was dissolved in chloroform followed by precipitation with a large excess of methanol. The precipitated polymer was filtered from the solution and dried under vacuum at 40 °C for 24 h. The polymer yield was calculated by gravimetry.

2.3. Instruments and measurement

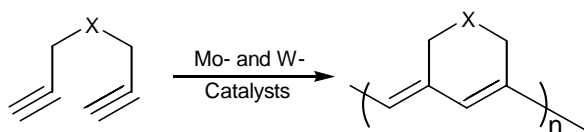
FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet, and frequencies are given in reciprocal centimeters. NMR (^1H and ^{13}C) spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA). Magic angle spinning, cross polarization ^{13}C NMR spectra of insoluble polymer were recorded on a Varian Infinity Plus 200 spectrometer (3-s repetition time, 5-ms cross polarization mixing time, and 6-kHz spinning). Elemental analyses were performed with FISONS EA1110 Elemental Analyzer. UV-visible spectra of polymer solution were taken on a Shimadzu UV-3100S spectrophotometer. The molecular weight and polydispersity were determined in THF solvent by a Waters GPC-150C calibrated with polystyrene standards. The electrical conductivity was measured by the four-point probe method. X-ray diffractograms were measured with a PHILIPS X-ray diffractometer (Model: X'Pert-APD). The polymer morphology was studied by scanning electron microscopy (ISI-SX-30E). TGA and DSC thermograms were obtained under a nitrogen atmosphere at a heating rate of 10 °C/min up to 700 °C with thermal analyzer of rheometric.

3. Results and discussion

3.1. Polymerization behaviors

The cyclopolymerization of 1,6-heptadiyne derivatives were performed by various transition metal catalysts (Scheme 1).

We mostly used the Mo- and W-based catalysts, which have been known to be very effective for the polymerization of substituted acetylenes [2–5]. The polymerization of 1,6-heptadiyne itself by MoCl_5 in chlorobenzene



[X = O, S, SO, SO₂, SiR₂, GeR₂, N⁺R₂, CH₂, C(CO₂Et)₂, CR₂ (R = mesogenic, NLO, photoconductive groups)]

Scheme 1. Cyclopolymerization of dipropargyl monomers.

proceeded well to give a quantitative yield of polymer [33]. The W-based catalysts showed lower catalytic activity in this polymerization (polymer yield = 11%). The polymer yields were slightly increased when such cocatalyst as EtAlCl₂ and Ph₄Sn are used. The resulting poly(1,6-heptadiyne) was mostly insoluble in organic solvents although the polymerization solution seems to be homogeneous during the polymerization in some cases.

It was also found that the catalytic activity of Mo-based catalysts are greater than those of W-based catalysts in the cyclopolymerization of some dipropargyl monomers such as DEDPM, diphenyldipropargylmethane, dipropargylfluorene, 4,4-bis(*tert*-butyldimethyl siloxy)-methyl-1,6-heptadiyne, etc.

Table 1 shows the results for the polymerization of DEDPM by various transition metal catalysts. The polymerization of DEDPM by MoCl₅ alone in 1,4-dioxane was well-proceeded to give a high yield of polymer which can be easily casted into a uniform thin film. In the polymerization of some substituted acetylenes containing oxygen atom, high catalytic activity of MoCl₅-based catalysts were generally known, which is originated from the self-activation of Mo-catalysts by the oxygen of monomer [34,35]. Mo(CO)₆ and Cp₂MoCl₂ catalyst systems were also found to be effective for this cyclopolymerization of DEDPM. The Mo-based catalysts were also found to be effective for the polymerization of dipropargyl derivatives containing heteroatoms.

High oxidation state alkylidene molybdenum complexes such as Mo(CHCMe₂R)(*N*-2,6-C₆H₃-*i*-Pr₂)(OCMe₂CF₃)₂ and Mo(CHCMe₂R)(*N*-2,6-C₆H₃-*i*-Pr₂)(*O*-*t*-Bu)₂, which were frequently used for the ring-opening metathesis poly-

merization of 2,3-difunctionalized-7-oxanorbornenes and 7-oxanorborn dienes [36,37] to give a polymer with narrow molecular distributions ($M_w/M_n = 1.17$), were also found to be effective for the cyclopolymerization of DEDPM. DEDPM 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 ($M_w/M_n = 1.25$), soluble polyene of a known type that contains a mixture of five- and six-membered moieties [38].

