Cyclopolymerization of Diphenyldipropargylmethane by Transition-Metal Catalysts

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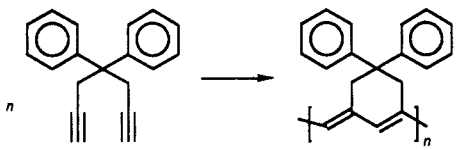
ABSTRACT: The polymerization of diphenyldipropargylmethane was carried out with various transition-metal catalysts. It was found that the $MoCl_5$- and WCl_6-based catalyst systems are very effective for the cyclopolymerization. The characterization of poly(diphenyldipropargylmethane) was carried out by IR, ^1H NMR, ^{13}C NMR, Raman, and UV–visible spectroscopies. The resulting polymer has a conjugated polyene backbone containing a six-membered cyclic structure. Poly(diphenyldipropargylmethane) was a dark violet solid of high molecular weight [$\bar{M}_n = (1–8) \times 10^4$], soluble in aromatic hydrocarbons, some ethers, and some ketones. The resulting polymer possesses excellent thermal and oxidative stability in air. In morphology studies of poly(diphenyldipropargylmethane), the fibrillar structure with a 200–300-Å-diameter range was observed by scanning electron microscopy. The electrical conductivity and the magnetic properties of the resulting polymer upon doping were changed and these changes were studied by morphology, IR, UV–visible, and ESR spectra.

Introduction

There have been many studies on polymerization of various substituted acetylenes by transition-metal catalysts.[1] Recently, the cyclopolymerization of terminal diacetylenes was attempted by preparing polyene through alternating double and single bonds, resulting in substituted polyacetylene.[2,3] In 1983, Gibson et al. reported the synthesis of cyclic polyene, poly(1,6-heptadiyne), by cyclopolymerization of 1,6-heptadiyne using Ziegler–Natta catalyst,[3,4] but the resulting polymer was insoluble in organic solvents and it was more readily oxidized than *trans*-polyacetylene in air. In our previous work, it was found that $MoCl_5$- and WCl_6-based catalyst systems are very effective for the cyclopolymerization of dipropargyl ether,[2a] dipropargyl sulfide,[2b] and dipropargylsilanes.[2c]

This paper deals with the cyclopolymerization of diphenyldipropargylmethane (DPDPM) by transition-metal catalysts and the characterization of the product polymer. We also studied the thermal and oxidative stability, morphology, electrical properties, and magnetic properties of the resulting polymer.



Experimental Section

The monomer, diphenyldipropargylmethane (DPDPM), was prepared according to the following reaction procedure by Grignard reaction: yield 45%; needlelike crystals; mp 89 °C; bp 110 °C (0.5 mmHg); ^1H NMR ($CDCl_3$) δ 7.2–7.4 (10 H, s), 3.2 (4 H, d), 2.0 (2 H, t); IR (KBr pellet, cm^{-1}) 3300, 3030, 2970–2870, 2150, 1600–1450.

Other Materials. Tungsten(VI) and molybdenum(V) chloride (Aldrich Chemical Co., resublimed 99%) were used without further purification. Palladium(II) chloride (Aldrich Chemical Co.) was used without further purification, and tetrabutyltin was distilled under reduced pressure. Organoaluminum compounds (Aldrich Chemical Co.) were used without further purification. All solvents used were analytical-grade materials.

Polymerization. All procedures for catalyst system preparation and polymerization were carried out under dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in the polymerization solvent before use as 0.05, 0.2, or 0.4 M solutions. A typical polymerization procedure is as follows: A monomer solution was prepared by mixing DPDPM and each solvent. To this monomer solution is injected the catalyst system [catalyst and cocatalyst (on the basis of need)]. When cocatalyst was used, these catalyst systems were aged at 30 °C for 15 min to reduce WCl_6 and $MoCl_5$. After the mixture stood at 60 °C for 24 h, the polymerization was stopped by adding a mixture (3 mL) of methanol and chloroform (1:4 volume ratio). Then, the polymerization mixture was dissolved in chloroform followed by precipitation with excess methanol. The precipitated polymer was filtered from the solution and dried to a constant weight under vacuum at 40 °C for 24 h. The polymer yield was calculated by gravimetry.

Instruments for Characterization. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian T-60A spectrometer and a Bruker AM-200 spectrometer. Infrared spectra were taken on a Perkin-Elmer 283B spectrometer with a potassium bromide pellet. UV–visible spectra were obtained with a Cary 17 spectrometer. Thermogravimetric analyses (TGA) was performed in a nitrogen atmosphere at a heating rate of 10 °C/min with a 1090 analyzer. Thermal transitions were measured with a Du Pont 910 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10 °C/min. The number-average molecular weight of the polymer was determined in THF solution by a Waters GPC-150C with a calibration curve for polystyrene. Elemental analysis was carried out with a 240C elemental analyzer. The Raman spectrum was obtained with a 0.85-m double spectrometer SPEX with an Ar^+ laser source for 488.0-nm excitation and 140-mW laser power. The morphology of resulting polymers was studied by scanning electron microscopy (ISI-SX-30E). The X-ray diffractogram was measured by an X-ray diffractometer with Cu Kα radiation at a scan speed of 4°/min.

