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Synthesis, characterization, and reactivity ratio studies on new sulfide copolymers containing ethylbenzene units

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Abstract

Soluble new sulfide copolymers were synthesized readily by the polycondensation of ethylene dibromide (EDB) (or methylene dibromide (MDB)) with styrene dibromide (SDB) and sodium sulfide (Na_2S) in the presence of phase transfer catalyst. The copolymers were characterized by using Fourier transform-infrared, ^{1}H NMR, ^{13}C NMR, gel permeation chromatography, and thermogravimetric analysis (TGA) techniques. The copolymer composition obtained from the ^{1}H NMR spectra led to the determination of reactivity ratios. The analysis of reactivity ratios revealed that both EDB and MDB are more reactive than SDB towards Na_2S, and copolymers formed are random in nature. Furthermore, it also gave an insight on the microstructure of the copolymers that both poly (ethylene sulfide-co-styrene sulfide) (p(ES-co-SS)), and poly(methylene sulfide-co-styrene sulfide) (p(MS-co-SS)) copolymers have more of blocky structure with increase in the concentration of ethylene sulfide (ES) or methylene sulfide (MS) units in the respective copolymers. The TGA was used to find out the thermal stability of these polymers. The XRD data indicated an increase in the amorphous content of the copolymers with an increase in the concentration of styrene sulfide (SS) units and thereby resulting in most of these copolymers being soluble in common organic solvents. The solubility and molecular weight of the polymers formed were dependent on the concentration of SDB taken in the feed.

Keywords: Polysulfide copolymers; Reactivity ratio; Soluble

1. Introduction

Polysulfide polymers are one of the important classes of polymers with extensive applications as sealants, adhesives, insulators, etc. [1–17]. They are commercially synthesized by condensing an organic dihalide with sodium polysulfide [3]. Earlier, methylene dichloride and ethylene dichloride have been extensively used in the manufacture of polysulfide polymers by Thiokol company [12]. But the resultant polysulfide polymers are insoluble in common organic solvents, hence could not be useful as industrial materials. Catsiff et al. [2] have reported that heating of poly(ethylene sulfide) at its melting point leads to evaluation of toxic gases such as carbon disulfide, hydrogen sulfide, etc. Later on, thiol-terminated liquid polysulfides that are soluble in organic solvents have been investigated but this procedure could not be applied to monosulfide polymers [3,12].

Introduction of kink structures in the backbone is known to reduce crystallinity and promote solubility of the polymers. In this paper, we intend to apply this concept to enhance the solubility of monosulfide polymers in common organic solvents by introducing kink structure in the form of ethyl benzene unit, whereby the phenyl substituents restrict the close packing of the polymer chain resulting in increasing in the amorphous content of the copolymers and soluble. New copolysulfide polymers based on ethylene dibromide (EDB) with styrene dibromide (SDB) and Na_2S is given by Eq. (1) in the presence of phase

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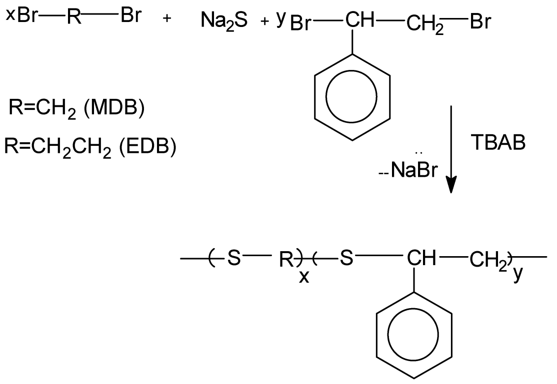
transfer catalyst such as



(1)

tetrabutylammonium bromide (TBAB) has been synthesized.

A plethora of information is available on the copolymer composition and reactivity ratio determination using free radical copolymerization [18,19]. However, determination of reactivity ratio on the condensation type copolymers is rare in the literature. This paper deals with the copolymer composition and reactivity ratio determination of polysulfide copolymers first time in the literature. The composition and reactivity ratios of these copolymers were determined from ^{1}H NMR analysis, and the copolymers were characterized by using FTIR, ^{13}C NMR, gel permeation chromatography (GPC), thermal analyses and XRD. It has been observed that the solubility behaviors of these copolymers were dependent upon the amount of styrene sulfide units incorporated into the copolymer backbone.

2. Experimental section

2.1. Materials

The starting material styrene dibromide was prepared according to the reported [20] procedure, and purified before use. Ethylene dibromide (Lancaster, UK), methylene dibromide (Lancaster, UK), and sodium sulfide nona hydrate (Aldrich, USA), tetrabutylammonium bromide (TBAB), tetrabutylammoniumhydrogen sulfate (TBAHS), and cetyltrimethylammonium bromide (CTAB) were obtained commercially and used as received.

2.2. Techniques

Molecular weight of the polymers were determined by GPC with 515 HPLC pump, calibrated with polystyrene narrow standards through 10^3, 10^4, 10^5 Å 'styragel' columns at 30 °C with tetrahydrofuran as solvent (flow rate 1 ml/min). Elemental analyses (C and H) were performed on Heraeus CHN-Rapid analyzer. Fourier Transform-Infrared (FT-IR) spectra of the polymers were recorded on a NICOLET Impact 400 spectrometer. The ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AC 200 F NMR spectrometer as solutions in $CDCl_3$ and $CHCl_3$, respectively, with TMS as an internal standard. A capillary tube containing D_2O was placed inside the NMR tube, which served as an external lock while recording the ^{13}C NMR spectrum. TGA spectra were obtained using a Seiko thermal analyzer with a 20 °C/min heating rate in an atmosphere of nitrogen gas flowing at 100 ml/min. Powder XRD measurements were carried out using a JEOL GSM 20A diffractometer using Cu Kα as the radiation source with a scan rate of 4 °C/min.

2.3. Synthesis of homopolymers

The PES and PMS were synthesized by using reported procedure [1]. Elemental analysis data of PES and PMS are as follows. Calcd for PES: C 39.96; H, 6.68. Found: C, 38.86; H, 6.22. Calcd for PMS: C, 26.06; H, 4.36. Found: C, 26.75; H 4.54. The synthesis of poly(styrene sulfide) (PSS) has been reported [21]. Elemental analysis of PSS is as follows. Calcd: C, 70.54; H, 5.92. Found: C, 71.22; H, 6.10.