The cyclopolymerization of dipropargyl monomers carrying an ionic nature is a facile synthesis method for self-dopable conjugated ionic polymers. Various dipropargyl quaternary ammonium salts were polymerized to yield the unusual ionic conjugated polymers. The potential counterions are ionically bound to the polymer. Dihexyldipropargylammonium salts (counterion = Br⁻, *p*-CH₃C₆H₄SO₃⁻) were firstly polymerized to give the corresponding conjugated polymers in high yields. The cyclopolymerization of 2-ethynyl-*N*-propargylpyridinium bromide having two different acetylene functionalities (acetylenic and propargyl) yielded an interesting conjugated polymer with cumulated pyridyl moieties. This polymerization proceeded well by the catalysts of PdCl₂, PtCl₂, and RuCl₃ to give a quantitative yield of polymer.

Double ring forming polymerization (DRFP) of triacetylenic compounds such as 1,4-dipropargyloxy-2-butyne (DPOB) and tripropargylammonium salts were also performed. In the polymerization of DPOB, the Mo-based catalysts were also found to be very effective to give a quantitative yield of polymer. The polymerization by MoCl₅ associated with cocatalysts gives slightly lower yields than that of MoCl₅ alone. The resulting poly(DPOB) were mostly insoluble in organic solvents as like with poly(dipropargyl ether). The polymerization of tripropargylammonium salts by MoCl₅-EtAlCl₂, WCl₆-EtAlCl₂, PdCl₂, etc. proceeded well to give a relatively high yield of polymers (Scheme 2).

The functional conjugated polymers were also synthesized by the cyclopolymerization of dipropargyl monomers with such function groups as side chain liquid crystalline, photoconductive, photorefractive, and nonlinear optical groups. The polymer yields by MoCl₅-based catalysts were

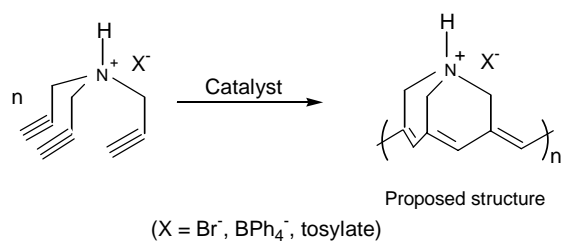
Table 1
Cyclopolymerization of diethyl dipropargylmalonate (DEDPM) by Mo- and W-based catalysts

Experiment number	Catalyst system ^a	Solvent	Polymer yield (%) ^b	M_n^c
1	MoCl ₅	1,4-Dioxane	91	97,000
2	MoCl ₅	Chlorobenzene	89	92,000
3	MoCl ₅ -(<i>n</i> -Bu) ₄ Sn	1,4-Dioxane	95	127,000
4	WCl ₆	1,4-Dioxane	12	–
5	WCl ₆ -(<i>n</i> -Bu) ₄ Sn	1,4-Dioxane	15	–
6	Mo(CO) ₆	1,4-Dioxane	94	110,000
7	Mo(CO) ₆	CCl ₄	70	73,000
8	Cp ₂ MoCl ₂ -EtAlCl ₂	Chlorobenzene	98	27,000

^a Mixture of catalyst and cocatalyst was aged at 30 °C for 15 min before use.

^b Methanol-insoluble polymer yield.

^c Determined by GPC with polystyrene standards.



Scheme 2. Double ring forming polymerization of tripropargyl monomers.

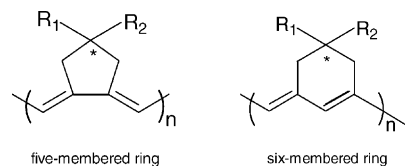
mostly quantitative, regardless of the bulkiness of functional substituents.