Doping and Electrical Conductivity. Rectangular pellets of the resulting polymer were made by exerting 15 000 lb of pressure with a Perkin-Elmer Cver laboratory press. Pressed pellets of the polymer were doped by exposure to the vapor of iodine under atmospheric pressure. The doping levels were determined by the weight uptake method. Electrical conductivity was measured by four-point probe DC method with a Keithley electrometer 642, Keithley nanovoltmeter 181, Keithley digital multimeter 195A, and Keithley programmable current source 220.

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Table I
Polymerization of Diphenyldipropargylmethane by Various Catalyst Systems[a]

exp no.	catalyst system[b] (mole ratio)	polymer yield, %	M_n	color[d]
1	$MoCl_5$	100	84 000	d-v
2	$MoCl_5$–$EtAlCl_2$ (1:2)	76	43 000	d-v
3	$MoCl_5$–$EtAlCl_2$ (1:4)	50		d-v
4	$MoCl_5$–Et_2AlCl (1:2)	67		d-v
5	$MoCl_5$–$(n\text{-}Bu)_4Sn$ (1:2)	53		d-v
6	WCl_6	23		d-b
7	WCl_6–$EtAlCl_2$ (1:4)	84	20 000	d-b
8	WCl_6–$EtAlCl_2$ (1:4)	62		d-b
9	WCl_6–Et_2AlCl (1:2)	77		d-b
10	WCl_6–$(n\text{-}Bu)_4Sn$ (1:2)	78		d-b
11	$PdCl_2$[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 catalyst. [c] Polymerization was carried out for 24 h at 90 °C in *N,N*-dimethylformamide. The initial monomer concentration ($[M]_0$) and the monomer to catalyst mole ratio (M/C) were 0.25 M and 100, respectively. [d] Color: d-v, dark violet; d-b, dark brown; r-b, red-brown.

Table II
Solvent Effect in the Polymerization of Diphenyldipropargylmethane[a]

exp no.	solvent	polymer yield, %
1	benzene	60
2	toluene	78
3	chlorobenzene	76
4	chloroform	88
5	tetrahydrofuran	7
6	*N,N*-dimethylformamide	0

[a] Polymerization was carried out by $MoCl_5$–$EtAlCl_2$ (1:2) at 60 °C for 24 h. The monomer to catalyst mole ratio (M/C) and initial monomer concentration ($[M]_0$) were 100 and 0.25 M, respectively.

Magnetic Properties. ESR experiments were conducted with a Varian E-line EPR spectrometer at a frequency of 9.5 GHz. The relative spin density could be directly obtained by integration of the resonance curve. The spin density was calculated by using standard material, powder coal (pitch) diluted with KCl (g = 2.0028, 3×10^{15} spins/cm). DPPH (α,α'-diphenyl-β-picrylhydrazyl) was used as a reference (apparent g factor = 2.0036) for the g factor and magnetic field calibrations.

Results and Discussion

Polymerization of Diphenyldipropargylmethane (DPDPM) by Various Catalyst Systems. Table I shows results for the cyclopolymerization of DPDPM by various transition-metal catalysts. $MoCl_5$ polymerized DPDPM more effectively than WCl_6 alone. The catalytic activity of $MoCl_5$ was somewhat decreased by using cocatalyst, whereas catalyst activity of WCl_6 was increased by using cocatalysts such as $EtAlCl_2$, Et_2AlCl, and $(n\text{-}Bu)_4Sn$. The same results were found in the cyclopolymerization of dipropargyl ether,[2a] dipropargyl sulfide,[2b] and dipropargylsilanes.[2c] It is found that a high mole ratio of catalyst to cocatalyst gives poor polymer yield. Therefore, the appropriate ratio is selected for the polymerization. The solvent effect on the polymerization of DPDPM was also investigated (Table II). DPDPM was easily polymerized in aromatic hydrocarbons and chloroform. They are good solvents for not only the catalyst but also the resulting polymer. On the other hand, DPDPM was not, or hardly, polymerized in *N,N*-dimethylformamide and tetrahydrofuran. In Figure 1, the time dependence of polymer yield for the polymerization of DPDPM is shown. The polymerization of WCl_6–$EtAlCl_2$ (1:2) proceeded rapidly within 2 h to the extent of 85%, whereas in the case of using $MoCl_5$–$EtAlCl_2$ (1:2), the polymerization proceeded slowly.