2.4. Synthesis of copolymers

The copolymers were synthesized by the interfacial polycondensation using a phase transfer catalyst. A typical procedure for the synthesis of p(MS-co-SS) copolymer IV is as follows. To a solution of $Na_2S\cdot9H_2O$ (2.8822 g, 12 mmol) in 20 ml of water, 20 ml of $CHCl_3$ solution containing MDB (1.303 g, 7.5 mmol) and SDB (0.659 g, 2.5 mmol) was added followed by the addition of TBAB (0.064 g, 0.2 mmol) as a PTC. The mixture was stirred for 24 h. The $CHCl_3$ layer was separated, washed several times with water to remove sodium bromide and dried over anhydrous sodium sulfate. Then the $CHCl_3$ solution was poured into a large excess of methanol to precipitate the copolymer. The copolymer was further purified by repeated washings using methanol and finally dried to a constant weight in vacuum. By using the same procedure, p(ES-co-SS) copolymer has been synthesized.

Elemental analysis data of p(ES-co-SS) and p(MS-co-SS) copolymers are as follows. Calcd (based on the copolymer composition obtained from ^{1}H NMR) for p(ES-co-SS): C 55.22; H, 6.30. Found: C, 54.52; H, 6.12. Calcd for p(MS-co-SS): C, 59.24; H, 5.14. Found: C, 58.54; H 4.86.

3. Results and discussion

Before attempting the copolymer synthesis, the effect of phase transfer catalysts such as TBAB, TBAHS, and CTAB on the molecular weight and yield was studied for copolymer IV. It could be seen from Table 1 that TBAB form a comparatively higher molecular weight polymer.

The effect of concentration of TBAB catalyst is also

Table 1
Molecular weight, yield of the copolymers, and PSS

Molecular weight, yield	Effect of catalyst[a] (30 °C, 0.2 mmol)		Effect of TBAB concentration[a] (30 °C)		Effect of temperature[a] (0.2 mmol, TBAB)		p(ES-co-SS)			p(MS-co-SS)			PSS
	TBAB (TBAHS)	CTAB	0.06 (0.1) mmol	0.2 (0.3) mmol	30 °C (60 °C)	100 °C	0.25^b $(0.50)^b$	(0.65) (0.75)	0.80 (0.90)	0.25^b $(0.35)^b$	0.50^b (0.65)	0.75 (0.90)	
M_w, × 10^4	3.82 (3.53)	3.35	1.78 (3.02)	3.82 (2.67)	3.82 (1.69)	1.70	–	– (3.82)	3.65 (4.46)	–	– (2.22)	1.86 (2.36)	2.28 $(1.60)^c$
Yield (%)	54.84 (63.14)	61.09	41.59 (51.74)	54.84 (66.00)	54.84 (76.28)	72.60	69.12 (65.28)	57.35 (54.84)	50.29 (46.24)	91.00 (87.90)	87.28 (51.18)	50.69 (44.78)	72.14 $(71.12)^c$

[a] 0.75 mol SDB, and 0.25 mol EDB with Na_2S.

[b] Due to limited solubility, unable to measure molecular weight.

[c] Polymer synthesized at reaction temperature of 100 °C under identical conditions of 30 °C.

shown in Table 1. The higher molecular weight polymer is obtained when the concentration of the catalyst was 0.2 mmol and the molecular weight decreased for 0.30 mmol catalyst concentration. The effect of the reaction temperature on the molecular weight and yield was examined over the temperature range of 30–100 °C (Table 1). The higher molecular weight polymer was obtained at 30 °C and decreases at higher temperatures. We believe that the formation of lower molecular weight at higher temperature could be either due to molecular weight reduction by alkaline hydrolysis of the resulting polysulfide [22] or the elimination of hydrobromic acid in alkaline condition from styrene dibromide [23]. This fact is confirmed when the molecular weight measurement was carried out for neat PSS, polymerized at 100 °C under identical conditions (Table 1).

As can be seen from Table 1, optimum amount of the catalyst, and polymerization temperature for TBAB were found to be at 0.2 mmol, and 30 °C, respectively. The other copolymers were synthesized by the above-mentioned procedure; molecular weight and yield are reported in Table 1. It could be seen that the molecular weight and yield decreases with an increase in the concentration of SDB in the feed (Table 1).

3.1. FT-IR

Fig. 1 shows the FT-IR spectrum of PSS and copolymers. In PSS (Fig. 1a) IR absorptions at 3058, 3027, 1598, 1491, 1450 cm^{-1} showed the presence of a phenyl group with overtones from 1679 to 1949 cm^{-1}. The strong bands at 697 and 763 cm^{-1} are indicative of monosubstituted aromatic ring. The aliphatic C–H stretching absorbs at 2919 cm^{-1}. FT-IR spectra of p(ES-co-SS), and p(MS-co-SS) are presented in Fig. 1(b) and (c), respectively. The absorptions due to aliphatic group frequencies of both ES, and SS (or MS, and SS) units are observed together.

3.2. Copolymer composition analysis

The ^1H NMR spectrum of $p(ES_{0.43}\text{-co-}SS_{0.57})$ in $CDCl_3$ is displayed in Fig. 2. The peak between 7.0 and 7.5 ppm is due to the phenyl protons and the broad absorption in the range of 2.3–4.4 ppm is due to the backbone CH–S and CH_2S protons. The compositions of the copolymers were determined by comparing the area of the phenyl peaks with the total backbone proton peaks. Table 2 lists the compositions of the copolymers determined by ^1H NMR spectroscopy and the same is shown graphically in Fig. 3. From Fig. 3, it is clear that the reactivity of SDB is less than EDB towards Na_2S. This reactivity difference is due to the nature of bromide groups; both are primary in EDB whilst in SDB, one primary bromide and a secondary bromide is present. It is well known that the primary bromides are more reactive

