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Course of conducting poly(1,6-heptadiyne) formation through ultraviolet–visible spectroscopy

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Abstract

Polymerization of the symmetrical non-conjugated diyne, 1,6-heptadiyne, was carried out in nitrogen atmosphere with different initiators in dimethyl formamide. The course of polymerization was followed through ultraviolet–visible spectroscopy. The rate of polymerization was determined under different conditions and used for comparing the efficiency of the initiators. The poly(1,6-heptadiyne) was isolated and characterized through infrared spectroscopy, conductivity measurements and cyclic voltammetry. The electroactivity of the polymer was revealed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymerization; Poly(1,6-heptadiyne); Different initiators

1. Introduction

The subject of electrically conducting organic polymers is a fast developing and fascinating field which has moved in recent years from pure theoretical fancy to a frontier area of modern materials science. Molecular engineering of these novel polymers are now a field of active research in an effort to bring the unique, electronic, magnetic and optical properties of the metals while keeping intact the attractive mechanical and processable advantages of their plastic nature. Ever since Shirakawa et al. [1] succeeded in preparing free standing films of *cis*- and *trans*-polyacetylene by passing pure acetylene gas over a Zeigler–Natta catalyst, a flurry of research activities on polyacetylene were found to follow with the additional discovery of the phenomenon of doping [2].

When it was realized that these polyacetylenes have poor stability and processing difficulty in air, search for other substituted polyenes continued. It was known and subsequently confirmed by using Shirakawa catalyst that substituted polyacetylenes (methyl and ethyl derivatives) polymerized sluggishly in comparison with acetylene [3,4].

A large number of monosubstituted acetylenes have then been polymerized using a wide range of catalysts and conditions involving homogeneous and heterogeneous Zeiglar–Natta catalyst, thermal polymerization, using free radical initiators, high energy radiation in solid and liquid state, cationic and anionic initiator, etc. [5–7].

Few terminal diacetylenes $R'C{\equiv}C{-}(CH_2)_n{-}C{\equiv}CR''$ (where R' and R'' are different/same substituents) have been successfully polymerized to give conducting polyacetylene derivatives [8–10]. The conditions and catalysts for the polymerization vary widely with the monomer structure. Anionic species such as I^-, Br^-, Cl^-, CN^- and SCN^- were used towards this purpose [11].

Butler et al. [12] succeeded in producing soluble non-cross-linked polymers from polymerization of series of symmetrical non-conjugated diolefins, with a probable cyclopolymerization mechanism. Then it was widely extended to several other difunctional monomers [13]. The versatility of using different possible initiators adds advantage of producing these types of soluble polymers. Earlier from this group of researchers, cyclopolymerization was effectively performed using different initiators [14–17].

The production of soluble polymers through cyclopolymerization can now be effectively extended to avoid the difficulty associated with the formation of insoluble and intractable conducting polymers when synthesized through conventional methods. The present work deals with the polymerization of 1,6-heptadiyne (HDY), a symmetrical non-conjugated diyne using different initiators in an attempt to produce soluble conducting polymer.

Various groups have developed different techniques to follow the course of polymerization. The depletion of

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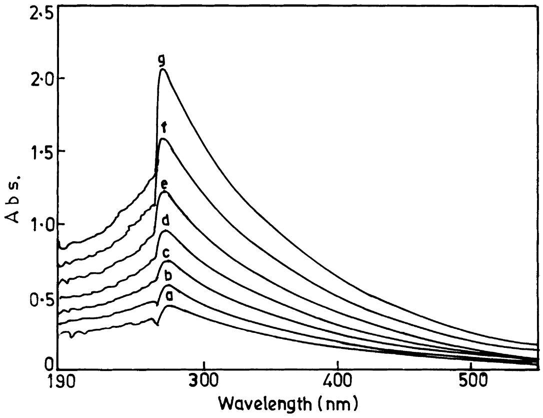

Fig. 1. UV–visible spectrum of poly(1,6-heptadiyne) taken in DMF for various concentrations: (a) 1.61×10^{-2}; (b) 2.02×10^{-2}; (c) 2.52×10^{-2}; (d) 3.15×10^{-2} (e) 3.94×10^{-2}; (f) 4.92×10^{-2}; (g) 6.16×10^{-2} g l^{-1}.

monomer was followed by cyclic voltammetry [18], gas chromatography [19], in situ Raman spectroscopy [20], micro-colorimetry [21] and UV–visible absorption spectroscopy [22]. Here the authors have used UV–visible spectroscopy to monitor the course of polymerization of 1,6-heptadiyne for the first time.

2. Experimental

2.1. Materials

1,6-Heptadiyne (Aldrich, USA) was used as received. Other chemicals used were of AnalaR grade and used as such.

