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Simultaneous synthesis and doping of poly(1,6-heptadiyne-*co*-dipropargyl ether) using ionic initiators

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Abstract

Cyclocopolymerization of 1,6-heptadiyne with dipropargyl ether was carried out under nitrogen atmosphere using KSCN, KBr and KI as initiators in *N*,*N*-dimethyl formamide. The course of polymerization was monitored through UV–Vis spectroscopy. The rate of cyclocopolymerization was determined at different polymerization conditions and the relative efficiency of different initiators was evaluated. KSCN was found to be particularly an effective initiator for the copolymerization. The resulting dark brown colour polymer exhibits good solubility in common organic solvents. ^{1}H-NMR, FTIR and UV–Vis spectra of poly(1,6-heptadiyne-*co*-dipropargyl ether) revealed that the copolymer possesses cyclic polyene units in the back bone. Doped nature of the polymer was evident from UV–Vis and FTIR spectroscopy. Thermal characteristics, conductivity and electroactivity of the copolymer were also explored. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclocopolymerization; Anionic initiators; Rate of polymerization

1. Introduction

Recent research attention has been very much focused on the development of conducting polymers with the view to use them for suitable applications. Polyacetylene is the simplest conducting polymer which has been studied extensively by many researchers because of their unique properties such as conductivity, paramagnetism and migration and transfer of energy. Shirakawa et al. [1] reported the formation of highly conducting polyacetylene films by Zeigler–Natta catalyst through great efforts with an additional phenomenon of doping [2]. However, characterization of polyacetylene has not been fully investigated owing to its insolubility and infusibility.

To increase the processability, studies on the synthesis and characterization of substituted polyacetylene have been extended [3,4] using a wide range of catalysts and conditions involving homogeneous and heterogeneous Ziegler–Natta catalysts, thermal initiation, free radical initiators, high energy radiation in solid and liquid state, cationic and anionic initiators, etc. [5,6]. Few conducting polyacetylene derivatives have been successfully synthesized from terminal diacetylenes [7,8]. The conditions and catalysts suitable for the polymerization vary widely with monomer structure. In all the cases of synthesis, doping has been done through external agents.

Butler [9,10] synthesized soluble, non-cross-linked polymers from the polymerization of series of symmetrical non-conjugated diolefins through cyclopolymerization. The versatility of using different possible initiators adds advantage for producing these types of soluble cyclo polymers. Earlier, cyclopolymerization of substituted vinyl, divinyl and diallyl monomers were effectively performed by our research groups by employing different methods of initiations [11–14]. Mathias [15] discussed in detail about the significant factors that can have control over the efficiency of different types of monomers for undergoing cyclopolymerization in the process of generating new materials. It is known that incorporation of rigid cyclic structures into commercial vinyl polymers leads to sufficient enhancement in glass transition and heat distortion temperatures which now opens up new markets for these classes of materials.

Studies on cyclopolymerization of non-conjugated diynes have been investigated in an attempt to prepare the polymers possessing alternating double and single bonds with a cyclic recurring units [16,17]. Polymers from 1,6-heptadiyne and its homologues of substituted diacetylenes have been effectively synthesized through cyclopolymerization. This

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method avoids the difficulty associated with the formation of insoluble and intractable conducting polymers when synthesized through conventional methods. Gibson et al. [16,18] reported the formation of insoluble free standing films with metallic lustre by performing polymerization of 1,6-heptadiyne with Ziegler type homogeneous catalysts. Choi et al. [19–21] reported the use of transition metal catalyst systems for cyclopolymerization of 1,6-heptadiyne and its derivatives to give conjugated double bonds in the polymer backbone with cyclic recurring units. However, the syntheses in these reports resulted only undoped conducting polymer.