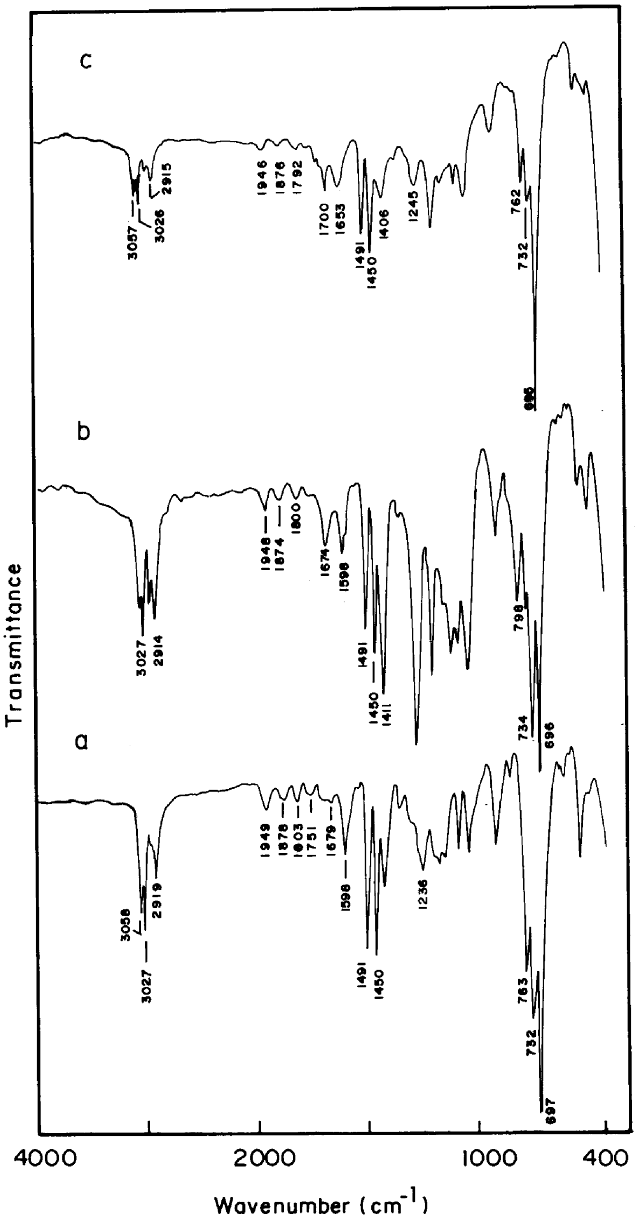


Fig. 1. FT-IR spectra of (a) PSS, (b) p(ES-co-SS), and (c) p(MS-co-SS).

than their secondary counterparts for the nucleophilic substitution reaction [24]. It has been reported in literature that the primary alkyl halides are more reactive than secondary and tertiary towards nucleophilic substitution reaction [3]. Hence, we have more EDB reacting than SDB in the present case.

A similar analysis could also be made for p(MS-co-SS) copolymer. In the ^{1}H NMR spectrum of the p(MS$_{0.5}$-co-SS$_{0.5}$) copolymer in $CDCl_3$ (figure is not presented here) the phenyl protons absorption was found between 7.0 and 7.5 ppm, the backbone CH_2S and CH–S protons resonances were observed in the region 2.5–4.6 ppm. Similar to the p(ES-co-SS) systems, in the present case also, the phenyl peaks area was compared with the total backbone protons area to get the composition. The compositions determined from the ^{1}H NMR spectra are listed in Table 2 and the same is graphically displayed in Fig. 3. Here also, the MDB was found to be more reactive than SDB towards Na_2S. The reason being, similar to EDB, here also the bromides of MDB are primary, hence more MDB is getting into the polymer backbone compared to SDB.

Table 2
Details of copolymerization and copolymerization characteristics

Copolymer system	Molefraction of SDB in the feed	Molefraction of SDB in the copolymer
p(ES-co-SS) (I)	0.25	0.09
(II)	0.50	0.26
(III)	0.65	0.35
(IV)	0.75	0.43
(V)	0.80	0.57
(VI)	0.90	0.76
p(MS-co-SS) (i)	0.25	0.12
(ii)	0.35	0.19
(iii)	0.50	0.39
(iv)	0.65	0.50
(v)	0.75	0.70
(vi)	0.90	0.84

3.3. Determination of reactivity ratios

The reactivity ratios were obtained below 10% conversion. Polymers were precipitated using petroleum ether as non-solvent for reactivity ratio determination.

SDB contains a primary and a secondary bromide group, which have different reactivities. For the determination of reactivity ratios, both the bromide groups in SDB are assumed to have a similar reactivity by us for mathematical simplicity.

In step-growth copolymerization, it is well known that the reactivities of the functional groups are independent of the chain length to which they are attached. Comonomers in such systems would be randomly distributed along the chain proportional to their concentrations in the feed [24]. Because of this, the reactivity ratios of comonomers in step-growth copolymerization are unity. However, deviation is observed due to reactivity differences on account of various structural factors like, for example, proximities of the functional groups and whether the functional group is primary or secondary, etc. It is natural that in such situations, the more reactive monomer would enter into the polymer first [24]. In the present system, the reactivities were found to be different and hence, it was thought necessary to obtain the reactivity ratios of the comonomers. A simple kinetic scheme and subsequent derivation for p(ES-co-SS) is discussed below.

The suffix 1 and 2 represents the SDB and EDB units in the chain, respectively. The four possible reaction

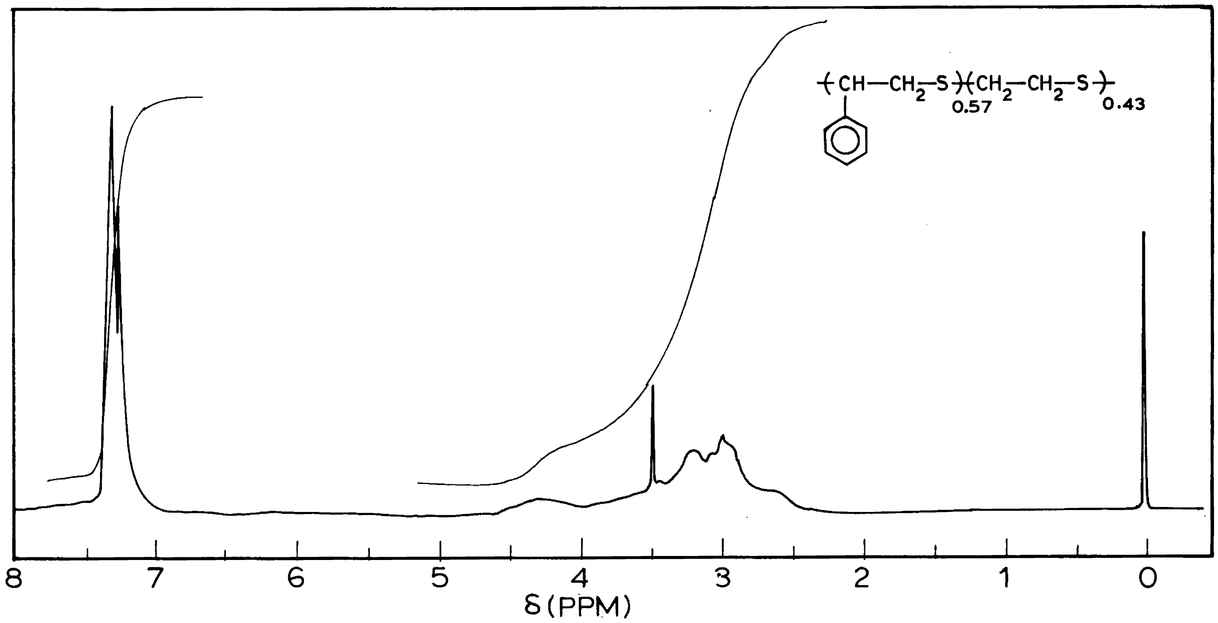
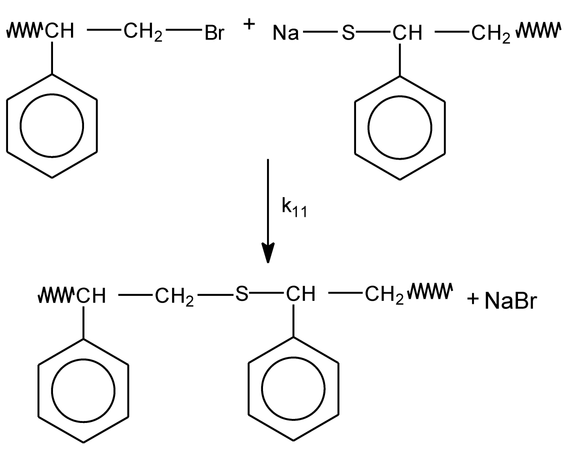