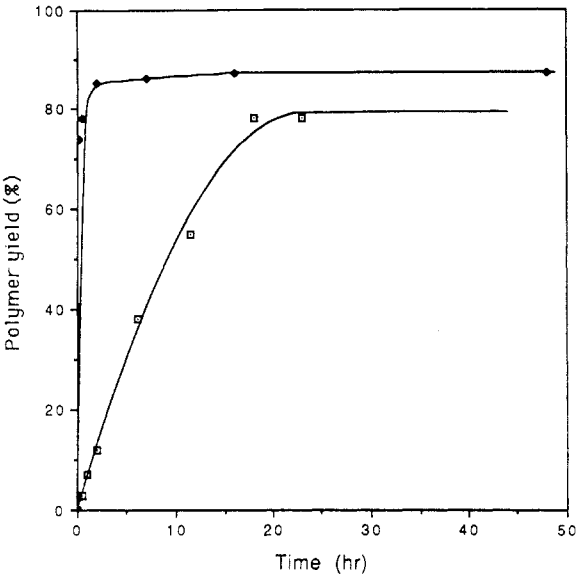

Figure 1. Time dependence curve for the polymerization of diphenyldipropargylmethane by WCl_6–$EtAlCl_2$ (1:1) (●) and $MoCl_5$–$EtAlCl_2$ (1:1) (□).

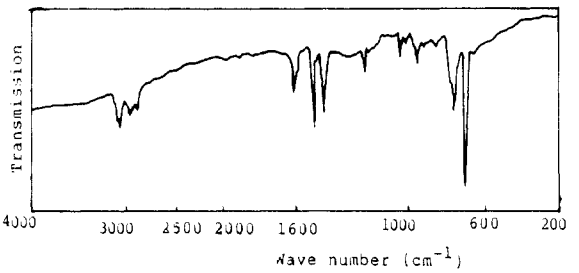

Figure 2. IR spectrum of poly(diphenyldipropargylmethane) in KBr pellet.

When 1,6-heptadiyne was polymerized (in the conditions $[M]_0$ = 0.5, M/C = 30, 24 h, 60 °C) by using $MoCl_5$–$EtAlCl_2$ (1:2), the obtained polymer was insoluble and polymer yield was 56%. However, DPDPM gave quantitative yield of 100% under the same polymerization conditions ($[M]_0$ = 0.5, M/C = 30, 24 h, 60 °C), and the obtained polymer was soluble. This result is explained by the substituent effect,[2a,5] which is the probability of cyclopolymerization enhanced by bulky substituents at the 4-position.

Polymer Structure. The result of elemental analysis [C, 93.1; H, 6.2) for poly(DPDPM) agrees well with the theoretical value (C, 93.4; H, 6.6). In the ^1H NMR spectrum, the vinylic protons of poly(DPDPM) broadly appeared at 6.2–7.4 ppm with the aromatic protons and the allylic protons of poly(DPDPM) at 2.8–4.0 ppm. Figure 2 shows the results of the IR spectrum of poly(DPDPM). The poly(DPDPM) shows neither the acetylenic hydrogen (3300 cm^{-1}) nor the carbon–carbon triple-bond stretching band (2150 cm^{-1}), which are shown in the IR spectrum of the monomer, DPDPM. Figure 3 exhibited the ^{13}C NMR of DPDPM and poly(DPDPM). The DPDPM, gave the acetylenic carbon peaks at 73 and 82 ppm. On the other hand, poly(DPDPM) did not show these peaks. Instead, the carbon peaks of the polyene backbone appeared at about 140 ppm in poly(DPDPM). The peak of methylene carbon adjacent to the polyene backbone shifted from 30 to 52 ppm on polymerization. The UV–visible spectra of poly(DPDPM) were obtained

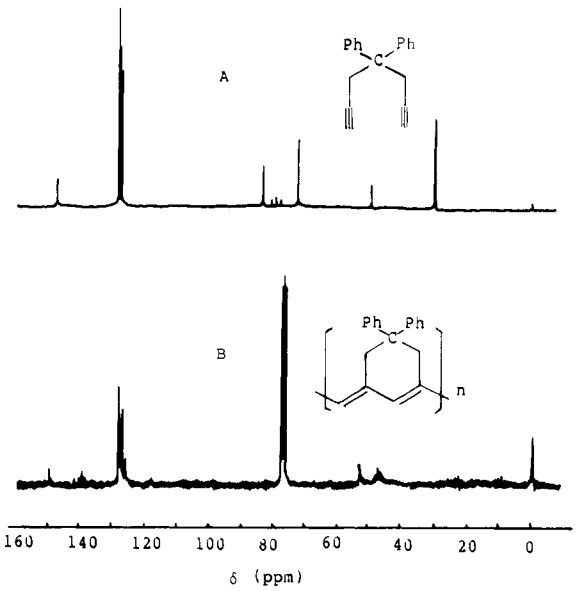

Figure 3. ^{13}C NMR spectra of diphenyldipropargylmethane (A) and poly(diphenyldipropargylmethane) (B) in $CDCl_3$.

