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Electrochemical preparation and characterization of conducting copolymers: poly(pyrrole-*co*-indole)

K. DHANALAKSHMI, R. SARASWATHI*
Department of Materials Science, Madurai Kamaraj University,
Madurai-625 021, Tamilnadu, India
E-mail: saraswathir@yahoo.com

Copolymerization of pyrrole and indole was achieved electrochemically in acetonitrile containing lithium perchlorate as supporting electrolyte. The copolymer compositions can be altered by varying the comonomer feed ratios during preparation. The copolymers were characterized by conductivity measurements, cyclic voltammetry, scanning electron microscopy, UV-visible and IR spectroscopic techniques. A possible scheme for the copolymerization mechanism has been suggested.

1. Introduction

Polypyrrole is one of the "model" conducting polymers investigated in detail with proposed applications in rechargeable batteries [1], supercapacitors [2], electrocatalysis [3], electromechanical and electrochemopositioning devices [4] and polymer/high T_c superconductor assemblies [5]. Several reports have appeared in literature on polyindole [6–9] and its substituted derivatives [10–14]. Polyindole-perchlorate film prepared from acetonitrile has been found to possess a conductivity of 10^{-1} ohm^{-1} cm^{-1} with a redox stability of over 450,000 cycles. The degradation of polyindole has been shown to be slower than that of polypyrrole [15]. However the poor mechanical properties of polyindole [16] have perhaps prevented it from being used in various applications.

The recent advancements in heteroaromatic copolymers have been reviewed [17]. Electrochemical copolymerization offers the advantages of preparing a wide array of materials with varying conductivity, redox activity and stability. The electrochemical copolymerizations of pyrrole with its N-substituted derivatives [18–22] and also with thiophene [23–25] and N-vinylcarbazole [26] have been documented in the literature. However, to our knowledge, copolymerization of indole with other aromatic/heteroaromatic monomers has not been reported so far. The closeness of the threshold polymerization potentials of pyrrole and indole suggests the possibilities for their electrochemical co-polymerization leading to the formation of an array of materials having increasing redox potentials from −0.15 V (polypyrrole) to +0.5 V (polyindole). These new copolymer electrode materials with higher redox potentials could offer the possibility of increasing the energy density when used as cathode materials in rechargeable batteries. Also, the copolymerization process might lead to films of enhanced electrochemical stability and better mechanical properties. In this paper, we report an analysis of the electrochemical, spectroscopic and morphological properties of a series of poly(pyrrole-*co*-indole) copolymer films.

2. Experimental

Pyrrole (SRL) was purified by vacuum distillation. Indole (SRL) was purified by recrystrallization from petroleum ether. Acetonitrile (Qualigens, AR) and lithium perchlorate (Alridch) were used as received. A platinum foil (24 mm^2) served as the working electrode for film deposition and cyclic voltammetric experiments. The polymers were deposited on an ITO coated glass for *in situ* UV-visible spectral measurements. A Ag/Ag$^+$ was used as reference. A large platinum foil (150 mm^2) served as the counter electrode. All experiments were carried out under N_2 atmosphere.

The conductivity measurements were made as follows. Two L-shaped platinum wires of length 25 mm each were fused into two separate glass tubes. The position of the two electrodes was adjusted such that the electrodes were fixed with a gap as minimum as possible. The gap was less than 1 mm. When polymerization was carried out simultaneously on both the wires, the polymer layer grew on the two wires and eventually bridged the gap between the wires. When the polymer was deposited in sufficient amounts, the two electrodes could be connected in the electrical sense. The two-probe electrode was then taken out of the polymerizing solution and rinsed carefully in the background electrolyte solution to get rid of the monomer and dried carefully. The resistance between the two polymer-coated wires was then measured. We have also measured the conductivity of pressed pellets for a few of the samples and we have found the order of conductivity to agree well with the two-probe method. We have varied the charge passed during copolymer deposition

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*Author to whom all correspondence should be addressed.

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for different comonomers feed ratios to have uniform gap geometry. The quantity of electricity needed to bridge the gap depended on the concentration of the comonomers. The measured resistance values are much higher than ($\sim 10^3$ to 10^5 for most of the samples) that of the lead contacts ($\sim$0.2 ohm). The above method seems to limit the scattering of values that may arise owing to variation in the film thickness and roughness of film surface [27]. The two-probe method we have used in the present work has been described in literature by several groups [28–30] for polyaniline.

A PAR model 362 scanning potentiostat and X-Y recorder (Houston-Digilog 2000) were used for recording cyclic voltammograms. UV-Visible (Jasco model 7800) and FT-IR (Nicolet model 510P) spectrophotometers were used. The film morphology was studied by a scanning electron microscope (Hitachi model 450).

3. Results and discussion

3.1. Copolymer growth

In order to check the possibility of copolymerization by electrochemical method, at first quasi steady-state voltammetric curves were recorded at various concentrations of pyrrole and indole. The representative plots are shown in Fig. 1. It can be seen that the threshold potential (0.75 V) for the initiation of polymerization of pyrrole and indole are very close to each other rendering copolymerization of the two monomers feasible. This threshold potential is applied to prepare the copolymers in thin films as well as in bulk. The thin films are investigated for redox stability and spectroelectrochemical behaviour while the bulk material is used for conductivity, IR and morphological studies.

The experiments can be classified into three groups on the basis of feed ratio of the two monomers. Group I consists of experiments carried out with equal molar concentration of the two monomers. Group II experiments involve the use of a higher molar concentration of pyrrole than indole. In group III, a higher molar concentration of indole is used.