Fig. 2. ^1H NMR spectra of p($ES_{0.43}$-co-$SS_{0.57}$) in $CDCl_3$.

sequences are shown in Eqs. (2)–(5):



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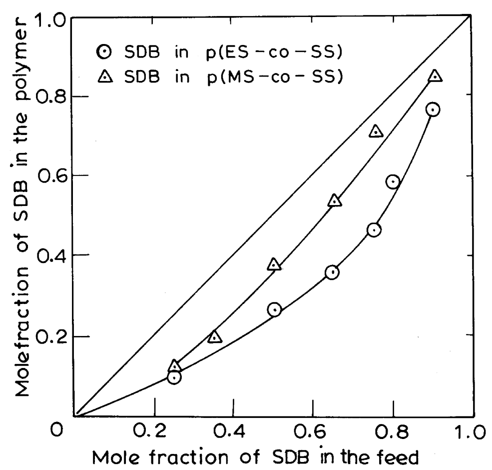
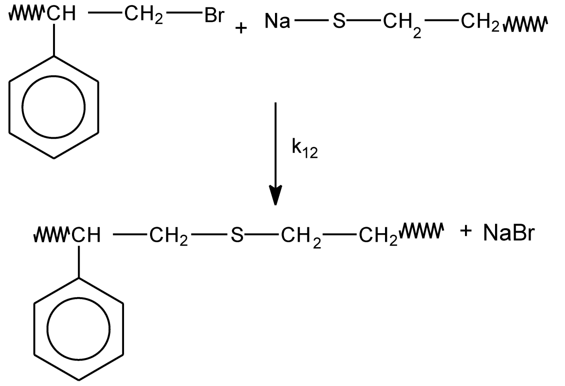


Fig. 3. Variation of the instantaneous copolymer composition as a function of SDB feed composition.



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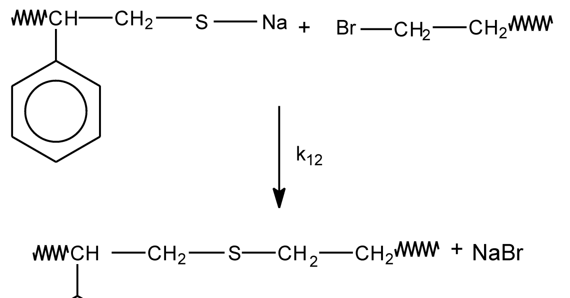

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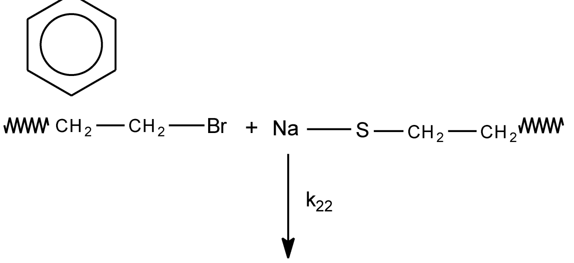


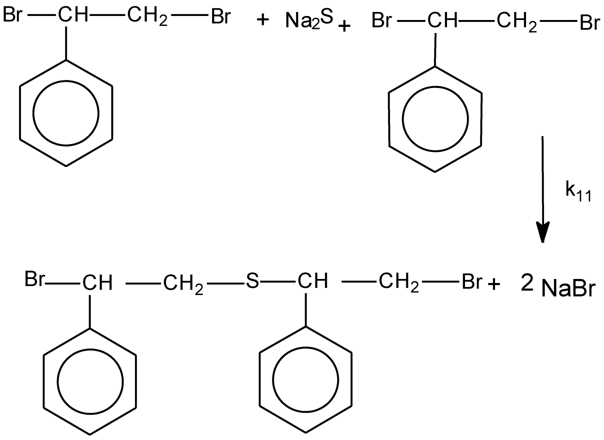
(5)

Since in condensation reaction, the reactivity of the growing end group does not depend on the chain length, Eqs. (2)–(5)

Table 3
Reactivity ratios of SDB, EDB and MDB

Copolymer system	Fineman–Ross	Kelen–Tudos
p(ES-co-SS)	$r_1 = 0.33$ $r_2 = 3.5$	$r_1 = 0.33$ $r_2 = 3.39$
p(MS-co-SS)	$r_1 = 0.55$ $r_2 = 1.5$	$r_1 = 0.4$ $r_2 = 1.73$

can be simplified as in Eqs. (6)–(8):



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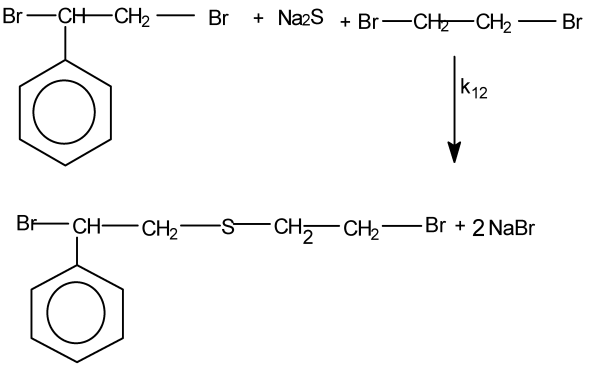

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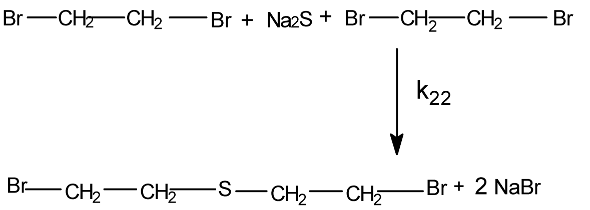

(8)