The cyclopolymerization mechanism of 1,6-heptadiyne derivatives was not clearly elucidated, although the polymerization using transition metal catalysts has been investigated over the past four 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. It was reported that the “alkylidene mechanism” for the living polymerization of 2-butyne [39] and acetylene itself [40] was operative in two systems that contained well-defined alkylidene complexes. And the controlled living polymerization of 1,6-heptadiynes by the well-defined Mo(CHCMe₂Ph)(NAr)[OR_{F6}]₂ [Ar = 2, 6-*i*-Pr₂C₆H₃, OR_{F6} = OMe(CF₃)₂] [38] and the MoOCl₄-Bu₄Sn-EtOH catalyst systems [28] were also reported.

3.2. Polymer structure

The polymer structures of the resulting conjugated polymers were characterized by ¹H NMR, infrared, and UV-visible spectroscopies and elemental analysis. The FT-IR spectrum of the poly(1,6-heptadiyne) did not show the acetylenic C≡C bond stretching (2118 cm⁻¹) and acetylenic ≡C-H bond stretching (3294 cm⁻¹) frequencies. Instead, the C=C stretching frequency peak of conjugated polymer backbone at 1604 cm⁻¹ was newly observed. Because of the insolubility of poly(1,6-heptadiyne), we measured the solid-state ¹³C NMR spectrum of poly(1,6-heptadiyne). This spectrum of poly(1,6-heptadiyne) did not exhibit any acetylenic carbon peaks, which was seen at 68.84 and 82.61 ppm in the ¹³C NMR spectrum of 1,6-heptadiyne. Instead, it showed the new vinyl carbon peaks of conjugated polymer backbone of poly(1,6-heptadiyne) at 110–150 ppm. It also showed two broad peaks due to the methylene carbons adjacent to the conjugated double bonds and the methylene protons of 4-position at 50–95 ppm and 10–43 ppm, respectively. The UV-visible spectrum of thin solid poly(1,6-heptadiyne) film (obtained from the casting of homogeneous polymer solution) showed the characteristic broad absorption peak at the visible region, which is originated from π → π* conjugation band transition of the polyene main chain.

Fig. 1 shows the ¹H NMR spectrum of a typical poly(DEDPM) prepared by Cp₂MoCl₂-EtAlCl₂ catalyst system. The peaks at 5.6–7.2 ppm are due to the vinyl protons of conjugated polymer backbone. The peaks at 2.6–3.6 ppm and 4.2 ppm are due to the methylene protons adjacent to the conjugated carbons and the methylene protons of ethyl groups, respectively. Fig. 2 shows the ¹³C NMR spectrum of the poly(DEDPM) in CDCl₃. This spectrum did not show any acetylenic carbon peaks, which were seen at 72.9 and 79.6 ppm in the ¹³C NMR spectrum of DEDPM. Instead, the vinyl carbon peaks of polymer backbone appeared recently at 123 and 136 ppm. More information on the microstructure of poly(DEDPM) can be obtained from the resonance of the quaternary carbon atoms [38]. It was known that the two clusters of resonance for the quaternary carbons in poly(DEDPM) can be assigned to the quaternary carbons in the five-membered rings (57–58 ppm), and in the six-membered rings (54–55 ppm), respectively [38].



From these viewpoints and Fig. 2, it was concluded the poly(DEDPM) prepared by Cp₂MoCl₂-EtAlCl₂ catalyst system was consisted with a mixture of five- and six-membered ring moieties, and the content of five-membered ring moiety was higher than that of six-membered ring moiety.

It has been also reported that the conjugated 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 [38]. 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 [41]. In general, the ratio of the five-membered rings to the six-membered rings was increased as the size and number of substituents at the 4-position of 1,6-heptadiynes increase. In particular, the five-membered polymer was only produced when an extremely bulky substituent such as the *tert*-butyldiphenylsiloxymethyl group was introduced at the 4-position of 1,6-heptadiyne. And also, Mo(CO)₆-catalyzed cyclopolymerization of DEDPM in 1,4-dioxane at 100 °C to gave exclusively a polyene containing only five-membered rings [42].