In the process of making non-linear optical materials, derivatives of 1,6-heptadiyne have been copolymerized with dipropargyl phosphonate using metathesis catalysts [22]. To our knowledge, a systematic study on the synthesis of conducting copolymer of 1,6-heptadiyne with other cyclopolymerizable monomer and characterization for the structure and electroactivity have not been made so far. It is also known from literature that polymerization of dipropargyl derivatives by metathesis catalysts [23] could yield conducting polymers in the undoped states requiring further doping with I_2 or other dopants. Hence, a comprehensive method, which would yield doped conducting polymer during synthesis itself is therefore warranted. The use of suitable initiators that can provide doping in a concomitant way with synthesis will produce the polymer in the doped state. Such initiation routes will be much useful for the synthesis of conducting polymers.

The present study has directed its attention towards the synthesis and characterization of the conducting copolymer from 1,6-heptadiyne (HDY) and another diacetylene derivative, dipropargyl ether (DPE). Few anionic initiators (KSCN/KBr/KI) were specifically selected to produce the conducting copolymer in the doped state. For following the course of conducting polymer formation, UV–Vis spectroscopy was employed. In our earlier work, the course of formation of a soluble conducting polymer, poly(1,6-heptadiyne), was followed by UV–Vis spectroscopy [24]. Here, UV–Vis and FTIR spectroscopy were used to obtain evidences for the doped nature of the copolymer. The copolymer was characterized for its conductivity, thermal characteristics and electroactivity.

2. Experimental

2.1. Chemicals

1,6-heptadiyne (HDY) (Lancaster, England), Dipropargyl ether (DPE) (Aldrich, USA) and other chemicals (AnalaR grades) were used as such.

2.2. Polymer synthesis

Cyclopolymerization was carried out in a polymerization tube of 80 ml capacity fitted with B_{24} ground joint head carrying inlet and outlet tubes. All experiments were carried out under oxygen free nitrogen atmosphere in *N*,*N*-dimethyl formamide (DMF). A typical polymerization procedure is outlined below:

Suitable volumes of monomers (HDY and DPE) and initiator solutions (KSCN/KBr/KI) in DMF (20 ml) were taken in the polymer tube. The reaction mixture was deaerated for 15 min 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. The course of polymerization was followed by recording the UV–Vis spectra of the mixture (cooled to room temperature) at various polymerization times using Shimadzu 2401 PC UV–Vis spectrophotometer.

2.3. Isolation of copolymer

After polymerization (mostly beyond 48 h), the unreacted monomer and DMF were distilled off under reduced pressure. The copolymer was isolated by washing with water to remove unreacted initiators, then dried in vacuum oven and used for characterization purposes.

2.4. Characterization

2.4.1. Molecular weight

The average molecular weight, $\bar{M}_n$ and $\bar{M}_w$ of the copolymer was determined by using Shimadzu R-7A (data module; LC-10AD pump) Gel permeation chromatograph. Two linear columns in series were used for separation. The flow rate for DMF was $2\ \mu l\ min^{-1}$ at 40 °C using polystyrene standards.

2.4.2. UV–Vis spectroscopy

UV–Vis absorption spectra of the separated copolymer were recorded by dissolving calculated amount of the copolymer in DMF. Spectra of the copolymers were also recorded in other solvents like NMP, THF, etc.

2.4.3. ^{1}H-NMR spectroscopy

^{1}H-NMR spectra (for the homopolymer and copolymer) were recorded with Bruker-AC-300 spectrometer and chemical shifts were recorded in ppm units with TMS as internal standard.

2.4.4. FTIR spectroscopy

The FTIR spectra of homo and copolymer were recorded in pressed KBr pellets using Pentagon-200 FTIR spectrophotometer.

2.4.5. Thermogravimetric analysis

Thermal properties of the dried copolymer were followed using a Perkin Elmer TGA 7/DX thermal analyzer over the temperature range of 100–800 °C in N_2 atmosphere, at a heating rate of $20\ °C\ min^{-1}$.

2.4.6. Conductivity measurements

The conductivity of the copolymer samples was determined by using four probe resistivity meter (Concord, India).