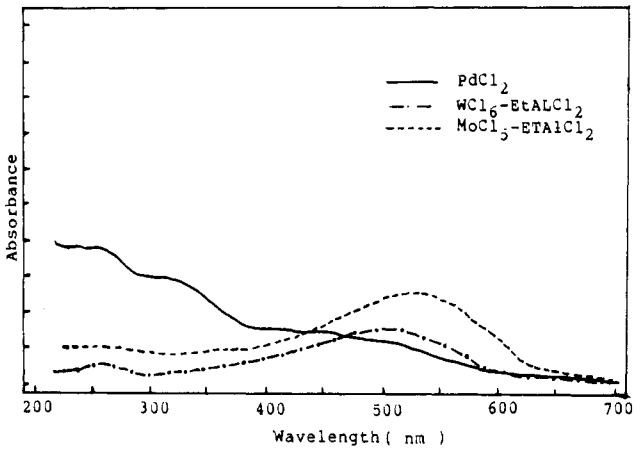

Figure 4. UV-visible spectra of poly(diphenyldipropargylmethane).

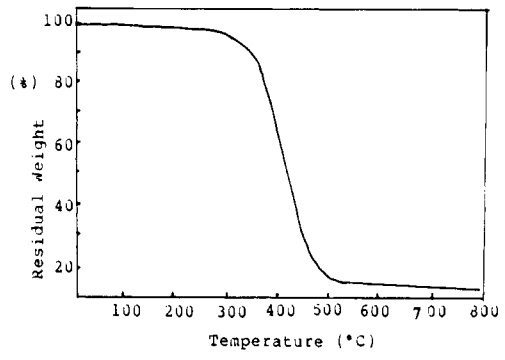

Figure 5. TGA thermogram of poly(diphenyldipropargylmethane).

in 1,2-dichloroethane (Figure 4). A broad $\pi \rightarrow \pi^*$ absorption appeared at the visible region, and it extends to the 700 nm. The maximum observed for various catalyst systems increased in the the following order; $PdCl_2$ (λ_{max} 310; ϵ 2900) < WCl_6 (λ_{max} 500; ϵ 3800) < $MoCl_5$ (λ_{max} 530; ϵ 4000).

Polymer Properties. The TGA thermogram of poly(DPDPM) is shown in Figure 5. It retains 95% of its weight at 320 °C, 90% at 350 °C, and 15% at 600 °C. The DSC curve of poly(DPDPM) shows two irreversible exothermic processes at 160 and 240 °C (Figure 6). The

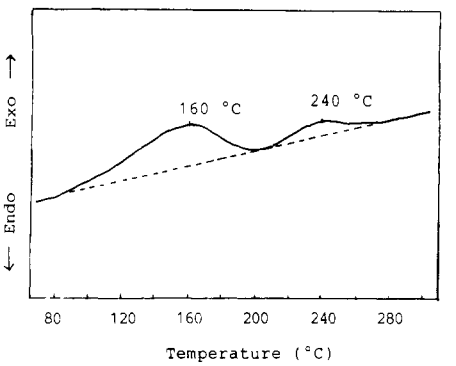

Figure 6. DSC curve of poly(diphenyldipropargylmethane).

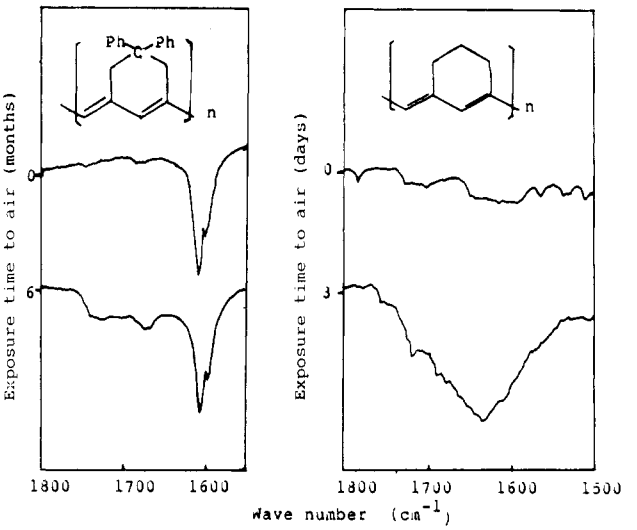

Figure 7. IR spectra for oxidation stability to air at room temperature of poly(diphenyldipropargylmethane) and poly(1,6-heptadiyne).