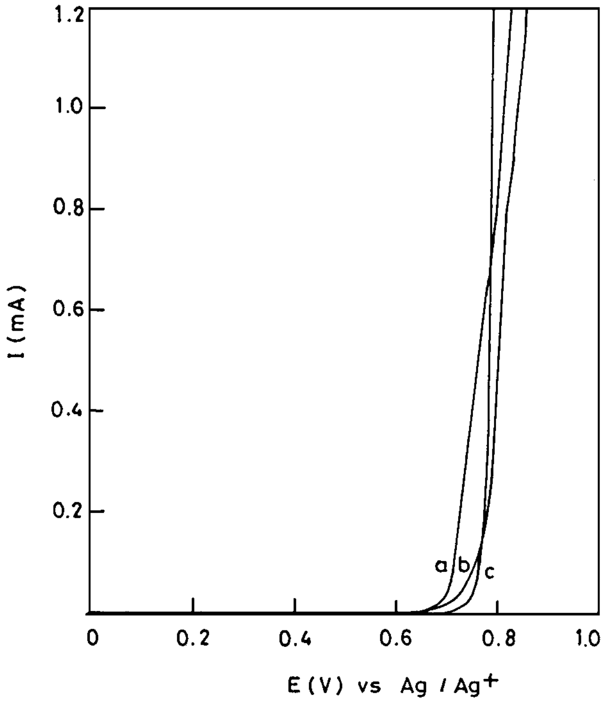


Figure 1 *I-E* curves of Pt electrodes in the presence of (a) 0.1 M pyrrole, (b) 0.1 M indole and (c) a mixture of both monomers in the above described concentration in acetonitrile containing 0.5 M LiClO4, dE/dt = 1 mV s^{-1}.

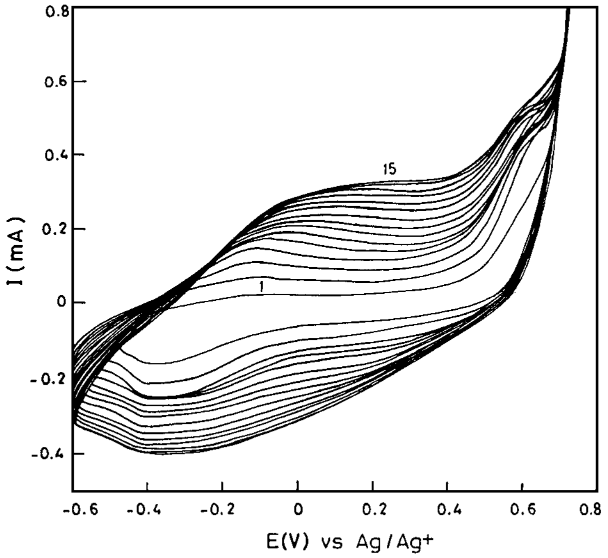


Figure 2 Cyclic voltammograms taken during homopolymerization of 0.5 M pyrrole in acetonitrile containing 0.5 M LiClO4, dE/dt = 20 mV s^{-1}.

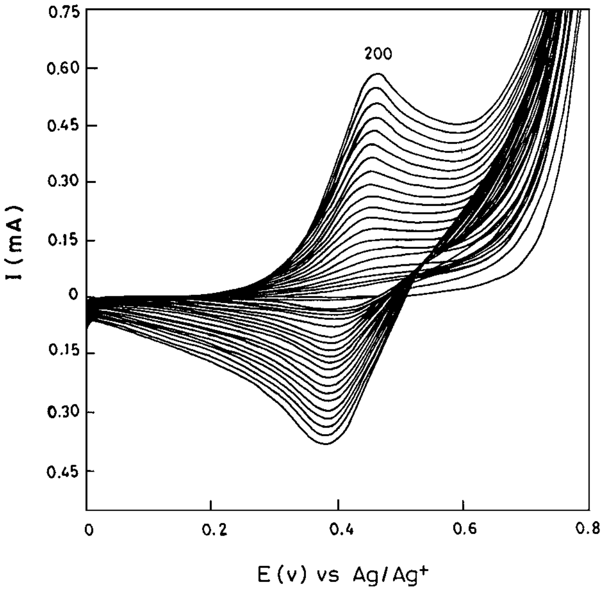


Figure 3 Cyclic voltammograms taken during homopolymerization of 0.5 M indole in acetonitrile containing 0.5 M LiClO4, dE/dt = 20 mV s^{-1}.

Owing to the differences in the cyclic voltammetric growth profiles (Figs 2 and 3) of polypyrrole ($E_p^A =$ 0.1 V, $E_p^C = -0.4$ V) and polyindole ($E_p^A = 0.48$, $E_p^C = 0.39$ V), the multisweep cyclic voltammograms during the growth of the copolymer were recorded. The copolymer growth profiles were found to depend on the feed ratio. Figs 4–6 show representative graphs for group I, II and III. The switching potentials (E_λ) were gradually decreased from 0.75 V to 0.6 V to avoid film degradation during growth. While only one anodic with a corresponding cathodic peak is observed for feed ratios in group I ($E_p^A = 0.25$ V,