2.2. Polymer synthesis

Polymerization was carried out in a polymerization tube of 80 ml capacity fitted with the B-24 ground joint head carrying inlet and outlet tubes. All experiments were carried out under oxygen-free nitrogen atmosphere in dimethyl formamide (DMF). The typical polymerization procedure and method to monitor the course of polymerization is outlined below.

Suitable volumes of monomer (HDY) and initiator solutions (KSCN/KBr/KCl/KI) in DMF was taken in the polymer tube and the total volume was made as 20 ml by using DMF. The mixture was deaerated with oxygen-free nitrogen and kept in a thermostatic bath at 110°C. The top portion of the polymer tube was cooled by a condenser circulated with ice cold water to avoid loss of DMF and monomer. Nitrogen gas was passed through the reaction mixture for 15 min and the inlets and outlets of the polymer tubes were closed with Teflon stoppers. The course of polymerization was followed at various polymerization reaction times by recording the UV–visible spectra of the mixture (cooled to room temperature) using Shimadzu 2401 PC UV–visible spectrophotometer.

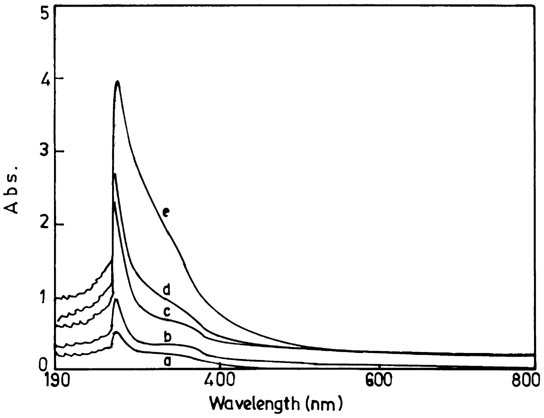

Fig. 2. UV–visible spectrum recorded during course of polymerization of 1,6-heptadiyne using KSCN as initiator (a–e): [HDY] = 4.883×10^{-3} mol l^{-1}; [KSCN] = 5.20×10^{-3} mol l^{-1}. (a) 3; (b) 6; (c) 12; (d) 15; and (e) 18 h.

After polymerization (mostly beyond 48 h of polymerization time), the unreacted monomer and solvent (DMF) were distilled off under reduced pressure. The polymer residue was then dried under vacuum and used for characterization purposes.

2.3. Characterization of the polymer

1. *UV–visible spectroscopy*: Calculated amount of the polymer was dissolved in DMF and the UV–visible spectrum was recorded using a Shimadzu UV-2401 PC UV–Visible Spectrophotometer.
2. *IR spectroscopy*: The IR spectrum of the polymer sample was recorded using a Brucker IFS 66v FT-IR Spectrophotometer.
3. *Conductivity measurements*: The conductivity of the polymer samples was determined by using a four-probe resistivity meter (Concord, India).
4. *Cyclic voltammetry*: Cyclic voltammogram (CV) was recorded using the EG&G PAR model Versostat II Potentiostat/Galvanostat. A conventional three-electrode cell (10 ml capacity) involving SCE as reference, a platinum disc electrode of area 0.02545 cm^2 as working and a platinum foil as counter was employed. The chemically synthesized poly(1,6-heptadiyne) was dissolved in acetone and casted into the film on a platinum disk surface and dried under vacuum. The CVs of the film coated electrodes were recorded using 2 M H_2SO_4 as background electrolyte and the potentials were cycled between −0.2 to 1.0 V vs. SCE with different scan rates.

3. Results and discussion

Polymerization of 1,6-heptadiyne (HDY) was performed in nitrogen atmosphere using KSCN as initiator in DMF. The colour of the reaction medium turned into deep brown

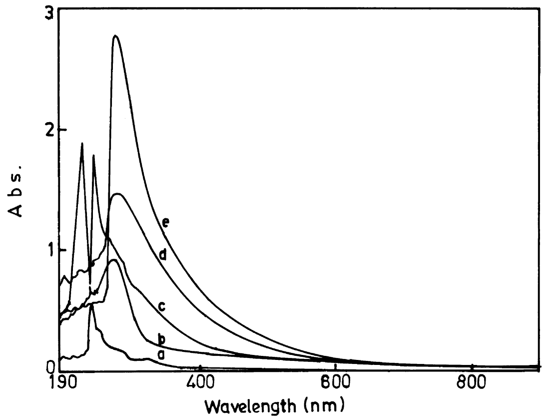

Fig. 3. UV–visible spectrum of poly(1,6-heptadiyne) taken in different organic solvents: (a) dichloromethane; (b) methanol; (c) tetrahydrofuran; (d) *N*-methyl pyrolidone; and (e) dimethyl formamide.

as the polymerization time increased. After 72 h of polymerization, the deep brown coloured reaction mixture was vacuum evaporated to obtain a brown residue, presumably poly(1,6-heptadiyne) (PHDY). This was washed with minimum distilled water to remove the unreacted monomer, the initiator and subsequently dried. The brown reside was dissolved in DMF and the UV–visible spectra were recorded for different concentrations of PHDY in DMF (Fig. 1).