3.3. Polymer functions and properties

Poly(1,6-heptadiyne) itself was insoluble in any organic solvents as like with polyacetylene. The introduction of substituents at poly(1,6-heptadiyne) structure made the polymers to be soluble in organic solvents and provide the oxidative stability. In most cases, the poly(1,6-heptadiyne)s

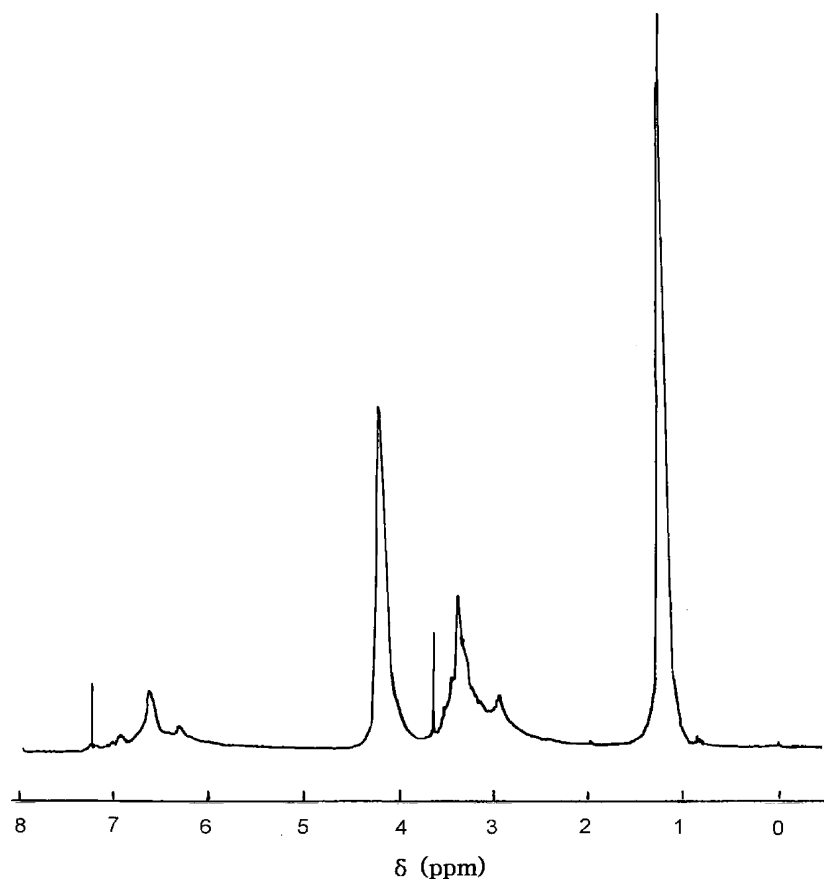


Fig. 1. ^1H NMR spectrum of a poly(DEDPM) prepared by Cp_2MoCl_2 – EtAlCl_2 catalyst system (in CDCl_3).