2.4.7. Cyclic voltammetry

Cyclic voltammograms (CV) were recorded using EG and G PAR Model Versostat™II Potentiostat/Galvanostat. A conventional three-electrode cell (10 ml capacity) involving SCE as reference, a platinum disk of area 0.02545 cm^2 as working and a platinum foil as counter was employed. Poly(HDY-*co*-DPE) was dissolved in acetone or NMP and casted as film on the surface of platinum disk electrode and dried under vacuum. CV's of the film coated electrodes were recorded in 2 M H_2SO_4 (background electrolyte) by cycling the potentials between -0.2 and 1.0 V for different scan rates (50–600 mV s^{-1}).

3. Results and discussion

3.1. Course of copolymerization

Polymerization of mixture of HDY and DPE was performed in DMF with KSCN/KCl/KBr/KI as initiator at 110 °C. UV–Vis spectroscopy was employed to follow the course of polymerization. The spectra recorded during the polymerization of mixture of HDY with DPE indicated the formation of copolymer. A close comparison of spectra recorded for the individual homopolymerization (HDY or DPE) with copolymerization clearly revealed the copolymer formation with mixture of HDY and DPE in the polymerization system. Spectra recorded with different initiators (KSCN/KBr/KI) showed variations in absorption characteristics and extent of copolymer formation. Doped nature of formed copolymer was also evident.

Fig. 1 shows the UV–Vis absorption spectra recorded during course of copolymerization of HDY with DPE using KSCN as initiator. A peak at 281 nm and broad band at 350–450 nm were observed during copolymerization. The peak at 281 nm showed decrease in absorbance with polymerization time. The band at 350–450 nm was found to grow progressively with time with an appearance of isobestic point at 330 nm. The assignments for these absorption bands were made by comparing the spectrum of the individual monomers (HDY and DPE) and spectrum observed during homopolymerization of HDY and DPE. The monomer spectrum of HDY and DPE had a peak at 269 and 268 nm, respectively (Fig. 1, inset), without having any absorption in the visible region. For the homopolymerization of HDY and DPE the absorption band corresponding to cyclic polyene units were found at 340–360 nm [24] and 320–340 nm (Fig. 2) respectively. Hence, the absorption peak at 281 nm and the broad band at 350–450 nm during copolymerization are assigned for the intermediate state during copolymer formation and π–π^* transition of the conjugated cyclic polyene units which is expected for the copolymer as a result of cyclopolymerization (Scheme 1). A clear red shift in π–π^* transition in comparison with PHDY and PDPE indicates an increase in the conjugation length of the copolymer as a result of copolymerization (Scheme 1). Through the above observations, the formation of copolymer becomes evident when HDY and DPE were polymerized with KSCN as initiator. Similar observations were noticed when KCl or KBr or KI was used as initiator for the copolymerization.

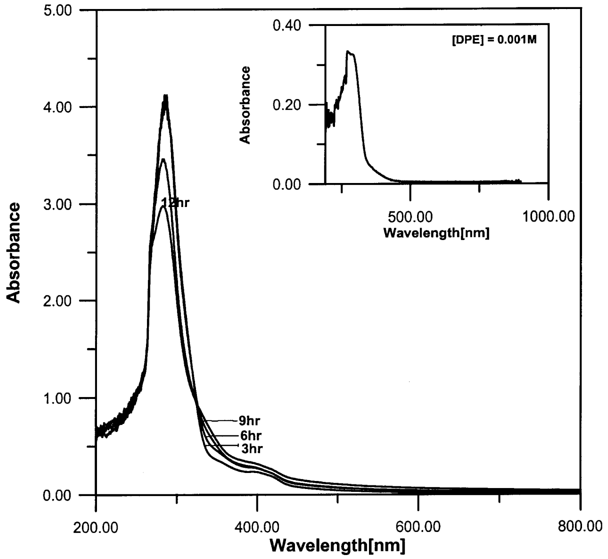


Fig. 1. UV–Vis spectra recorded during the cyclocopolymerization of HDY with DPE in DMF [HDY] = 5.43×10^{-3} mol l^{-1}; [DPE] = 5.43×10^{-3} mol l^{-1}; [KSCN] = 5.0×10^{-3} mol l^{-1}.