PHDY showed a broad band at 340–360 nm with progressive increase in absorption in the visible region with increase in concentration of PHDY. The optical density values at 340 nm showed linearity with concentration of PHDY. This calibration was used to estimate the amount of PHDY formed during polymerization while following the course of the reaction.

For different experimental conditions of monomer and initiator concentrations in DMF, polymerization was performed for various time intervals. After a definite polymerization time interval, the reaction mixture was analysed for the extent of PHDY formation. The spectrum during the course of polymerization showed a peak at 269 nm, a shoulder 340–360 nm and continuous absorption in the visible region with increasing polymerization time. The optical density 340–360 nm showed progressive increase with increase in the polymerization time (Fig. 2).

It is interesting to compare the spectrum during the course of polymerization and the corresponding concentration of monomer taken in the polymerization time. The monomer spectrum showed only a single peak at 269 nm with negligible absorption in the visible region. In contrast, the spectrum during the course of polymerization at any time interval has distinct absorption in visible region. This is in accordance with the spectrum of poly(1,6-heptadiyne) (Fig. 1) where such an increasing absorption band was noticed with increasing concentration of the polymer. The amount of polymer formed was determined by estimating the extinction coefficient at $\lambda = 340$ nm. The value was calculated to be 16.9 $\mathrm{l\,g^{-1}\,cm^{-1}}$. The amount of polymer was estimated using optical density values at $\lambda = 340$ nm observed for various polymerization time intervals. The rate of polymerization R_p (amount of polymer formed per unit time) was then calculated and presented in Table 1. It was noted that R_p showed an increase with increase in [HDY] and also with increase in [KSCN] when [HDY] was kept as constant (Table 1). The increase in rate was significant with increase in monomer concentration than with the conditions of increasing initiator concentration (Table 1). Experiments with KCl, KBr and KI as initiators of comparable conditions, revealed the following.

Table 1
Course of polymerizaton of 1,6-heptadiyne with KSCN as initiator using UV–visible spectroscopy [[HDY] = 5.43×10^{-3} (a–c); 9.70×10^{-3} (d); 1.1×10^{-2} mol $\mathrm{l^{-1}}$ (e). [KSCN] = 3.0×10^{-3} (a); 7.45×10^{-3} (b); 9.0×10^{-3} (c); 5.0×10^{-3} mol $\mathrm{l^{-1}}$ (d,e)]

Time (h)	R_p^a ($\times 10^5$ g $\mathrm{l^{-1}\,min^{-1}}$)	R_p^b ($\times 10^5$ g $\mathrm{l^{-1}\,min^{-1}}$)	R_p^c ($\times 10^5$ g $\mathrm{l^{-1}\,min^{-1}}$)	R_p^d ($\times 10^4$ g $\mathrm{l^{-1}\,min^{-1}}$)	R_p^e ($\times 10^4$ g $\mathrm{l^{-1}\,min^{-1}}$)
9	6.07	11.40	19.30	1.66	4.46
12	9.70	11.00	26.40	4.01	4.07
15	10.60	12.10	27.60	4.00	3.54
18	11.02	19.80	28.60	4.05	3.64

Table 2
Comparison of rate of polymerization of 1,6-heptadiyne using different initiators [[HDY] = 4.883×10^{-3} mol $\mathrm{l^{-1}}$; [KSCN] = 5.0×10^{-3} (a); [KCl] = 5.0×10^{-3} mol $\mathrm{l^{-1}}$ (b); [KBr] = 5.0×10^{-3} (c); [KI] = 5.0×10^{-3} mol $\mathrm{l^{-1}}$ (d)]

Time (h)	R_p^a ($\times 10^5$ g $\mathrm{l^{-1}\,min^{-1}}$)	R_p^b ($\times 10^5$ g $\mathrm{l^{-1}\,min^{-1}}$)	R_p^c ($\times 10^5$ g $\mathrm{l^{-1}\,min^{-1}}$)	R_p^d ($\times 10^5$ g $\mathrm{l^{-1}\,min^{-1}}$)
6	7.27	5.60	5.25	4.75
9	6.34	5.46	4.73	3.43
12	5.37	5.15	4.51	2.79
15	5.33	4.71	3.61	2.48
18	4.98	4.62	3.26	2.24