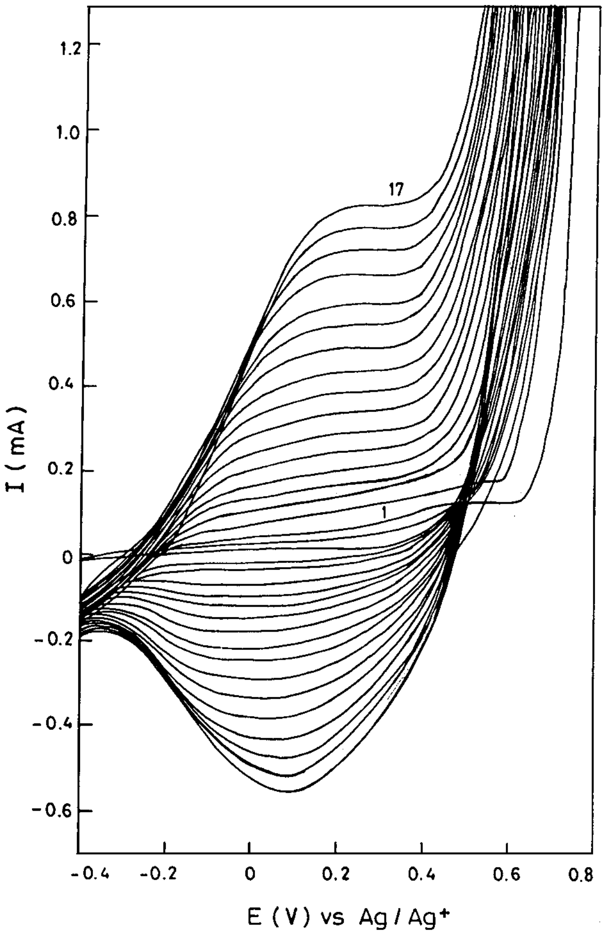


Figure 4 Cyclic voltammograms taken during copolymerization of pyrrole (0.1 M) and indole (0.1 M) (group I) in acetonitrile containing 0.5 M $LiClO_4$, dE/dt = 20 mV s^{-1}.

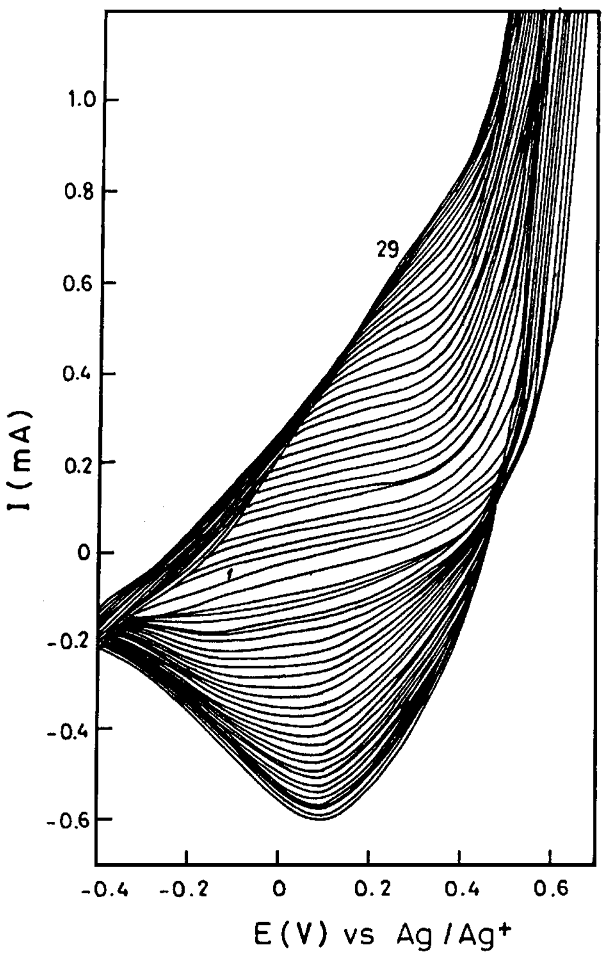


Figure 5 Cyclic voltammograms taken during copolymerization of pyrrole (0.5 M) and indole (0.25 M) (group II) in acetonitrile containing 0.5 M $LiClO_4$, dE/dt = 20 mV s^{-1}.

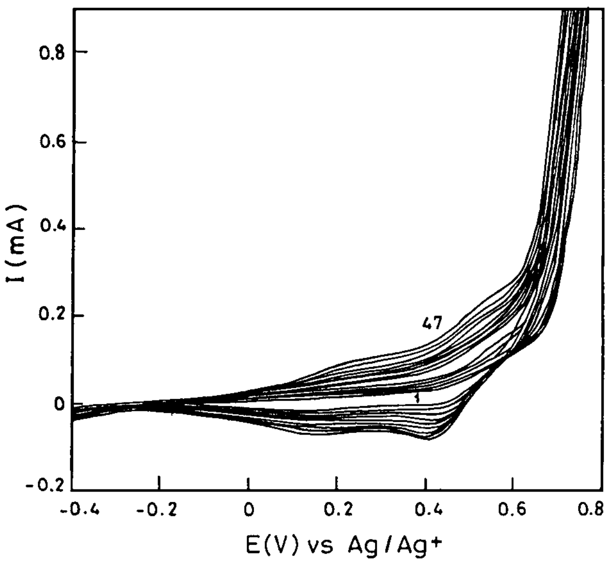


Figure 6 Cyclic voltammograms taken during copolymerization of pyrrole (0.1 M) and indole (0.5 M) (group III) in acetonitrile containing 0.5 M $LiClO_4$, dE/dt = 20 mV s^{-1}.

$E_p^C = 0.08$ V) and group II ($E_p^A = 0.25$ V, $E_p^C = 0.1$ V), two processes ($E_{p1}^A = 0.2$ V, $E_{p1}^C = 0.14$ V; $E_{p2}^A = 0.55$ V, $E_{p2}^C = 0.42$ V) occur whenever the concentration of indole exceeds that of pyrrole (group III).

The evolution of a new peak at a potential different from the growth potentials of polypyrrole and polyindole suggests the formation of a copolymer. In the case of group III, the first peak can be assigned to the formation of the copolymer. The second peak potential is close to that of polyindole as can be compared with Fig. 3. In other words, a higher concentration of indole than pyrrole in the feed ratio leads to the formation of a mixture of polyindole and the copolymer.

3.2. Characterization

The dry state conductivity values for the various copolymers are given in Table I. The values lie between those of the two homopolymers. It is generally observed that increasing the pyrrole concentration in the feed ratio increases the conductivity.