polymer consists of a mixture of two structures; the helical and the planar structures. The first thermal process at 160 °C proves this fact, and it is attributed to the exo double-bond rearrangement from a helical structure to a nearly planar polyene backbone configuration.[3] The next thermal process at 240 °C arises from the loss of the backbone configuration. The polymer is converted from dark violet to reddish brown during the last process. This process involves the rearrangement from exocyclic to endocyclic double bonds, proton migration, cross-linking, and bond scissoring.[6] It is found that the X-ray diffractogram of poly(DPDPM) films did not exhibit crystallinity. These results are caused by the presence of bulky substituents.

As to the solubility behavior of poly(DPDPM), it is completely soluble in aromatic hydrocarbons (benzene, toluene, xylene), halogenated hydrocarbons (CCl_4, $CHCl_3$, CH_2Cl_2, chlorobenzene), some ethers (anisole, tetrahydrofuran), and some ketones (acetophenone). However, it is not soluble in ethyl ether, aliphatic hydrocarbons, and alcohols.

Oxidative Stability. Polyacetylene[7] and poly(1,6-heptadiyne)[3,8,9] are easily oxidized in air at room temperature. On the other hand, poly(DPDPM) has excellent oxidative stability in air. The air oxidation of the polymer was studied by IR spectroscopy (Figure 7). The IR spectrum of poly(1,6-heptadiyne), which had been standing at room temperature exposed to air for 3 days, showed a new carbonyl absorption band at 1650 cm^{-1}. In the case of poly(DPDPM), it was not until it had stood for 6 months that a band of the carbonyl group appeared at 1650 cm^{-1}.

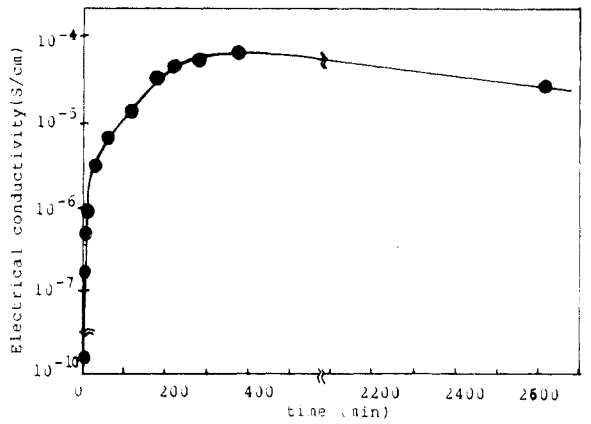

Figure 8. Conductivity of a poly(diphenyldipropargylmethane) pellet as a function of exposure time to iodine at 25 °C under nitrogen.

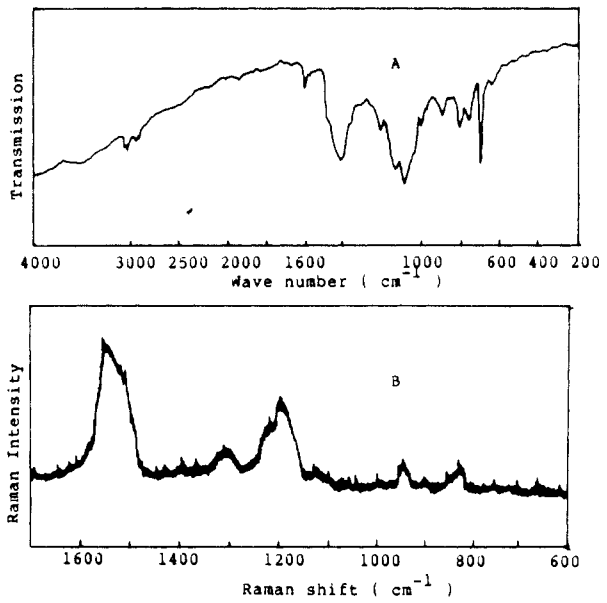

Figure 9. IR spectrum of iodine-doped poly(diphenyldipropargylmethane) (A) and Raman spectrum of undoped poly(diphenyldipropargylmethane) (B).

Electrical Properties. The electrical conductivity of a poly(DPDPM) pellet as a function of exposure time is displayed in Figure 8. In 5 h, the poly(DPDPM) pellet exhibited a maximum in the conductivity and then began to decrease slowly. This decrease could be the result of iodination chemistry causing loss of conjugation. When the film-type polymer was exposed to iodine vapor, it changed from dark violet to blue-black and the electrical conductivity increased from 10^{-10} to 10^{-4} S 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} S cm^{-1}.[3] The steric interaction of the phenyl group in poly(DPDPM) brings about a more twisted backbone. Therefore, the poly(DPDPM) lacks planar conjugation of the backbone and results in the loss of electrical conductivity. The activation energy for conduction is determined from the conductivity dependence on temperature. For the undoped poly(DPDPM), the activation energy is found to have a value of 12–13 kcal/mol, which is comparable to that of polyacetylene (11 kcal/mol) and poly(1,6-heptadiyne (12.2 kcal/mol).[3] The doped film of poly(DPDPM) has a value of only 3.5 kcal/mol.