The amount of copolymer formed at different time intervals of copolymerization was followed by the absorbance

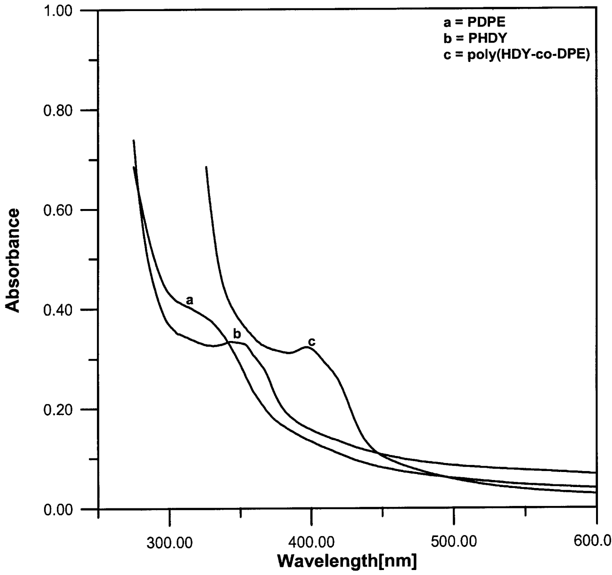
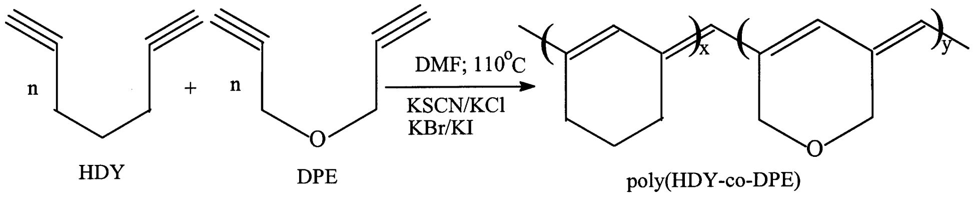


Fig. 2. UV–Vis absorption spectra of PDPE, PHDY and ploy(HDY-*co*-DPE) in DMF.



Scheme 1. Copolymerization of HDY with DPE.

values corresponding to the copolymer. Towards this purpose, the formed copolymer was isolated from the reaction medium. Calculated amount of copolymer was dissolved in DMF and UV–Vis absorption spectra were recorded for various concentrations. The optical density values at 400 nm found linearity with the concentration of the formed copolymer, poly(HDY-*co*-DPE). This calibration was further used to estimate the amount of copolymer formed at any time of polymerization. The molar extinction coefficient at 400 nm was calculated to be 8.61×10^{-1} l g^{-1} mol^{-1}. This value was also used to determine the amount of copolymer formed at any polymerization time.

Rate of copolymerization, R_P (amount of polymer formed per unit time) was determined for different experimental conditions. Table 1 summarizes the R_P values obtained for the copolymerization of HDY with DPE while using KSCN/KBr/KI as initiator in DMF. R_P was found to increase with increase in initiator (KSCN/KBr/KI) concentrations while using any of the initiator. The efficiency of the initiator towards initiation of copolymerization was compared by using the R_P values obtained under identical conditions and found to be in the order KSCN > KI > KBr ≈ KCl. The obtained yield of copolymer (Table 2) while using KSCN or KBr or KI as initiator also indicated highest efficiency to KSCN towards initiating the cyclopolymerization. The weight average molecular weight ($\bar{M}_w$) of the copolymer was determined as 13.2×10^4 relative to the polystyrene standards in GPC. The ratio of $\bar{M}_w/\bar{M}_n$ was found to be 3.74.