In order to confirm further the formation of copolymers, IR spectra were recorded for all the samples and the data were compared with those of the homopolymers (Table II). A detailed analysis of the spectral manifestations indicates the formation of copolymers containing pyrrole and indole units. The bands at 790 cm^{-1} and 3100 cm^{-1} in the spectrum of polypyrrole correspond to the 2–2′ coupling and the stretching mode of the secondary amine respectively [25]. In the case of polyindole, the spectral band at 1320 cm^{-1} induced by C-N amine shows the participation of the nitrogen atoms in indole in the electropolymerization [6]. The bands at 1145, 1984 and 626 cm^{-1} indicate the

TABLE I Cyclic voltammetric and conductivity data for the copolymers in acetonitrile containing 0.5 M $LiClO_4$. Charge = 300 mC, sweep rate = 50 mV s^{-1}

Conc. of pyrrole (M)	Conc. of Indole (M)	E_p^A (V)	E_p^C (V)	I_p^A (mA)	I_p^C (mA)	σ (ohm^{-1} cm^{-1})
0.05	0.05	0.33	0.17	1.07	0.93	3.2×10^{-4}
0.1	0.1	0.30	0.20	1.14	1.10	8.6×10^{-4}
0.25	0.25	0.35	0.20	0.69	0.53	1.1×10^{-3}
0.5	0.5	0.23	0.22	0.35	0.25	2.6×10^{-3}
0.5	0.1	0.01	−0.14	1.62	1.15	7×10^{-2}
0.5	0.25	0.03	−0.04	1.10	1.07	4×10^{-2}
0.1	0.25*	0.30	0.20	0.30	0.27	2.4×10^{-3}
		0.55	0.45	0.05	–	
0.1	0.5*	0.38	0.30	0.17	0.19	7.5×10^{-4}
		0.58	0.47	0.20	0.15	
0.1	0	−0.14	−0.39	2.10	1.62	7.3
0.5	0	−0.15	−0.44	2.40	2.13	3.9×10^{-1}
0	0.1**	0.18	0.11	0.43	0.61	4.7×10^{-2}
		0.55	0.47	0.35	0.48	
0	0.5**	0.11	0.03	0.05	0.03	10^{-4}
		0.49	0.38	0.23	0.18	

*Two redox couples—first couple is due to copolymer and the second is polyindole.

**Two redox couples—first couple is assigned to indole trimer and the second is polyindole [35].

TABLE II FT-IR data of homopolymers and copolymers

Homopolymer/copolymer	IR band positions (cm^{-1})												
Polypyrrole	3100			1520	1470		1275	1144 1121	1089	964	890	790 711	626
Polyindole	3261	2923 2852		1598 1567	1497 1451	1319	1248	1145 1112	1086	943 914	883 842 800	741	669 628
Co-polymer (0.1 M pyrrole/0.1 M indole)	3398	2924 2853	1710	1559	1456 1401	1301	1205	1146 1112	1083	926		798 741	669 628
Co-polymer (0.5/0.25)	3458	2925 2854	1716	1629 1552	1462 1402	1325	1205	1146 1116	1084	961 930		781 742	669 628
Co-polymer (0.1/0.5)	3395	2923 2852	1710	1615	1491 1457 1418	1325	1245 1211	1144 1114	1086	965 925	876	802 744	671 629

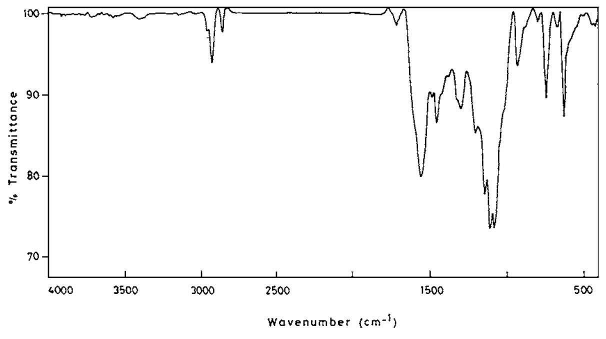


Figure 7 FT-IR spectrum of perchlorate-doped copolymer. Sample was prepared from acetonitrile containing 0.5 M $LiClO_4$ using a comonomer feed ratio of 0.1 M pyrrole and 0.1 M indole (group I).

presence of perchlorate dopant. The bands at 1475, 1600 and 750 cm^{-1} correspond to the stretching and bending modes of aromatic alkene. The presence of both bands at 790 and 1325 cm^{-1} in the spectra of all the copolymer samples (Fig. 7) indicate that the 1,3 coupling of the pyrrole moiety in the indole and 2–2′ coupling in pyrrole are retained during copolymer formation. The IR spectra of all the copolymer samples show a new band at 1710 cm^{-1}. This band is assigned to the 2,3 coupling (α-β unsaturated coupling in 5-membered rings) of the pyrrole units in the two monomers [31]. The IR spectra of samples belonging to group III contain additional bands at 1491 cm^{-1} and 1245 cm^{-1} which are also present in the spectrum of pure polyindole. This indicates the formation of a mixture of both the copolymer and polyindole supporting the inference made from their cyclic voltammetric growth data shown in Fig. 6.

The *in situ* UV-visible spectral characteristics of the copolymer films at various potentials were recorded. The as-grown films of the two homopolymers, polypyrrole and polyindole, change their colour from yellow to black and green respectively when switched from the reduced state to the oxidised state. The copolymer films are found to switch from light brown to black. The sharpness of this colour change in the copolymer films is somewhat less compared to that of the homopolymers. However, the spectral data (Fig. 8) show a definite and linear increase in absorbance in the visible region with increasing oxidation potentials.