The rates of disappearance of the two bromides, i.e. SDB and EDB are given by

$$\frac{-\mathrm{d[SDB]}}{\mathrm{d}t} = k_{11}[\mathrm{SDB}]^2[\mathrm{Na_2S}] + k_{12}[\mathrm{SDB}][\mathrm{Na_2S}][\mathrm{EDB}] \tag{9}$$

$$\frac{-\mathrm{d[EDB]}}{\mathrm{d}t} = k_{22}[\mathrm{EDB}]^2[\mathrm{Na_2S}] + k_{12}[\mathrm{SDB}][\mathrm{Na_2S}][\mathrm{EDB}] \tag{10}$$

The ratio of Eq. (9) by Eq. (10) gives,

$$\frac{\mathrm{d[SDB]}}{\mathrm{d[EDB]}} = \frac{k_{11}[\mathrm{SDB}]^2[\mathrm{Na_2S}] + k_{12}[\mathrm{SDB}][\mathrm{Na_2S}][\mathrm{EDB}]}{k_{22}[\mathrm{EDB}]^2[\mathrm{Na_2S}] + k_{12}[\mathrm{SDB}][\mathrm{Na_2S}][\mathrm{EDB}]} \tag{11}$$

$$\frac{\mathrm{d[SDB]}}{\mathrm{d[EDB]}} = \frac{[\mathrm{Na_2S}]}{\mathrm{Na_2S]}}\,\frac{k_{11}[\mathrm{SDB}]^2 + k_{12}[\mathrm{SDB}][\mathrm{EDB}]}{k_{22}[\mathrm{EDB}]^2 + k_{12}[\mathrm{SDB}][\mathrm{EDB}]} \tag{12}$$

Dividing Eq. (12) by k_{12} and by defining $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{12}$ the composition of the copolymer being formed, is given by

$$\frac{\mathrm{d[SDB]}}{\mathrm{d[EDB]}} = \frac{r_1[\mathrm{SDB}]^2 + [\mathrm{SDB}][\mathrm{EDB}]}{r_2[\mathrm{EDB}]^2 + [\mathrm{SDB}][\mathrm{EDB}]} \tag{13}$$

By defining $\mathrm{d[SDB]} = F_1$, $\mathrm{d[EDB]} = F_2$ and $[\mathrm{SDB}] = f_1$, $[\mathrm{EDB}] = f_2$, where f_1 and f_2 are the mole fraction of the monomers SDB, EDB; and F_1 and F_2 are their instantaneous compositions (mole fractions) in the copolymer, Eq. (13) can be written as

$$\frac{F_1}{F_2} = \frac{r_1 f_1^2 + f_1 f_2}{r_2 f_2^2 + f_1 f_2} \tag{14}$$

which is identical to the copolymer equation given by Mayo and Lewis [25].

Using Fineman and Ross procedure [26], Eq. (14) was further rearranged to

$$\frac{f_1\{F_1 - F_2\}}{f_2 F_1} = \frac{F_2}{F_1}\left\{\frac{f_1^2}{f_2^2}\right\} r_1 - r_2 \tag{15}$$

A plot of the $f_1/f_2\{F_1 - F_2/F_1\}$ versus $F_2/F_1\{f_1^2/f_2^2\}$ gives a straight line with slope equal to r_1 and intercept equal to $-r_2$. The Fineman–Ross plot for p(ES-co-SS) system is shown in Fig. 4a. The reactivity ratios obtained are tabulated in Table 3. Similar to p(ES-co-SS) system, for the p (MS-co-SS) system also, the r_1 and r_2 (Table 3) were determined graphically (figure is not presented here). The method of Kelen–Tudos [27] makes use of the equation

$$\eta = (r_1 + r_2/\alpha)E + r_2/\alpha \tag{16}$$

where η and E are functions of the molar ratio of the monomers in the copolymer, and the monomer mixture as defined elsewhere. r_1 and r_2 are found from the linear plot of η versus E and finding the values of η when $E = 0$ (r_2/α) and $\eta = 1(r_1)$. The Kelen–Tudos plot for p(ES-co-SS) system is shown in Fig. 4b and the corresponding reactivity ratios are tabulated in Table 3. Similar to p(ES-co-SS) system, for the p(MS-co-SS) system also, the r_1 and r_2 were determined (Table 3). The reactivity ratios determined by both the methods were found to be nearly the same for the individual systems (Table 3).

3.4. Significance of r_1 and r_2

3.4.1. p(ES-co-SS) system

Although the product of r_1 and r_2 ($r_1 \times r_2 = 1.155$)