3.2. Copolymer structure

The copolymer structure was identified by ^{1}H-NMR, FTIR and UV–Vis spectroscopy. The ^{1}H-NMR spectrum of poly(HDY-*co*-DPE) in DMSO-d_6 is shown in Fig. 3a. Absence of the acetylenic peak at 2.0 ppm indicates the conversion of –C≡C– bonds in the monomer to –C=C– during the polymerization. The multiple peaks around 6.6–8.2 ppm are assigned for the protons on the conjugated double bonds in the copolymer backbone [25]. The peak at 3.9 ppm indicates the allylic protons on the carbon adjusted to oxygen of the polyene units present in the copolymer backbone. The peak at 4.4 ppm is assigned for the other allylic protons in the cyclic ring. It is important to note that multiple peaks for the protons on the conjugated double bonds for poly(1,6-heptadiyne) and poly(dipropargyl ether) appeared at 6.8–7.6 and 6.4–7.5 ppm, respectively.

The shoulder at 2925 cm^{-1} in FTIR spectrum of SCN$^-$ ion doped poly(HDY-*co*-DPE) (Fig. 3b) is assigned for the –C=C–H stretches in the backbone. The peaks at 1405, 1430 and 1450 cm^{-1} are assigned for the methylene scissor vibrations. For poly(1,6-heptadiyne) [24], the methylene scissor vibrations have been noticed at 1420–1450 cm^{-1}. An intensive band at 1626 cm^{-1} (–C=C– stretching) indicates the extended conjugation in the copolymer backbone [20]. The peaks at 1380 and 1124 cm^{-1} (for copolymer prepared with KSCN) represent the doping induced vibrational changes as noticed for trans polyacetylene [26]. Otherwise, the copolymerization initiated with KSCN/KCl/KBr/KI as initiators resulted the copolymer in the doped state. This can be taken as the chief advantage of using ionic initiators (SCN$^-$, Cl$^-$, Br$^-$, I$^-$) in contrast to metathesis catalyst, which could produce the polymer in the undoped state. There were variations in the stretching frequencies around 1370–1380 and 1124 cm^{-1} for the copolymers prepared with KSCN/KCl/KBr/KI as initiator (Fig. 3c) which indicated the association of different

Table 1
Effect of initiator concentrations on rate of copolymerization. [HDY] = 5.43×10^{-3} mol l^{-1} (a–h), [DPE] = 5.43×10^{-3} mol l^{-1} (a–h), [KSCN] = 5.0×10^{-3} mol l^{-1} (a); 7.5×10^{-3} mol l^{-1} (b); 10.0×10^{-3} mol l^{-1} (c), [KI] = 5.0×10^{-3} mol l^{-1} (d); 7.5×10^{-3} mol l^{-1} (e), [KBr] = 5.0×10^{-3} mol l^{-1} (f); 7.5×10^{-3} mol l^{-1} (g); 10.0×10^{-3} mol l^{-1} (h)

Time (h)	$R_P^a \times 10^4$ (g l^{-1} min^{-1})	$R_P^b \times 10^4$ (g l^{-1} min^{-1})	$R_P^c \times 10^4$ (g l^{-1} min^{-1})	$R_P^d \times 10^4$ (g l^{-1} min^{-1})	$R_P^e \times 10^4$ (g l^{-1} min^{-1})	$R_P^f \times 10^4$ (g l^{-1} min^{-1})	$R_P^g \times 10^4$ (g l^{-1} min^{-1})	$R_P^h \times 10^4$ (g l^{-1} min^{-1})
3	15.2	17.8	20.6	9.2	10.5	8.45	9.11	10.3
6	7.64	11.0	11.5	5.61	7.06	4.42	4.72	5.45
9	5.28	7.56	8.17	4.09	5.45	3.06	3.52	4.06
12	4.18	5.86	6.58	3.32	4.57	2.39	3.11	3.39
15	3.55	4.86	5.59	2.88	3.82	2.28	2.61	2.91

Table 2
Comparison of the yield of copolymer formation with different initiators. [HDY] = 5.43×10^{-3} mol l^{-1} (A–E); 10.86×10^{-3} mol l^{-1} (F, G), [DPE] = 5.43×10^{-3} mol l^{-1} (A–C, F); 8.15×10^{-3} mol l^{-1} (D, G); 10.86×10^{-3} mol l^{-1} (E), [KSCN] = 5.0×10^{-3} mol l^{-1} (A, D–G); 7.5×10^{-3} mol l^{-1} (B); 10.0×10^{-3} mol l^{-1} (C), [KI] = 5.0×10^{-3} mol l^{-1} (A, D–G); 7.5×10^{-3} mol l^{-1} (B); 10.0×10^{-3} mol l^{-1} (C), [KBr] = 5.0×10^{-3} mol l^{-1} (A, D–G); 7.5×10^{-3} mol l^{-1} (B); 10.0×10^{-3} mol l^{-1} (C)