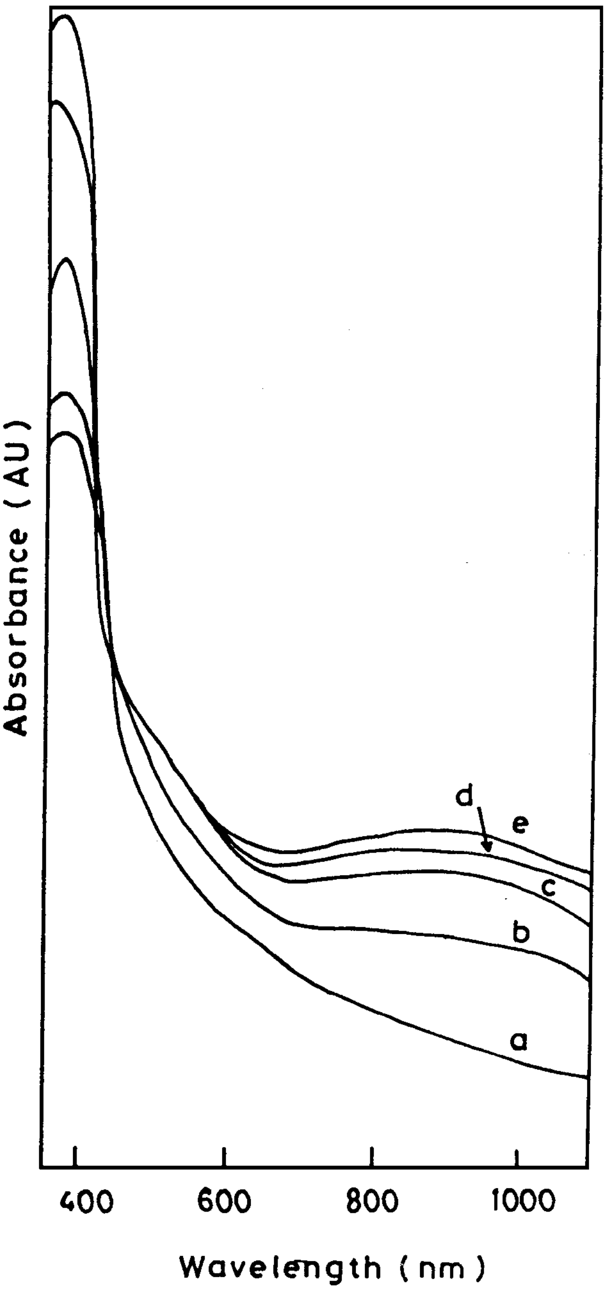


Figure 8 In-situ optical absorption spectra of the copolymer film coated on an optically transparent indium tin oxide electrode at (a) −0.4 V, (b) −0.2 V, (c) 0 V, (d) +0.2 V and (e) +0.4 V vs Ag/Ag$^+$. Film was prepared from acetonitrile containing LiClO$_4$ using a feed ratio of 0.1 M pyrrole and 0.1 M indole (group I).

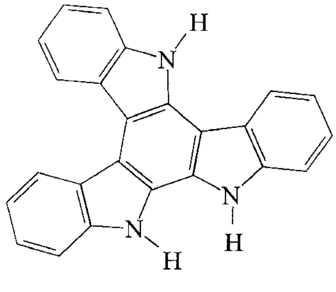
Polypyrrole-perchlorate films prepared in acetonitrile has been reported to have fibrous [32, 33] and micro-spheroid morphologies [16]. Detailed investigations on polyindole showed that the polymer morphology depended on the preparation conditions, counter ion and nature of solvent and a cauliflower shape is the most commonly observed morphology [8]. We have got a fibrous morphology for our polyindole sample (Fig. 9a). The poly(pyrrole-co-indole) samples show a dispersed granular morphology (Figs 9b–e). The granular regions are more for the sample prepared with a higher concentration of indole than pyrrole (group III). It may be noted that it is this sample which shows a lower conductivity of all the copolymer samples (Table I).

3.3. Cyclic voltammetry

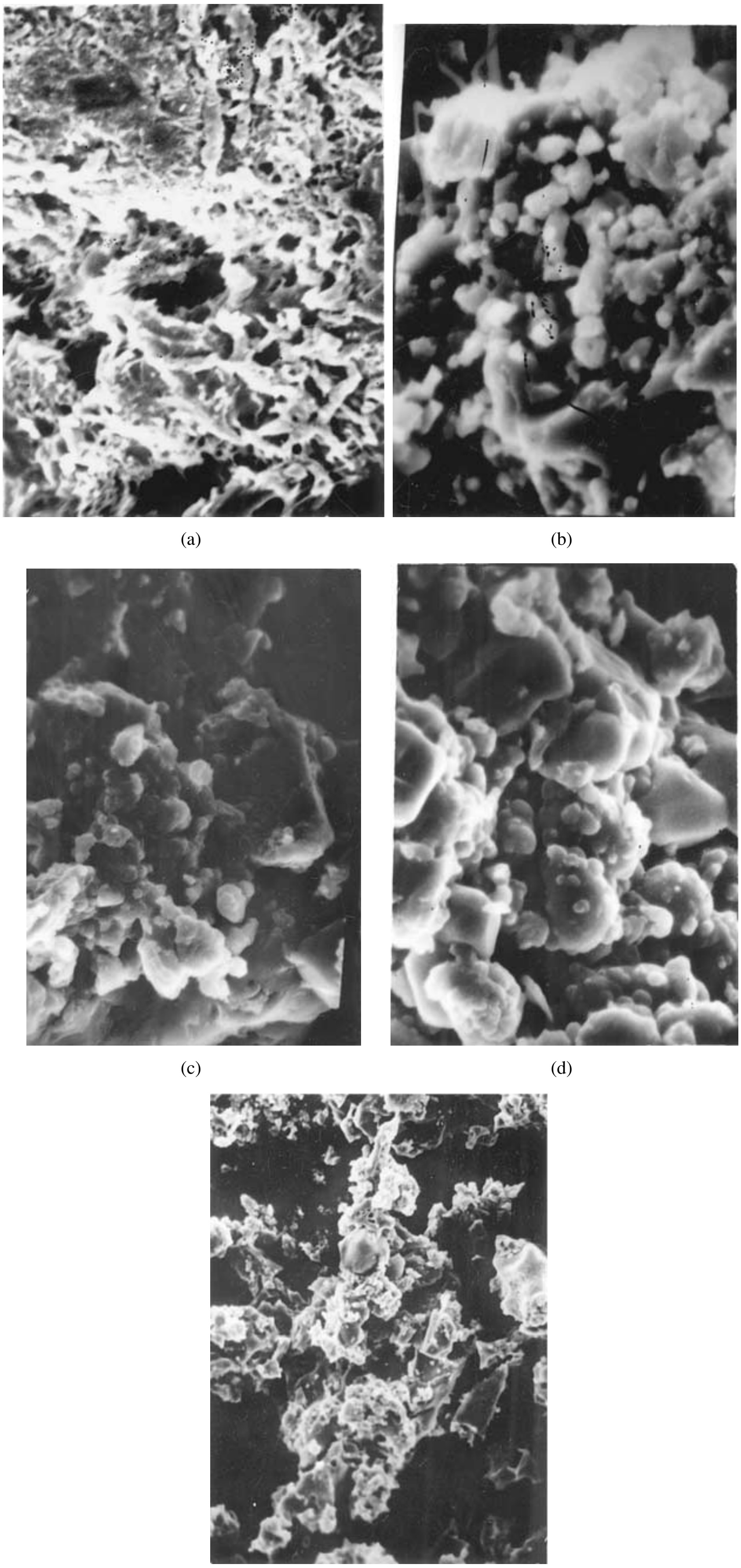
Table I shows the complete cyclic voltammetric data obtained with thin films of various copolymers in the background electrolyte solution of acetonitrile containing 0.5 M LiClO$_4$. Representative cyclic voltammograms under the three groups are shown in Figs 10–12.

