



β -Cyclodextrin Mediated Synthesis of Sterically Controlled Styrene-acrylonitrile Copolymer

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Abstract. Sterically controlled styrene-acrylonitrile (SAN) copolymers were prepared by inclusion polymerization using molar equivalents of β -cyclodextrin (β -CD) and its derivative. Comonomer compositions, reactivity ratios, monomer sequence and average styrene and acrylonitrile sequence lengths were determined using ^{13}C NMR spectroscopy. The molecular weight of the polymers prepared increased with decreasing β -CD concentration, but was found to be less than the control. With increase in the styrene: β -CD ratios the average acrylonitrile sequence length and run number of the polymers increased. The glass transition temperature (T_g) also increased along with the melting temperature (T_m) of the polymers at higher styrene: β -CD ratios.

Key words: β -cyclodextrin, styrene-acrylonitrile, copolymer, monomer sequence, comonomer composition.

1. Introduction

There have been numerous studies on the copolymerization of styrene (S) with acrylonitrile (AN) [1, 2]. Styrene and acrylonitrile copolymers are prepared commercially by all three types of polymerization [3, 4], namely, bulk, emulsion and suspension.

An alternating SAN copolymer was obtained in the presence of ZnCl_2 by Arita *et al.* [5]. High molecular weight linear SAN copolymer could be prepared [6] by emulsion polymerization, using 1-octadecanol and $\text{K}_2\text{S}_2\text{O}_8$ in water resulting in 91% SAN copolymer with an average molecular weight of 3.13×10^6 . Micro-emulsion polymerization was used to produce high molecular weight copolymers [7]. Random SAN copolymers were prepared by bulk polymerization using benzoyl peroxide as the initiator [8]. The complete mechanism of copolymerization of styrene and AN was investigated by several workers [3, 5].

The monomer feed ratio and the method of copolymerization decide the reactivity ratio and the stereosequence of the copolymers, which can be explained by the terminal model or penultimate model. Styrene-acrylonitrile copolymer prepared in

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bulk by free radical polymerization at 60 °C can be satisfactorily explained by the penultimate model [9].

Inclusion copolymerization of various pairs of monomers such as dimethylbutadiene, dichlorobutadiene, cyclohexadiene, vinylidene chloride, cyclopentadiene and cyclooctadiene included inside thiourea was carried out for the first time by Brown and White [10]. Later, the copolymerization of monomers inside DCA (deoxycholic acid) was studied by Takemoto and Miyata [11], who showed the existence of considerable differences between inclusion copolymerization and free copolymerization. Also, they have shown that the inclusion copolymerization is dependent on the ease with which the two monomers are included in the host and not on the reactivity of the growing chain ends. Random copolymerization of monomers in perhydrotriphenylene (PHTP) and the sequence distribution of monomers in the copolymers were studied extensively [12, 13]. In general, it has been observed that inclusion copolymerization produces random sequences of copolymers.

The present investigation deals with the results of inclusion copolymerization of styrene and acrylonitrile inside the β -CD cavity. No work on this aspect has been carried out so far. The effect of inclusion copolymerization on the monomer sequence length, reactivity ratios and the monomer mole fraction in the copolymer, as well as the molecular weight and differential scanning calorimetry (DSC) results were investigated.

2. Experimental

β -Cyclodextrin purchased from Cyclo Labs Ltd (Hungary) was used as such. Acrylonitrile and styrene purchased from SD Fine Chemicals Ltd. were used after distillation. Acrylonitrile monomer was purified by distilling over calcium carbonate and sulphuric acid to remove impurities. The sodium oleate, hydroxyapatite and benzoyl peroxide employed were purchased from SD Fine Chemicals Ltd.

2.1. INCLUSION COPOLYMERIZATION

A 2:1 molar mixture of styrene (0.105–0.035 mole), acrylonitrile (0.047–0.024 mole) and β -CD (amount varied depending upon molar ratio with respect to styrene) were placed in a three-necked round bottom flask and stirred for 0.5 h to form an inclusion complex [14]. Sodium oleate (0.02–0.006 mL), benzoyl peroxide (0.005–0.025 g), and hydroxyapatite (emulsifier, 0.3–0.08 g) in 10 to 30 mL of water were added to the mixture. The reaction mixture was stirred at 80 to 90 °C for 10 to 12 h under nitrogen. The polymer precipitate was filtered, washed with hot water repeatedly to remove cyclodextrin and dried in vacuum.

β -CD polymer was also used as an additive in polymerisation reactions. β -CD formed a polymer when reacted with epichlorohydrin which was water insoluble. This polymer exhibited comparable complexation abilities to β -CD.

The viscosity average molecular weights (\bar{M}_V) of the SAN copolymers were determined by an Oswald viscometer using the Mark–Houwink equation

$$[\eta] = K M_V^a$$

where $K = 3.6 \times 10^{-4}$ and $a = 0.62$ for *n*-butanone (MEK) as the solvent at 30 °C, [15].