Figure 9 shows the IR spectrum of poly(DPDPM) after iodine doping and the Raman spectrum of undoped

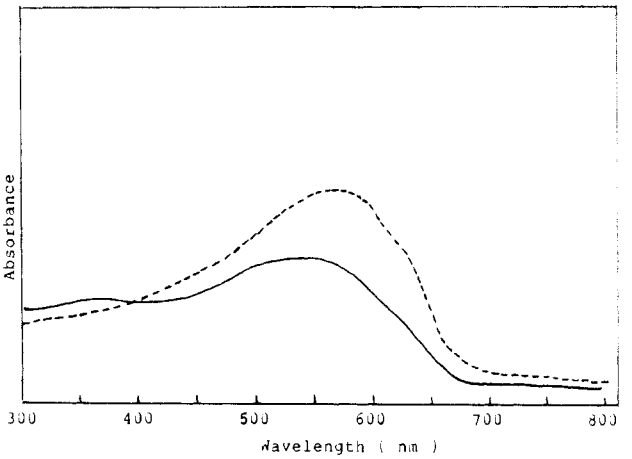

Figure 10. UV–visible spectra of undoped poly(diphenyldipropargylmethane) (—) and I_2-doped poly(diphenyldipropargylmethane) (- - -).

polymer. The Raman spectrum of undoped poly(DPDPM), excited with 488.0-nm radiation, showed several broad bands. Among them, especially, the stretching mode of a conjugated double bond at 1550 cm^{-1} and the coupling mode of the CH in-plane bending and C–C stretching appeared at 1200 cm^{-1}.[10-12] Doping induces two broad bands at 1420 and 1100 cm^{-1} in the IR spectrum. These two IR bands correspond to the Raman bands of undoped poly(DPDPM). Their frequencies are shifted to the lower frequencies because the band is weakened when electrons transfer from the polymer chain to the dopant.[13] These two modes become IR active upon doping because of their coupling with charge oscillation in the backbone.

In the UV–visible spectrum, λ_{max} of the $\pi \rightarrow \pi^*$ transition for the undoped poly(DPDPM) appeared at 530 nm, whereas the same band for the doped poly(DPDPM) appeared at 570 nm (Figure 10). The I_2-doped sample shows the broad absorption that is due to the charge-transfer band at 600–800 nm.[14] The partial localization of electrons along the polyene chain by the steric interaction of phenyl substituent brings about a somewhat hypsochromic shift in the λ_{max} of the $\pi \rightarrow \pi^*$ transition in comparison with polyacetylene (653 nm)[14] and poly(1,6-heptadiyne) (620 nm).[3]

Morphology. Figure 11 exhibits the morphological structure of poly(DPDPM) gained through scanning electron microscopy (SEM). The films were cast from chloroform and washed with methanol. The resulting polymer presents fibrillar morphology. The dull side of the film (facing toward air) is very porous with identifiable fibrils. The shiny side of the film (facing the glass wall) is very smooth with the fibrils matted. The fibrils range from 200 to 300 Å in diameter. The poly(DPDPM) morphology is similar to that of polyacetylene with the fibers generally having diameters of 200–500 Å.[15] On doping with iodine, an increase in fibrillar diameter to 400 Å is observed.

Magnetic Properties. The doping process was monitored by electron spin resonance (ESR) spectroscopy. The spin density of undoped poly(DPDPM) is 10^{18} spins/g, and the line width (H_{pp}) is 33 G at $g = 2.0011$. Figure 12 represents changes of the relative spin population and the line width as a function of iodine exposure time in situ. The line width of 33 G narrows to a sharp intense band of only 9 G upon doping. The poly(DPDPM) has a significantly larger H_{pp} than that of polyacetylene. It is explained by the following: the probability that the radicals are placed in the trapped state[16] is increased because poly(DPDPM) has a more twisted backbone due to the bulky