Ratio of HDY/DPE and initiators concentrations	Copolymer yield (%)		
	KSCN	KI	KBr
(1:1:1)^A	37^a	36^a	30^a
(1:1:1.5)^B	52^b	49^b	41^b
(1:1:2)^C	73^c	68^c	52^c
(1:1.5:1)^D	57^d	49^d	34^d
(1:2:1)^E	71^e	46^e	38^e
(2:1:1)^F	41^f	37^f	34^f
(2:1.5:1)^G	47^g	42^g	33^g

dopants (SCN^- or I^- or Cl^- or Br^-) with copolymer and the consequent different extent of induced doping. For PDPE, the doping induced vibrational band appeared at 1340 cm^{-1}. These IR bands are also indicative of the cyclic six membered type ring structure with alternative double bonds in the polymer backbone [27].

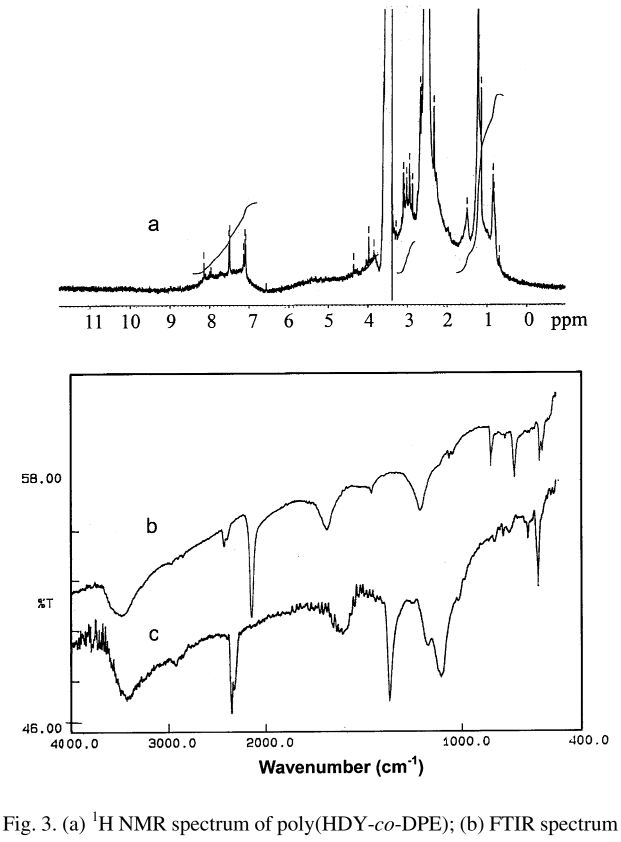


Fig. 3. (a) ^{1}H NMR spectrum of poly(HDY-*co*-DPE); (b) FTIR spectrum of poly(HDY-*co*-DPE) doped with SCN^- ion c. poly(HDY-*co*-DPE) doped with I^- ion and (c) PDPE doped with I^- ion.