¹H-NMR spectra were recorded on a Brüker WH 270 MHz NMR instrument, fitted with a Spectrospin magnet operating at 20 °C and an Aspect 2000 computer. About 200–300 scans were collected for each spectrum. All the spectra were recorded at 100 °C in DMSO-*d*₆. ¹³C-NMR spectra were recorded on a Brüker WH 67.5 MHz instrument, fitted with a Spectrospin magnet operating at 20 °C and an Aspect 2000 computer. For each spectrum, about 2500–3000 scans were accumulated with the total recycle time of 3 sec. All the samples were prepared in CDCl₃. Signals were referenced to CDCl₃ at 77 ppm to within ± 0.1 ppm. A region from 0 to 200 ppm was scanned for all the samples.

A 9900 Du Pont instrument with 910 DSC module was used for determining T_g and T_m values. About 5 to 10 mg sample was employed for the above study. Heating at 10 °C/min from room temperature to 300 °C was employed.

3. Results and Discussion

The molar ratio of styrene to acrylonitrile employed in copolymerisation was 2 : 1 (styrene : acrylonitrile). In the case of inclusion copolymerisation, the β -CD concentration employed was always expressed in molar proportions to that of styrene. The yields obtained in the case of 5 : 1 (styrene : β -CD) copolymer were low (<10%) while yields for the other polymers were 61–76%.

The viscosity average molecular weights of the prepared SAN copolymers are given in Table I. The copolymer prepared in the control reaction was found to possess a higher molecular weight (3.0×10^5) than those prepared in the presence of β -CD and its derivative. When the molar ratio of styrene : β -CD increased from 10 : 1 to 20 : 1, the M_V of the copolymers also increased. However, the copolymer prepared in the presence of β -CD-polymer exhibited almost the same M_V as that of 20 : 1 (styrene : β -CD) copolymer.

¹H-NMR spectra of all the SAN copolymers prepared by inclusion polymerization were recorded on a Brüker 270 MHz NMR instrument at 100 °C in DMSO-*d*₆ solvent (Figure 1). The styrene –CH₂ protons in the copolymer resonated at 0.90 ppm and the –CH protons at 2.51 ppm. Signals at 3.3 ppm and 2.1 ppm were contributed from the –CH and –CH₂ protons of acrylonitrile in the copolymer, respectively. Broad signals from 7.94 to 6.77 were attributed to the aromatic protons of styrene. For copolymers prepared in the presence of β -CD, a doublet at 5.85 ppm and a singlet at 5.75 ppm were from the 2-OH and 3-OH protons respectively of β -CD. Also, signals at 4.84 ppm and 4.51 ppm were due to 6-OH and H-1 of the β -CD, respectively. These signals were seen in the polymer samples even

Table I. Preparation and molecular weights of SAN copolymers

Styrene: β -CD	Conditions ^a	Viscosity average molecular weights ^b
Control	Styrene –0.096 mole Acrylonitrile –0.047 mole Yield = 76%	3.0×10^5
10:1	Styrene –0.0524 mole Acrylonitrile –0.0243 mole Yield = 63%	2.8×10^4
20:1	Styrene –0.1047 mole Acrylonitrile –0.0486 mole Yield = 71%	5.6×10^4
10:1(β -CD-polymer) ^c	Styrene –0.096 mole Acrylonitrile –0.0243 mole Yield = 61%	5.6×10^4

^aOther components for the reaction are: sodium oleate –0.02 mL; benzoyl peroxide –0.02 g; hydroxyapatite –0.3 g in 17 mL water. Mixture stirred at 90°C for 10 h under nitrogen atmosphere.

^bError range for determining M_V will be in the range $\pm 5\%$.

^cA water insoluble β CD-epichlorohydrin polymer was prepared initially and this polymer was used as additive like β -CD in polymerisation reactions.

after repeated washing with hot water. The 3-OH and 6-OH proton signals of β -CD in the copolymers were shifted upfield of their position in the free state. This might be due to the ring current effect of the phenyl ring π electron cloud on β -CD protons. This is clearly due to the presence of β -CD molecules in the polymer chain probably present as rotaxanes. The ratio of area of aromatic protons of styrene to H-1 protons of β -CD showed that for every 9.6 styrene units, one β -CD molecule was present on the chain on average. ¹H-NMR spectra of the SAN copolymers were complex due to overlapping of the signals from –CH and –CH₂ groups.

3.1. ¹³C-NMR SPECTROSCOPIC STUDY

The co-monomer composition (M_A and M_S where M_A = mole fraction of acrylonitrile and M_B = mole fraction of styrene) in the final copolymer with respect to the monomer feed composition was determined by ¹³C-NMR spectroscopy, (Figure 2). This could be obtained either from the ratio of the area of the –CN carbon peak of acrylonitrile to that of the aromatic carbons of styrene [16] or from the ratio of the area of the C-1 carbon peak of styrene (at 141.5 ppm to 146.5 ppm) to that of the –CN carbon peak of AN [17] (at 121.0 ppm to 122.5 ppm), Table II.