The peak potentials of all the copolymers lie between the redox potentials of polypyrrole (−0.15 V) and polyindole (0.5 V). The anodic and cathodic peak currents for the same deposition charge are found to depend on the feed ratio. It is generally observed, that films prepared with a larger concentration of pyrrole yield higher peak currents. On the other hand, a higher concentration of indole does not help in improving the redox currents. This can be explained by the fact that the conductivity of polyindole is about three orders less than that of polypyrrole. In all cases, a 10% decrease in peak currents has been observed for about 250 continuous redox cycles. Further, it may be interesting to note from the peak current values among group I in Table II, that the film prepared with a lower concentration of the two monomers in the feed ratio gives higher peak currents. This behaviour is similar to that of polyindole (Fig. 13) [34]. The electrochemistry of polyindole, particularly at low concentrations of the monomer, gets complicated by its trimer formation during polymerization [35]. The trimer is electroactive ($E_p^A = 0.12$ V, $E_p^C = 0.08$ V) and proposed to have a structure with free N-H linkages as shown in Scheme 1. In Fig. 13, the first anodic peak is assigned to the oxidation of the trimer while the second peak is due to the doping of polyindole. The decrease in current with increasing concentration of indole does not seem to be associated with the trimer. The anomaly seems to originate from the growth pattern of polyindole. The current-time curves recorded during the growth of polyindole at various concentrations of the monomer are shown in Fig. 14. The transients obtained at low concentrations indicate progressive nucleation whereas those at higher concentrations correspond to instantaneous nucleation [36, 37]. The latter possibly leads to the formation of a randomly oriented cross-linked polymer resulting in a decrease in electroactivity.

Fig. 12 shows the cyclic voltammograms of the copolymers prepared with a higher concentration of indole than pyrrole in the comonomer feed ratio (group III). Based on the agreement of peak potential values, the first redox process ($E_p^A = 0.38$ V, $E_p^C = 0.30$ V) is assigned to the doping-dedoping of the copolymer while the second process ($E_p^A = 0.60$ V,



Scheme 1 Structure of indole trimer.



(a) (b)

(c) (d)

(e)

Figure 9 Scanning Electron Micrographs of (a) polyindole (0.1 M), (b) copolymer prepared with 0.5 M pyrrole and 0.5 M indole, (c) copolymer prepared with 0.1 M pyrrole and 0.1 M indole (group I) (d) copolymer prepared with 0.5 M pyrrole and 0.25 M indole (group II) and (e) copolymer prepared with 0.1 M pyrrole and 0.5 M indole (group III). Magnification for all figures: 3000.

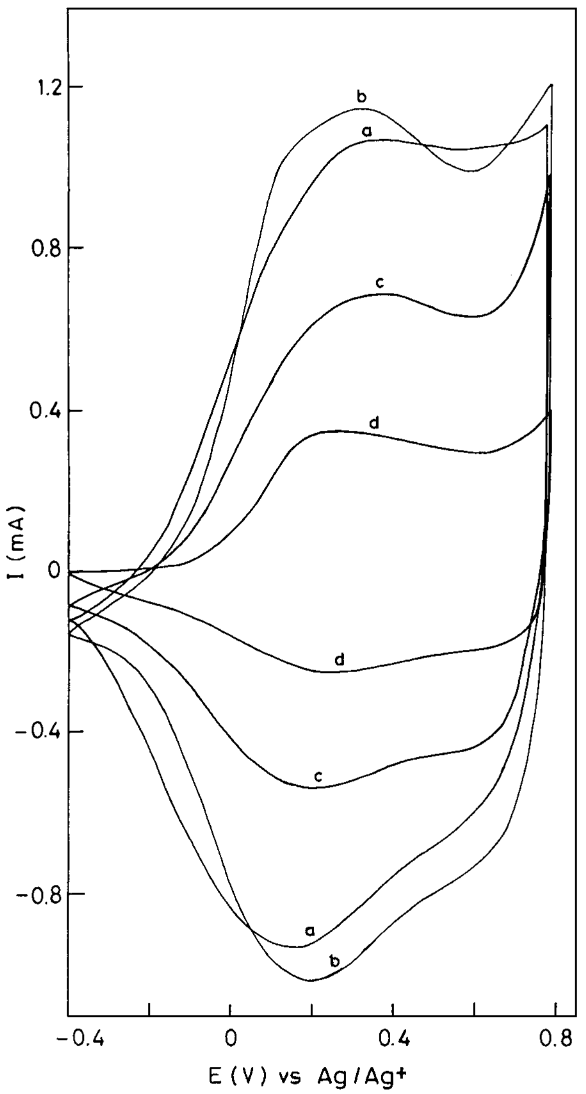


Figure 10 Cyclic voltammograms of copolymer films electrodeposited on a Pt electrode, in background electrolyte solution of acetonitrile containing 0.5 M $LiClO_4$. Samples were prepared using a feed ratio containing equal concentration of pyrrole and indole (group I). Concentration of each of the monomers in the feed ratio (a) 0.05 M, (b) 0.1 M, (c) 0.25 M and (d) 0.5 M. $dE/dt = 50$ mV s^{-1}; deposition charge = 300 mC.