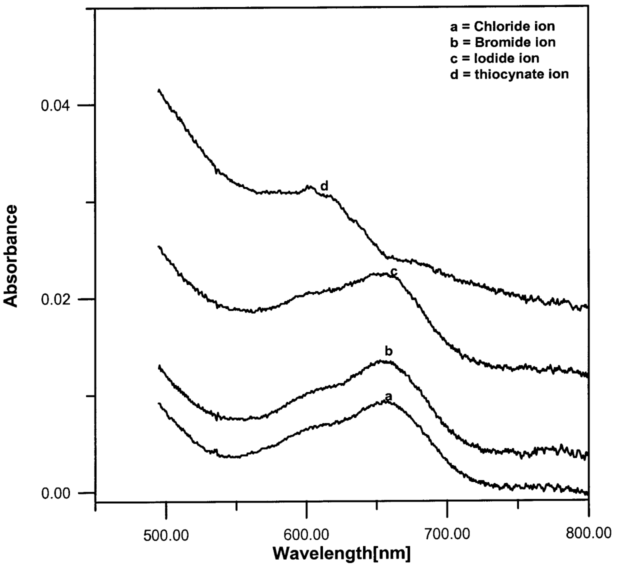


Fig. 4. UV–Vis absorption spectra of poly(HDY-*co*-DPE) in DMF for different dopants.

The doped nature of the formed copolymer was also evident from the presence of a broad band around 640–720 nm in the UV–Vis spectrum (Fig. 4) recorded during the course of copolymerization with KI/KBr/KCl as initiator and a broad band around 605 nm for KSCN initiated copolymerization. The differences in band positions also signify the nature of dopant ions (halide or SCN ion). These assignments confirm the cyclic polyene structure for the copolymer (Scheme 1).

3.3. Properties of the copolymer

It is known from Refs. [24,25,28] that polymers formed through cyclopolymerization are soluble in organic solvents. Poly(HDY-*co*-DPE) was tested for its solubility in different solvents. Poly(HDY-*co*-DPE) was found to be soluble in DMF, tetrahydrofuran [20], *N*-methyl pyrrolidone (NMP) and methanol. The UV–Vis absorption spectra of poly(HDY-*co*-DPE) was recorded in various organic solvents. A shoulder appeared at 400 nm in DMF was found to be blue shifted to 361 nm in NMP, 350 nm in THF and 320 nm in methanol. These kinds of solvatochromic shifts have been observed for the polymers of *N*-substituted dipropargyl amine derivatives [29,30] produced through cyclopolymerization.

The thermogram of poly(HDY-*co*-DPE) is shown in Fig. 5. The initial weight loss occurring below 220 °C indicates the loss of dopants from cyclic polyene units. The major weight loss was observed between 220 and 650 °C. This can be attributed to proton migration, cross-linking, bond scissoring and loss of cyclic polyene units [28]. For similar thermal transition, PDPE showed only 20% weight loss in comparison to the copolymer (40% weight loss). The additional weight loss in the case of copolymer is assigned

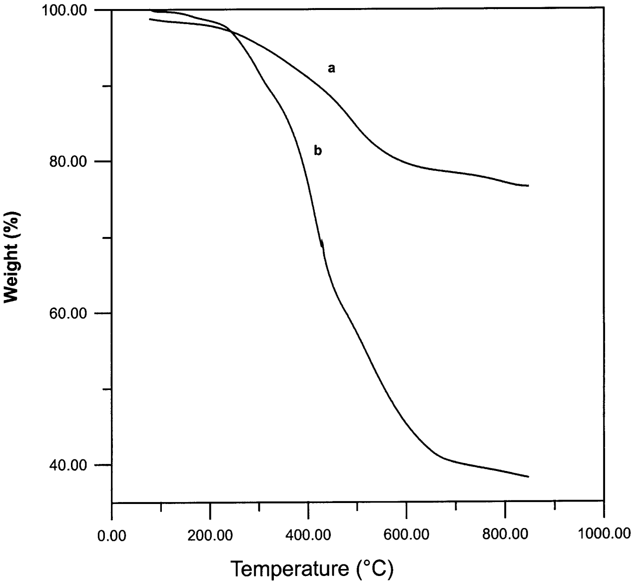


Fig. 5. Thermogram of (a) PDPE; (b) poly(HDY-*co*-DPE).