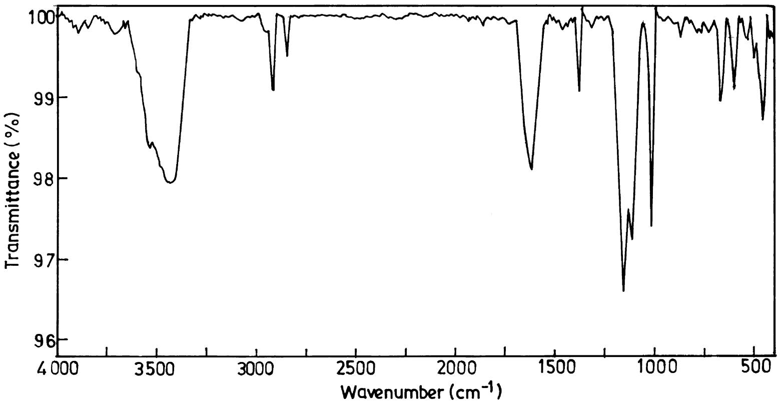

Fig. 4. IR spectrum of poly(1,6-heptadiyne).

The UV–visible spectrum recorded during the course showed variations. The shoulder occurring at 340 nm was found to be shifted to 355, 310 and 370 nm for the polymerization with KCl, KBr, KI as initiator. Besides that, R_p was also found to be different in the four cases (Table 2). Incidently, the effectiveness of initiation of polymerization with these four initiators were found to be in the order KSCN > KCl > KBr > KI. This trend was evident when the results are compared at various polymerization time intervals (Table 2).

PHDY was found to be soluble also in methanol, tetrahydrofuran, *N*-methyl pyrolidone (NMP) and dichloromethane. The UV–visible spectrum of PHDY was also recorded in these solvents (Fig. 3). The peak at 272 nm gets shifted to 270 and 275 nm, respectively, for methanol and NMP. The bathochromic shifts to 307 and 313 nm were significant in THF and dichloromethane.

The IR-spectrum of the poly(1,6-heptadiyne) (Fig. 4) showed bands that could be identified corresponding to C=C–H stretches (shoulders at 3020 and 3000 cm^{-1}), methylene scissor vibrations (bands at 1420–1450 cm^{-1}) and the tri-substituted olefinic C–H out of plane vibrations (bands at 960, 940 cm^{-1}). These types of assignments were earlier made for poly(1,6-heptadiyne) for a stable six-membered ring containing polyene units [13]. On the basis of these observations, PHDY can have the structure containing six-membered units with alternating polyene units. The non-observation of bands here at 1890, 1780, 1600, 870 and 820 cm^{-1} can be ascribed as due to absence of oligomeric products [23].

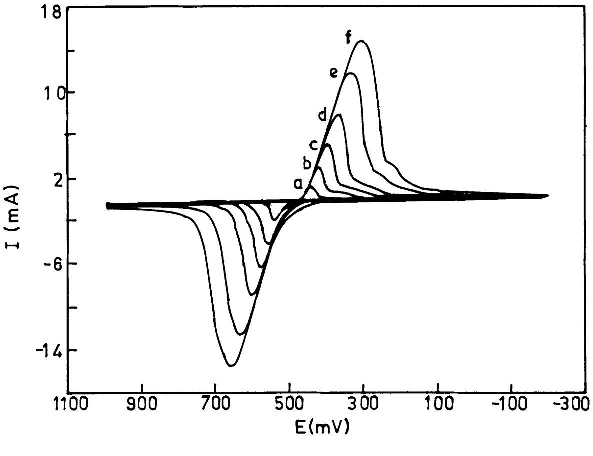

Fig. 5. Cyclic voltammograms of poly(1,6-heptadiyne) coated platinum electrode. Sweep rate: (a) 20; (b) 50; (c) 100; (d) 200; (e) 400; and (f) 600 mV/s.

PHDY was found to show enhanced electrical conductivity from the undoped level of 10^{-12} S cm^{-1} to a maximum value in the range 10^{-2}–10^{-1} S cm^{-1} with different dopants [13]. PHDY was found to have the conductivity in the order 0.2×10^{-1}–0.3×10^{-1} S cm^{-1} which indicated the doped nature of the formed polymer in the present study.

Further, the electroactivity of the PHDY was tested by recording the cyclic voltammogram of the polymer coated platinum electrode for various sweep rates (Fig. 5).

The CVs of the PHDY coated platinum electrode had an anodic peak at 542 mV at the sweep rate (ν) 20 mV/s which showed shifting to more anodic values whilst the cathodic peak at 442 mV showed movement to less positive values with increase in ν. This made an increase in a $E_p^a - E_p^c$ with increase in ν. The current values of anodic (i_p^a) and cathodic (i_p^c) peaks showed increase with ν suggesting electrochemical characteristic of this film surface as similar to bound electroactive film on working electrode [24].

Acknowledgements

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