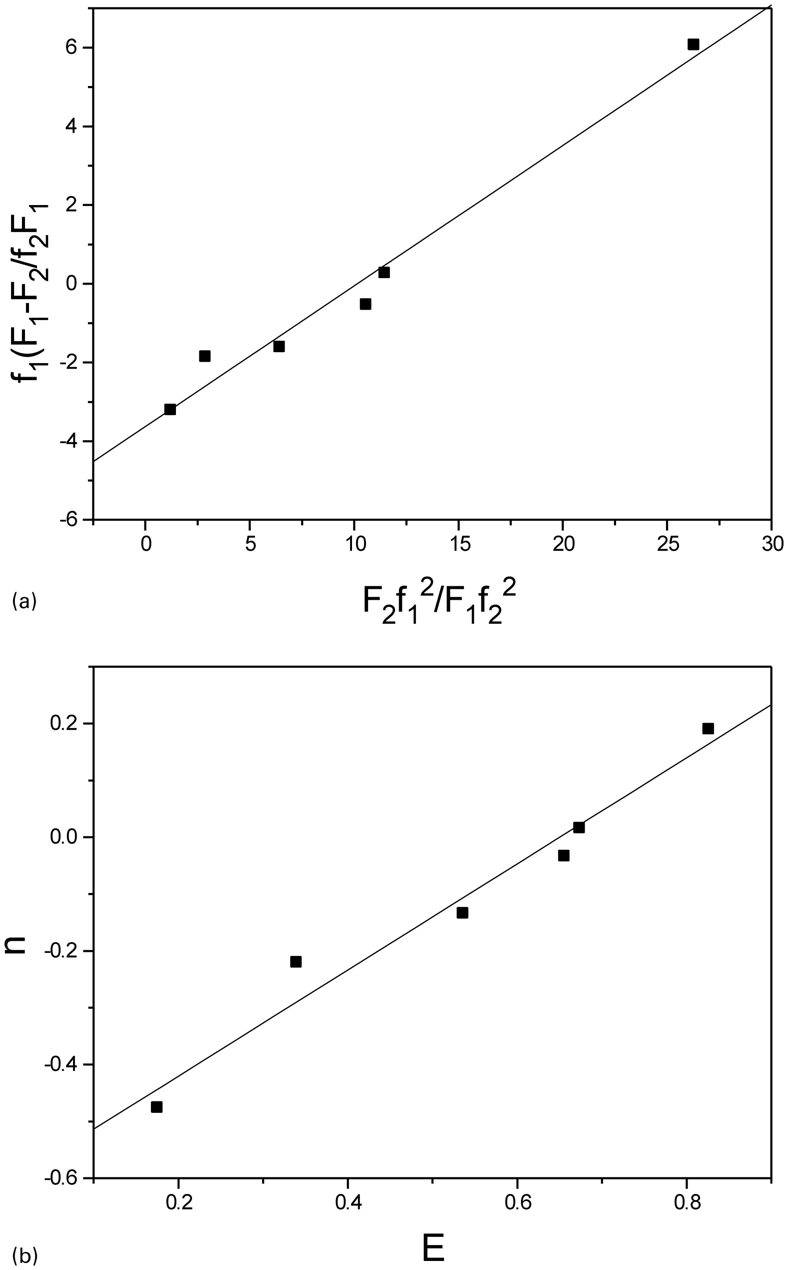

Fig. 4. (a) Fineman–Ross plot for p(ES-co-SS) system; (b) Kelen–Tudos plot for p(ES-co-SS) system.

represents the copolymer to be ideal in nature, the individual r_1 and r_2 values indicate that the copolymer will have blocks of CH_2-CH_2S units followed by a block of styrene sulfide units. This is further explained as follows.

$$r_2/r_1 = 10.6 \tag{17}$$

$$\frac{k_{22}/k_{12}}{k_{11}/k_{12}} = 10.6 \tag{18}$$

$$k_{22} = k_{11} \times 10.6 \tag{19}$$

The above equation clearly reveals that EDB is 10 times more reactive than SDB towards Na_2S. Hence during the polymerization process, although both monomers are being consumed from the start, the EDB monomer being get consumed faster rate than SDB units.

The direct pyrolysis mass spectrometry and pyrolysis–gas chromatography/mass spectrometry studies confirms that the copolymers formed are random in nature based on the thermal degradation products observed [21].

3.4.2. p(MS-co-SS) system

The product of r_1 and r_2 ($r_1 \times r_2 = 0.83$) approaches ideal copolymer structure, but a deeper analysis of r_1 and r_2

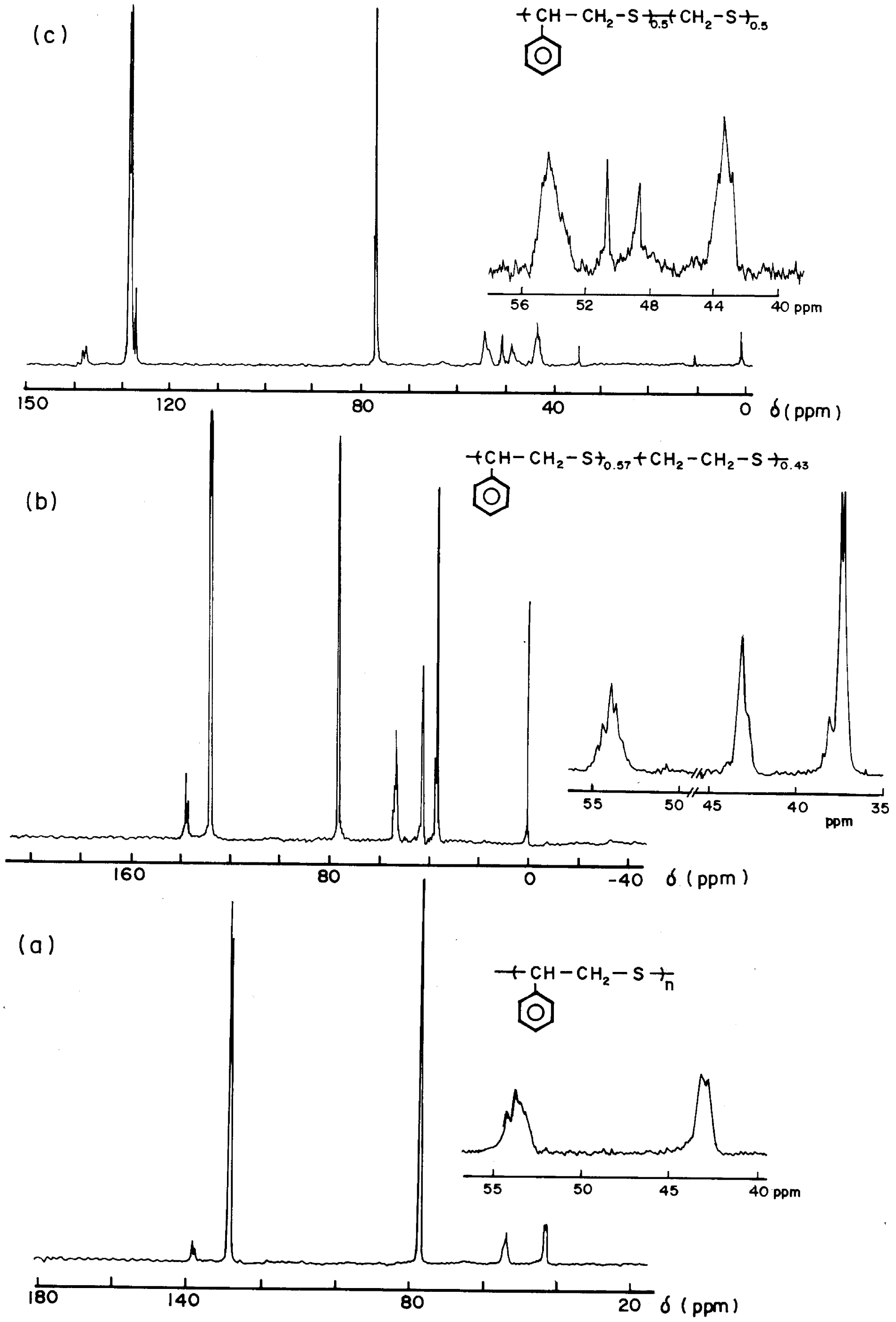

Fig. 5. ^{13}C NMR spectra of neat poly(styrene sulfide) and the copolymers in $CHCl_3$ (inserts shows the horizontal expansions).

proposes a different structure. This is explained as follows.

$$r_2/r_1 = 2.72 \quad (20)$$

$$k_{22} = k_{11} \times 2.72 \quad (21)$$

Since MDB is about three times more reactive than SDB, here also, MDB will get into copolymer first followed by SDB. But the block length of CH_2S units may not be as high as that of $CH_2{-}CH_2{-}S$ units in the p(ES-co-SS) system.