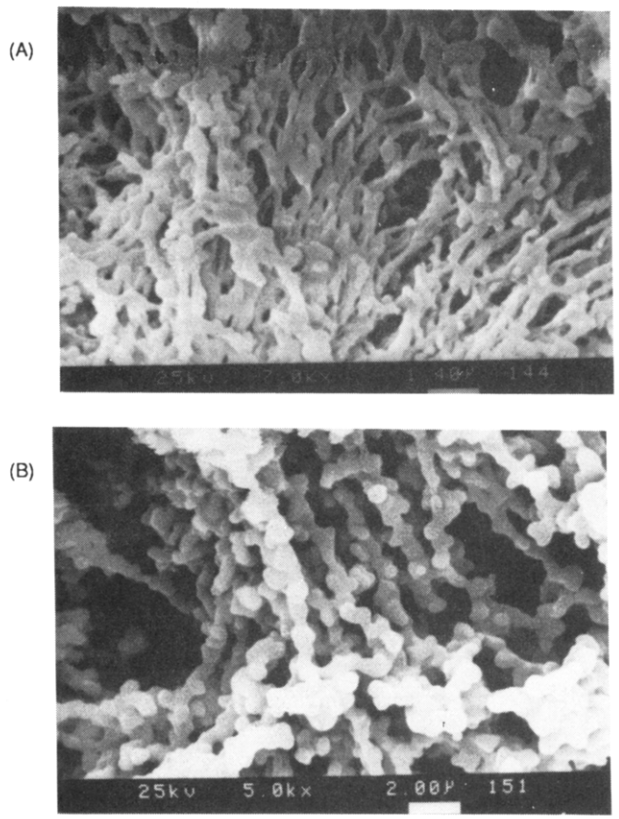

Figure 11. Scanning electron microscopy of poly(diphenyldipropargylmethane): (A) undoped dull side; (B) iodine-doped dull side.

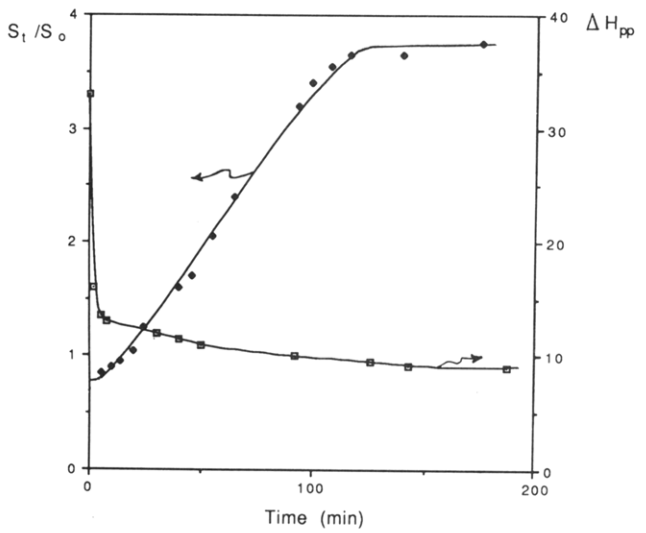

Figure 12. Line width (■) and free spin population (⊡) of poly(diphenyldipropargylmethane) as a function of exposure time to iodine at 25 °C in vacuo: S_0, initial spin population; S_t, spin population at each *t*ime (t).

phenyl substituents and the nonequivalent double bonds of the polymer backbone. The relative spin population increased, with first-order kinetics, as a function of the exposure time to iodine, and it was saturated in 2 h. The result of the increase of the spin population is similar to that of poly(1,6-heptadiyne).[3] Upon heating, the ESR spectrum changed as shown in Figure 13. As poly(DPDPM) is transformed from helical to linear, the ESR signal sharpens (α). Moreover, as heating is continued for a long time, the conjugation of backbone structure becomes ruptured, resulting in a new ESR signal (β) as shown in Figure 13.

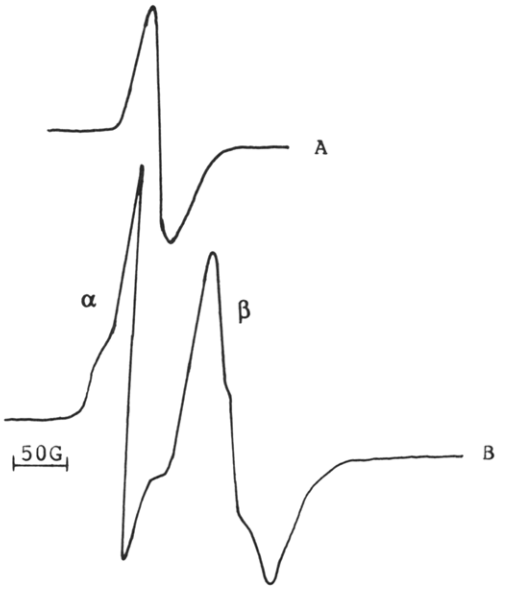

Figure 13. Electron spin resonance (ESR) spectra of poly(diphenyldipropargylmethane) as function of heating time at 230 °C under nitrogen gas: (A) zero time; (B) after 15 min.