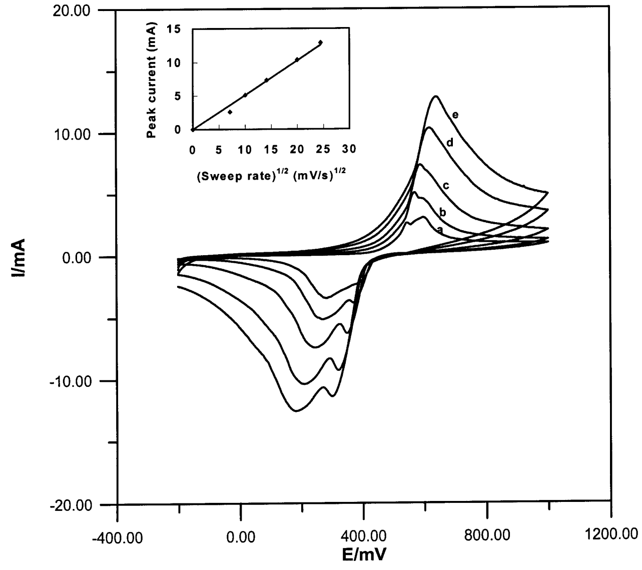


Fig. 6. Cyclic voltammograms of Poly(HDY-*co*-DPE) film coated platinum electrode. Scan rate is (a) 50; (b) 100; (c) 200; (d) 400; (e) 600 mV s^{-1}.

to the presence of HDY units in the copolymer [31]. It is pertinent to note that the first thermal process for PDPE occurred at 200 °C and loss of backbone units due to proton migration and cross-linking beyond 550 °C. The copolymer showed better thermal stability than PDPE only below the temperature (240 °C) at which the first thermal transition starts. The results from differential scanning colorimetry reveal the thermal properties of copolymer. The glass transition temperature of the copolymer was observed at 144 °C. The observed exothermic peak at 270 °C indicates the loss of cyclic polyene units and can be correlated with weight losses through TGA measurements.

Conductivity measurements of poly(HDY-*co*-DPE) revealed that the thiocyanate ion and halide ion doped nature of the copolymer was formed in the present study. The copolymer was found to have conductivity values in the order of 5.0×10^{-2}–8.0×10^{-2} S cm^{-1}. It is important to note that cyclic polyenes have conductivity in the order of 10^{-12} S cm^{-1} for undoped states and higher values in the order of 10^{-2}–10^{-1} S cm^{-1} for doped states [18,24,32].

3.4. Electroactivity

Fig. 6 shows the cyclic voltammograms recorded for the copolymer film coated Pt electrode in the potential range between 0.20 and 1.0 V vs. SCE for various scan rates. The film coated Pt electrode showed two well defined redox processes. The twin oxidation peaks appearing at 545 and 590 mV with a scan rate of 50 mV s^{-1}, were found to be shifted to more anodic values with increase in scan rate whilst the reduction peaks at 390 and 284 mV showed movement to less positive values with increase in scan rates [24,33]. Otherwise, the separation between anodic and cathodic peaks corresponding to these redox process was found to increase progressively with scan rate. This implied the slow kinetics for the process of insertion–desertion of dopant ions in the copolymer. The two oxidation peaks observed in the lower scan rates merged into a single peak at higher scan rates (>400 mV s^{-1}). The peak current for the first anodic peak was found to be a square root dependence on scan rate (Fig. 6, inset). This result is in accordance with the occurrence of diffusion controlled process at the film modified electrode.

4. Conclusion

The use of ionic initiators (KSCN/KCl/KBr/KI) for cyclopolymerization of HDY with DPE resulted the copolymer in the doped state. The doped nature of the copolymer was evident from the appearance of broad band around 640–720 and 605 nm for KI/KBr/KCl and KSCN initiated copolymerization, respectively. The copolymer synthesized with KSCN/KCl/KBr/KI as initiator showed variations in the doping induced vibrational frequencies and this becomes obvious from FTIR results. The efficiency of the initiator towards copolymerization was found to found to be in the order: KSCN > KI > KBr ≈ KCl. The copolymer was soluble in NMP, DMF, THF and methanol and showed solvatochromic shifts. The presence of multiple peaks around 6.8–8.2 ppm and a peak at 3.9 ppm in ^{1}H-NMR spectrum of the copolymer indicates the cyclic polyene structure for the copolymer and this proposal is supported by FTIR results.

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