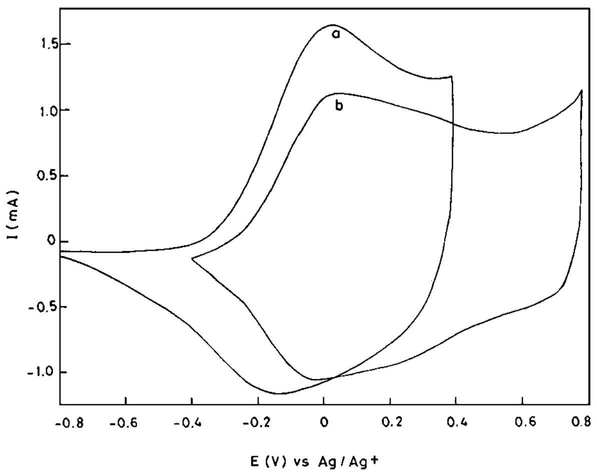


Figure 11 Cyclic voltammograms of copolymer films electrodeposited on a Pt electrode, in background electrolyte solution of acetonitrile containing 0.5 M $LiClO_4$. Samples were prepared using a feed ratio containing a higher concentration of pyrrole than indole (group II) Concentration of the monomers in the feed ratio (a) 0.5 M pyrrole and 0.1 M indole and (b) 0.5 M pyrrole and 0.25 M indole. $dE/dt = 50$ mV s^{-1}; deposition charge = 300 mC.

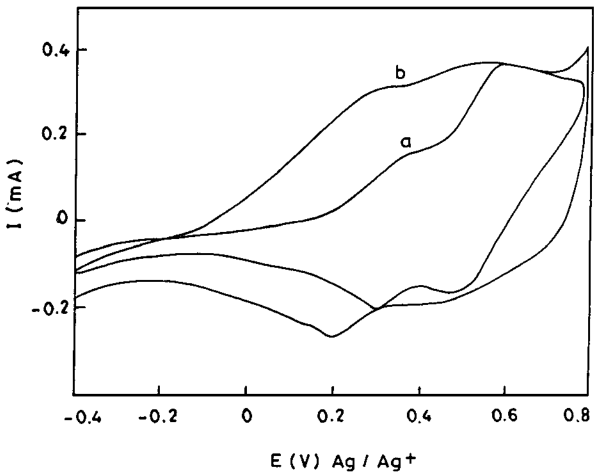


Figure 12 Cyclic voltammograms of copolymer films electrodeposited on a Pt electrode, in background electrolyte solution of acetonitrile containing 0.5 M $LiClO_4$. Samples were prepared using a feed ratio containing a higher concentration of indole than pyrrole (group III). Concentration of the monomers in the feed ratio (a) 0.1 M pyrrole and 0.5 M indole and (b) 0.1 M pyrrole and 0.25 M indole. $dE/dt = 50$ mV s^{-1}; deposition charge = 300 mC.