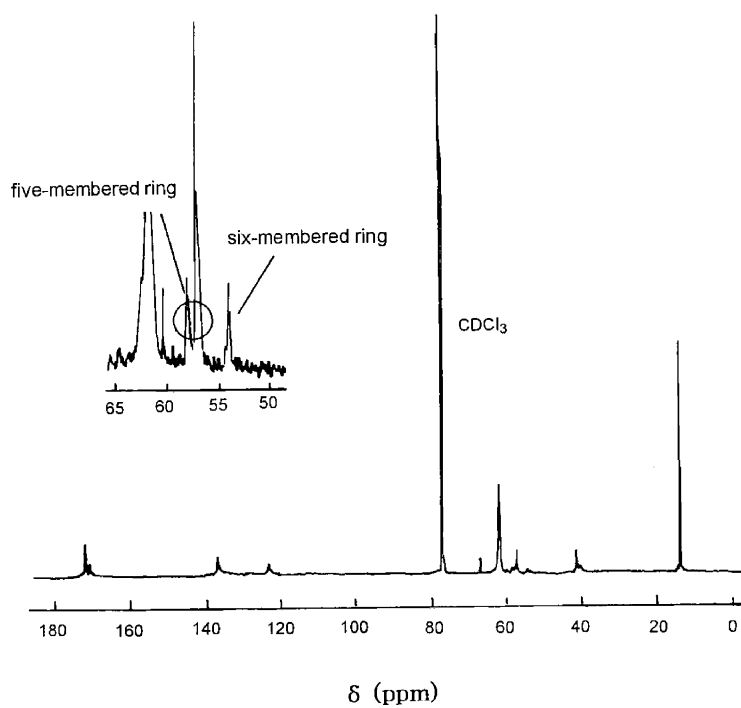


Fig. 2. ^{13}C NMR spectrum of a poly(DEDPM) prepared by Cp_2MoCl_2 – EtAlCl_2 catalyst system (in CDCl_3).

having substituents were soluble and easily solution castable [3–5]. Poly(1,6-heptadiyne)s having substituents were found to be generally stable to air oxidation, whereas the poly(1,6-heptadiyne) itself was very susceptible to air oxidation, reducing the π -conjugation.

Poly(1,6-heptadiyne) is distinct from polyacetylene in its morphology. Polyacetylene is highly porous, being comprised of fibrils of diameter 100–800 Å [43], and has an apparent density of about 0.4 g/cm³ [25]. 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 [25]. Poly(diphenyldipropargylmethane) presents a fibrillar morphology [44]. 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(diphenyldipropargylmethane) morphology is similar to that of polyacetylene with the fibers, generally having diameters of 200–500 Å [32]. 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 [32].

The electrical conductivity of poly(1,6-heptadiyne) with iodine-doping changes by a factor of 10^{10} from 10^{-12} to $10^{-2} \Omega^{-1} \text{cm}^{-1}$ 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), poly(dipropargyl sulfide), poly(dipropargylsilane)s, and poly(diphenyldipropargylmethane) [5]. 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 electrochemical properties of poly(1,6-heptadiyne)s have also been studied. The electrochemical measurements of poly(bis(*N*-carbazoyl)-*n*-hexyldipropargyl malonate) (PBCHDPM) films were performed in a 0.1 M tetrabutylammonium perchlorate ((TBA)ClO₄)/acetonitrile solution. 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 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 [45,46].

In order 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 were synthesized and characterized [3]. Second-order NLO polymers were also prepared 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 pendant NLO chromophore for both third- and second-order nonlinear optical materials, respectively.

The metathesis polymerization reaction was also applied 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. Photorefractive polymers based on the previous works for the photoconductivity of poly(1,6-heptadiyne) derivatives containing a carbazole moiety and electro-optical activity of poly(1,6-heptadiyne) derivatives containing NLO chromophores were also developed. Herein, all functional groups are covalently linked to the polymer backbone [47].

4. Conclusions

In this article, we presented the research results on the synthesis and properties of poly(1,6-heptadiyne)-based conjugated cyclopolymers with various functional substituents. The cyclopolymerization of 1,6-heptadiynes by Mo-based catalysts proceeded well to give a high yield of polymer. Poly(1,6-heptadiyne) derivatives 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. The effect of size and type of substituents upon the fine and conformational structure and the unusual optical absorption behaviors was found to be very important factor. Various poly(1,6-heptadiyne)s having functional groups such as side-chain liquid crystalline, nonlinear optical, photoconductive, self-dopable ionic, and photorefractive functionalities were designed and prepared.

Acknowledgements

The authors thank Prof. Won-Chul Lee, Dr. Hyun-Nam Cho, Dr. Mun-Sam Ryoo, Dr. Yun-Hi Kim, Dr. Sung-Ho Han, Prof. Jong-Wook Park, Dr. Sang-Jun Choi, Dr. Hyung-Jong Lee, Dr. Sung-Hyun Kim, Prof. Ji-Hoon Lee, and Dr. Sang-Seob Lee for their helpful advice and encouragement.

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