Conclusion

The terminal diacetylene of diphenyldipropargylmethane is most effectively cyclopolymerized to a cyclic polyene by a transition-metal catalyst, such as $MoCl_5$ and WCl_6. A bulky phenyl substituent at the 4-position of the 1,6-heptadiyne structure sterically favors cyclopolymerization and is also the primary cause of differences in the observed physical data from that of polyacetylene. Poly(DPDPM) is very soluble in many organic solvents and is stable toward air oxidation. The X-ray diffraction of poly(DPDPM) films did not reveal any evidence of crystallinity. On the other hand, SEM shows the fibrillar structure with a 200–300-Å-diameter range. The electrical conductivity of doped poly(DPDPM) is 10^{-4} S cm^{-1}. In this work, we found that poly(DPDPM) has different properties due to its specific cyclic structure in comparison with polyacetylene, and also it is different from poly(1,6-heptadiyne) due to the introduction of a bulky phenyl substituent at the 4-position.

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Registry No. DPDPM (homopolymer), 127974-83-8; WCl_6, 13283-01-7; $MoCl_5$, 10241-05-1; $(n\text{-}Bu)_4Sn$, 1461-25-2; $PdCl_2$, 7647-10-1; $EtAlCl_2$, 563-43-9; Et_2AlCl, 96-10-6; I_2, 7553-56-2.

Cholesteric Helical Pitch of Near Persistence Length DNA

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ABSTRACT: Simple aqueous solutions of DNA, a semirigid, strong polyelectrolyte, at high concentration in a 1:1 supporting electrolyte medium, undergo a series of transitions between anisotropic phases including a cholesteric liquid-crystalline phase with a pitch of ≈ 2 μm.[19] Measurements were made, by polarized light microscopy and laser light diffraction, of the cholesteric helical pitch in buffered aqueous solutions of DNA molecules with a contour length near the persistence length (500 Å) as a function of increasing DNA concentration, 1:1 supporting electrolyte concentration, and ionic species. The lowest density anisotropic DNA phase, termed precholesteric, exhibited weakly birefringent periodicities with a spacing strongly dependent on local DNA concentration, ranging from 10 to 50 μm. As the DNA concentration was increased, a highly regular cholesteric phase with a pitch of ≈ 2 μm came into coexistence with the precholesteric phase, and ultimately the solutions became fully cholesteric. No change in pitch of this cholesteric was noted with increasing DNA concentration or ionic strength over a DNA concentration range of $\approx$130–300 mg/mL and a supporting electrolyte concentration of 0.01–1.0 M NaCl. Transition to a high-density phase at DNA concentration > 300 mg/mL was preceded by unwinding of the pitch from 2.2 ± 0.2 to >10 μm. The constant ≈ 2-μm-pitch cholesteric phase was stable to higher DNA concentrations when sodium rather than ammonium was the principal counterion. These results are discussed in the context of theories of the phase behavior of lyotropic liquid crystals of chiral rods.

Introduction

The formation of ordered, liquid-crystal-like phases in biological systems has been the focus of a growing number of studies (reviewed in refs 1–5). There is strong electron microscopic evidence that DNA, in particular, exists in cholesteric-like liquid-crystalline phases in the chromosomes of dinoflagellates and other primitive organisms.[6] A lamellar phase has also been proposed for DNA packing in certain virus capsids.[7]

Onsager,[8] Flory,[9,10] and others[11,12] showed as long as 40 years ago that ordering of solutions of rodlike molecules and semirigid polymers in good solvents is expected above some critical volume fraction because of requirements for minimizing the polymer excluded volume. For nonchiral, uncharged rods this is manifested by an isotropic to nematic liquid-crystalline phase transition. DNA rods are both highly charged and inherently chiral; hence, it is expected and observed that at least one of the ordered DNA phases is cholesteric, i.e., exhibits a long-wavelength twist of the molecular director along a single axis. Odijk and co-workers have recently examined the theoretical basis for forming a cholesteric phase in solutions of charged rod polymers (reviewed in ref 13).

Observations of liquid-crystalline DNA (lcDNA) phases in vitro date to the early 1960s when Robinson showed by polarized light microscopy that relatively high molecular weight DNA solutions spontaneously form cholesteric-like liquid-crystalline phases as the DNA concentration is increased.[14] Cholesteric-like phases have been described subsequently for a number of other double-stranded DNA and RNA systems.[4,15-32] Maret and co-workers[20,21] examined the cholesteric phase of polydisperse poly(A)·poly(U) ribonucleic acid duplexes with an average length of about 1700 Å by small-angle neutron scattering, light diffraction from magnetically oriented samples, and measurements of the magnetic birefringence. Iizuka and co-workers investigated the isotropic to cholesteric

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