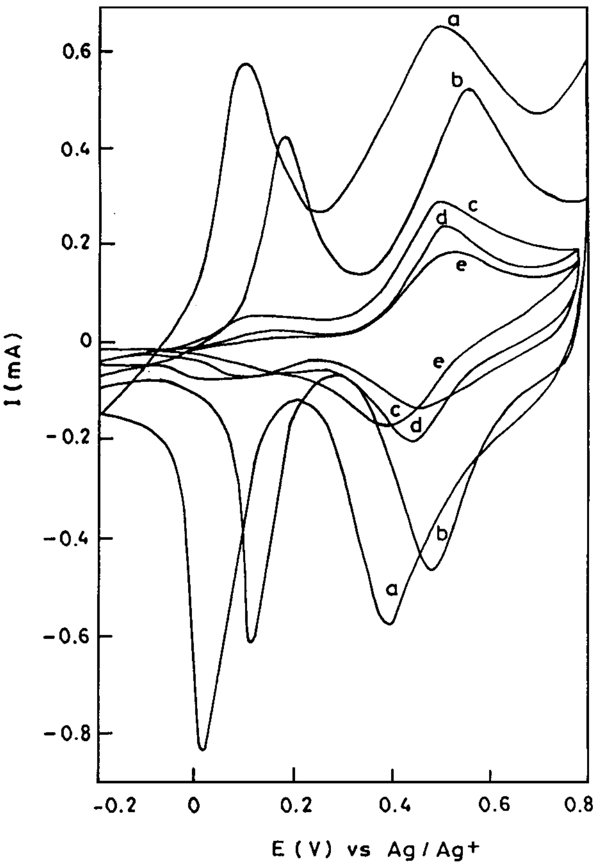
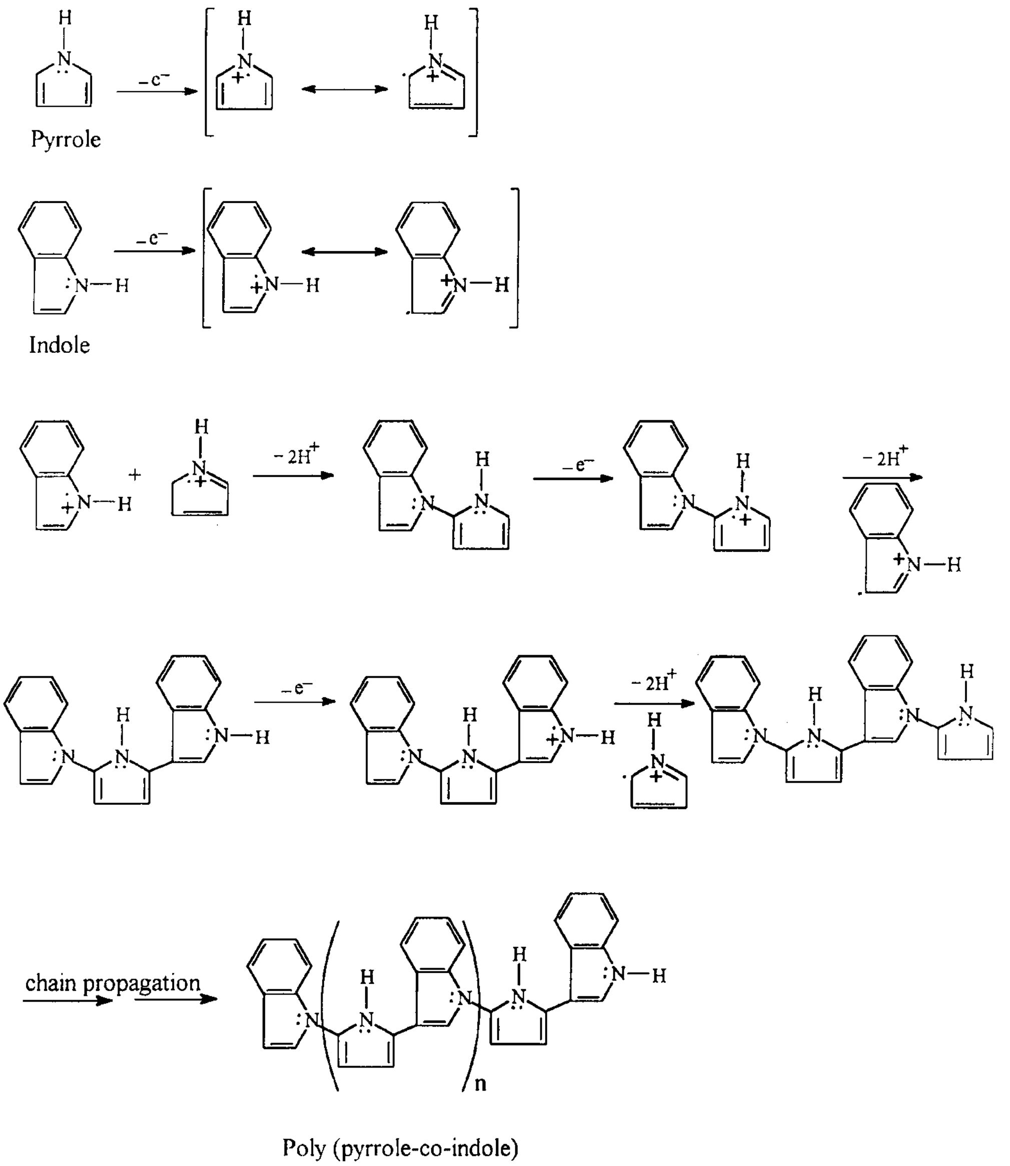


Figure 13 Cyclic voltammograms of polyindole electrodeposited on a Pt electrode using various concentrations of indole (a) 0.1 M, (b) 0.25 M, (c) 0.5 M and (d) 0.75 M and (e) 1 M. $dE/dt = 50$ mV s^{-1}; deposition charge = 300 mC.

$E_p^C = 0.51$ V) is due to that of polyindole. The indole trimer peak is less predominant at such high concentrations of the monomer (see Fig. 13).

3.4. Mechanism of copolymerization

The onset potentials for the oxidation of the two monomers are very close to each other. The IR spectral



Scheme 2 Copolymerization of pyrrole and indole.

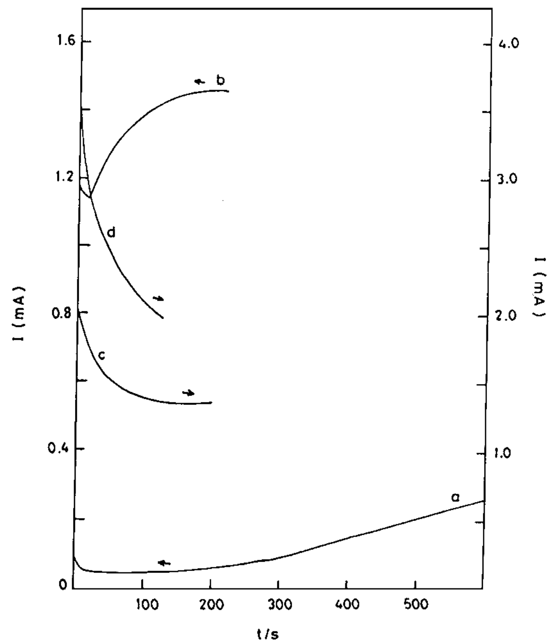


Figure 14 I-t transients in response to potential steps from 0 to 0.75 V vs Ag/Ag^+ as a function of indole concentration (a) 0.1 M, (b) 0.25 M, (c) 0.5 M and (d) 1 M in acetonitrile containing 0.5 M $LiClO_4$.

data suggests the presence of α-β (2–3′) coupling in the copolymer. Assuming equal reactivity for the two monomer cation radicals, the following scheme (Scheme 2) is speculated for the mechanism of copolymerization from a solution containing equal concentrations of pyrrole and indole (group I). It is likely that under the conditions employed for group II and group III, the structure of the copolymer would contain more number of pyrrole and indole units respectively.

4. Conclusions

We have demonstrated that pyrrole and indole can be electrochemically copolymerized to get an array of materials with different redox potentials. The compositions of the copolymers can be altered by varying the comonomer feed ratio. The results indicate that the highest electroactivity can be obtained when the copolymer is prepared from a feed ratio containing 0.1 M of each of the two monomers.

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