3.5. ^{13}C NMR

The broadband ^{13}C NMR spectrum of neat PSS, and copolymers in $CHCl_3$ are displayed in Fig. 5. In PSS (Fig. 5a), the peak arises at 53.71 and 43.22 ppm is due to the CH–S and CH_2–S absorptions, respectively. The aromatic phenyl group absorbs between 126.26 and 126.52 ppm, and the quaternary carbon absorbs at 136.12 ppm. In p(ES-co-SS), the peaks arises at 37.29 and

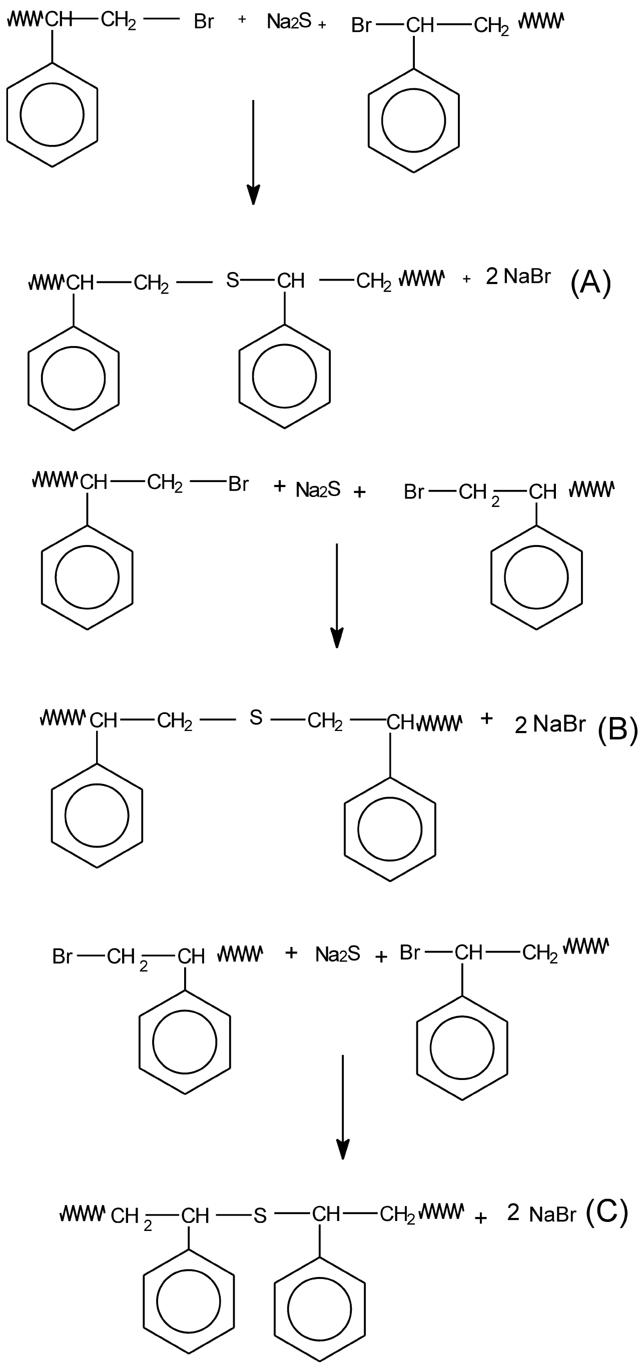

Fig. 6. Formation of different configurational sequences (head–tail (A), tail–tail (B), and head–head (C)) in poly(styrene sulfide).

37.52 ppm (the assignment of this peak is done in comparison with poly(propylene sulfide) [28] in which CH_2S group absorbs at 37.66 ppm. The higher value of chemical shift in poly(propylene sulfide) is due to the presence of CH group next to CH_2) is due to the CH_2S absorptions (Fig. 5b) of the ES unit, while the CH–S and CH_2–S from SS unit absorbs at 53.97 and 43.24 ppm, respectively. The aromatic phenyl group absorbs between 126.13 and 126.61 ppm, and the quaternary carbon absorbs between 136.47 and 138.19 ppm. In p(MS-co-SS), the peaks at 46.69 and 50.69 ppm is due to CH_2S absorptions (Fig. 5c) of MS unit, while the CH–S and CH_2–S from SS unit absorbs at 54.31 and 43.39 ppm, respectively. The aromatic phenyl group absorbs between 126.91 and 128.62 ppm, and the quaternary carbon absorbs between 137.19 and 138.59 ppm. The peak at 77 ppm in homo, and copolymers is due to $CHCl_3$.

3.6. Configurational analysis

In PSS, it has been found that the CH, CH_2 and the quaternary carbon of the phenyl ring, all show peak splitting, basically a doublet. This is explained as in Fig. 6. Since styrene dibromide contains a primary as well as secondary bromide groups, on condensation with Na_2S, it forms all the three structures (head–head, head–tail and tail–tail, Fig. 6). From Fig. 6, it is clear that both the backbone CH and CH_2 carbons are having two configurations; either the next carbon is CH or CH_2 and most probably, the doublet that is observed in the ^{13}C NMR spectrum of neat PSS is due to this. It is noted here that poly(styrene disulfide) synthesized by condensing SDB with aqueous Na_2S_2 also showed similar configurational splittings [4]. Even in some of the p(ES-co-SS) as well as p(MS-co-SS), we observe multiple splitting (or broadening) in CH, CH_2 and the quaternary carbon peaks indicating different configurational sequences which are not only due to the structures discussed in Fig. 6, but also due to random sequencing of EDB (or MDB) and SDB units in the copolymer (one composition for each copolymers system is presented in Fig. 5(b) and (c)).

3.7. Thermal stability

The thermal stability of PES, PSS, and copolymers were carried out by TG analysis. The thermal stability of PES is less compared to PSS. On copolymerization with SDB, the onset of thermal degradation of PES is shifted to a higher temperature. The DTG curve of PES shows two steps degradation, while PSS and copolymers show one-step degradation. In the case of PES, initial degradation temperature (T_i) and final degradation temperature (T_f) are 149.7 and 256.2 °C, respectively, for first step; and 256.2 and 338 °C, respectively, for second step. The T_i and T_f for PSS are 211 and 365 °C, respectively; and 204 and 358 °C, respectively, for p($ES_{0.50}$-co-$SS_{0.50}$).

The onset of thermal degradation is shifted from lower temperature in PMS to higher temperature in copolymers. DTG trace of PMS shows three steps of degradation, whereas the copolymers degrade in single step. It has been reported in literature that the PMS shows a single step degradation [29], while we observe three step degradations ((T_i); 147.0, 253, and 290 °C: (T_f); 254, 290, and 338 °C). We believe that the differences observed could be due to the difference in the methodology adopted in the synthesis of

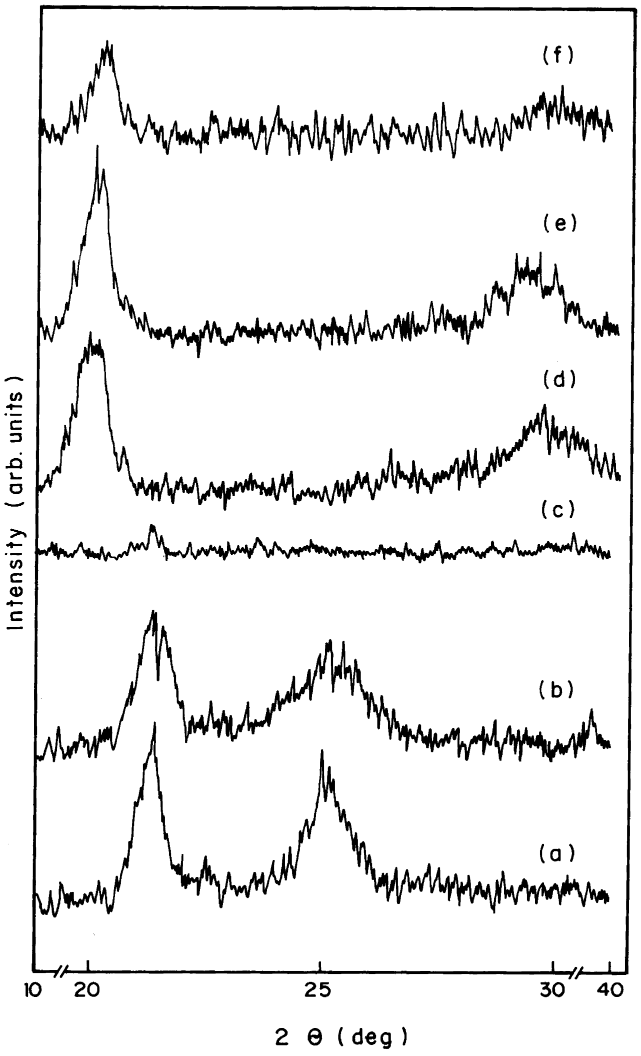

Fig. 7. Powder X-ray diffractograms of (a) neat poly (ethylene sulfide), (b) p(ES-co-SS) (0.85–0.15 mole fraction in the feed), (c) p(ES-co-SS) (0.75–0.25 mole fraction in the feed (d) neat poly(methylene sulfide), (e) p(MS-co-SS) (0.90–0.10) mole fraction in the feed, and (f) p(MS-co-SS) (0.75–0.25) mole fraction in the feed.

the polymer. The T_i and T_f for p($MS_{0.5}$-co-$SS_{0.5}$) are 204, 317 °C, respectively.

3.8. X-ray diffraction data

Fig. 7(a) and (d) represents the powder XRD spectrum of neat PES and PMS, respectively, and the sharp peaks observed show the crystalline nature of the polymers. On copolymerization with SDB, the crystallinity is reduced which is confirmed from the peak broadening (Fig. 7(b) and (c)). Further increase in the concentration of SDB in the copolymer resulted in the polymer precipitating as a viscous mass indicating total loss of crystallinity. It is to be mentioned here that pure PSS is a viscous solid indicating that it is completely amorphous. A similar trend was observed for p(MS-co-SS) systems also (Fig. 7(e) and (f)).

Table 4
Solubility of p(ES-co-SS) system

Polymer	$CHCl_3$	DMF	DMAc	THF	NMP	C_6H_6
(I)	+ −	−	+ −	+ −	+ −	−
(II)	+ −	−	+ −	+ −	+ −	+ −
(III)	+ −	−	+ −	+ −	+ −	+ −
(IV)	+	−	+	+	+	+
(V)	+	+ −	+	+	+	+
(VI)	+	+ −	+	+	+	+

+ , (Soluble); + − , (partially soluble); −, (insoluble).

3.9. Solubility

It is well known that crystallinity decreases the solubility of polymers, since the process of solution involves overcoming the heat and entropy factors associated with crystallization as well as those of the intermolecular interactions in the amorphous regions. The solubility of the polymer is also strongly dependent on crystallinity, since solubility is usually confined to the amorphous regions. Unlike PES, and PMS, the copolymers in the present study of having upto 0.65 mol SDB (p(ES-co-SS) copolymer), 0.50 mol SDB (p(MS-co-SS) copolymer) taken in the feed are found to be limited solubility and beyond these concentrations, freely soluble in common organic solvents (Tables 4 and 5). This difference in solubility behavior is either due to the difference in reactivity of SDB towards EDB and MDB or the amount of SS unit that requires to disturb the close packing of the polymeric chain (due to presence of bulky side group) and simultaneously to increase the amorphous fraction in the copolymer. The difference in reactivity ratio, and block length formation shown by SDB towards EDB and MDB as discussed earlier in reactivity ratio analysis, reflects the change in solubility phenomenon. This can be explained as follows; 0.75 mol of SDB is required to make the copolymer soluble in p(ES-co-SS) copolymer, whereas 0.65 mol of SDB is enough to make p(MS-co-SS) copolymer soluble.

4. Conclusions

Copolymers of SDB with either EDB or MDB and Na_2S were synthesized and characterized by ^{1}H NMR spectroscopy to determine the composition. It was found that the reactivity of SDB with Na_2S is less when compared to either

Table 5
Solubility of p(MS-co-SS) system

Polymer	$CHCl_3$	DMF	DMAc	THF	NMP	C_6H_6
(i)	+ −	−	−	+ −	−	+ −
(ii)	+ −	−	+ −	+ −	+ −	+ −
(iii)	+ −	−	+ −	+ −	+ −	+ −
(iv)	+	+ −	+	+	+	+
(v)	+	+ −	+	+	+	+
(vi)	+	+ −	+	+	+	+

+ , (Soluble); + − , (partially soluble); −, (insoluble).

EDB or MDB. The reactivity ratio analysis, and kinetic scheme was derived for the condensation copolymers. The block length formed is higher in p(ES-co-SS) copolymer, whereas it is less in p(MS-co-SS) copolymer. The microstructures of the copolymers were analyzed by using ^{13}C NMR. The weight average molecular weight, $M_w = 18{,}600-44{,}600$ were obtained by GPC.

The increase in solubility with copolymerization, depending on the composition taken in the feed has been explained by the loss of crystallinity and consequent increase in the amorphous content in the copolymer.

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