The monomer sequence distribution was also determined by ¹³C-NMR spectroscopy. The –CN and C-1 carbons were sensitive to the triad sequence [2, 4]. So the acrylonitrile-centered triads (SAS, AAS, or SAA and AAA, where S-styrene and A-acrylonitrile) were examined from the nitrile carbon signal of AN and styrene-

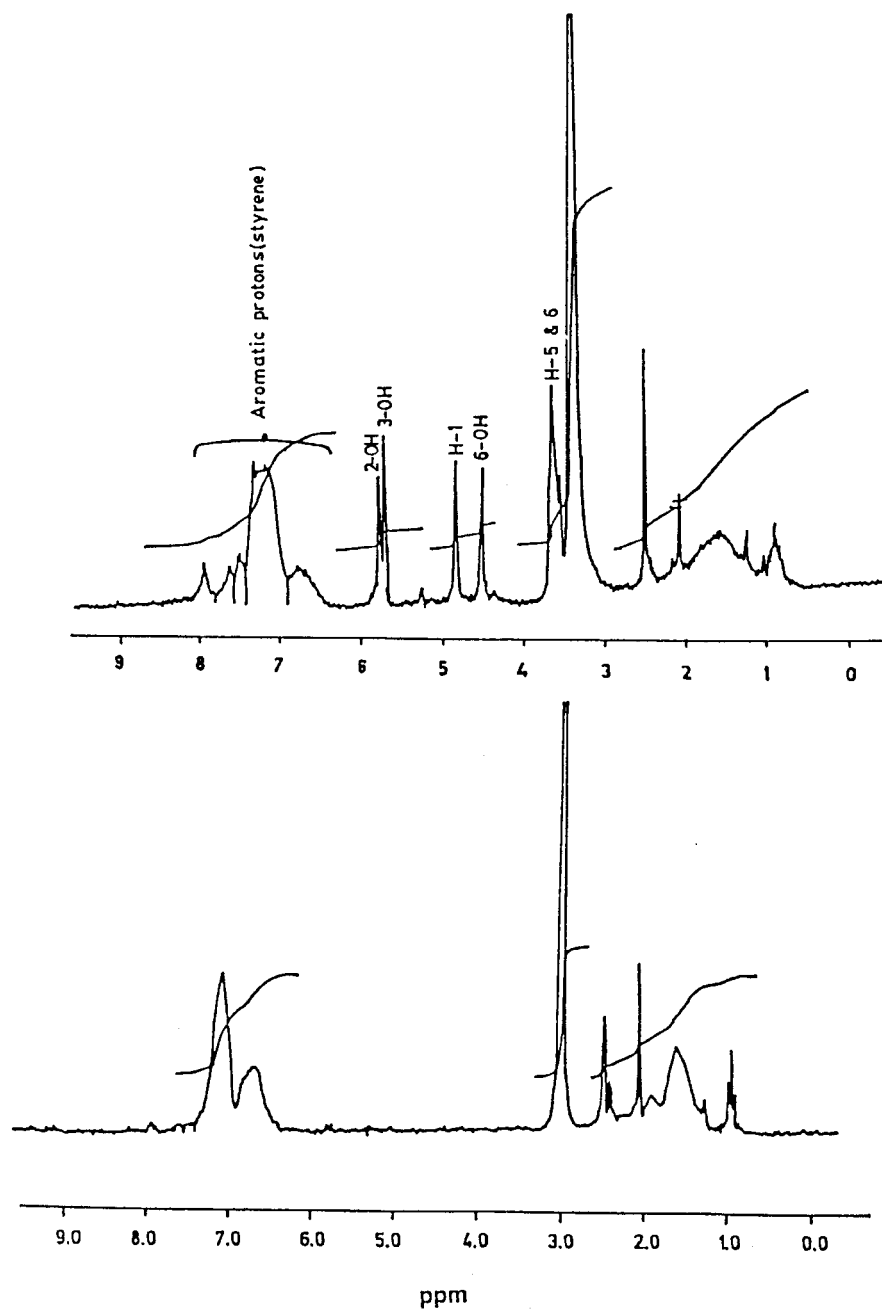


Figure 1. ¹H-NMR spectra of SAN polymers prepared in the presence and in the absence of β-CD recorded on the 270 MHz instrument at 100 °C. Lower trace: SAN prepared without β-CD; Upper trace: SAN prepared with β-CD (styrene : β-CD 20 : 1). About 300 scans were recorded in DMSO-d₆.

centered triads (*ASA*, *ASS* or *SSA* and *SSS*) were examined from the C-1 signal of styrene. The aromatic C-1 signal consists of three main peaks [18, 19]. The peak at 145.5 ppm corresponds to *SSS* triads and the peak at 142.5 ppm corresponds to *SSA* or *ASS* triads [20]. In the present study, the higher field peak at 139.0 ppm corresponding to *ASA* triads was absent in all the prepared polymers. Similarly, the nitrile carbon signal consists of three peaks, the one at 122.2 ppm corresponded to the *SAS* sequence, while the peak at 121.8 ppm corresponded to *SAA* or *ASS* triads. The peak at 120.0 ppm due to *AAA* triads and the one at 139.0 ppm corresponding to *ASA* were absent due to the lower monomer content of acrylonitrile compared to styrene in the copolymer. Areas of the styrene centered and acrylonitrile centered triad sequences determined from ^{13}C -NMR spectra are given in Table II. Although the noise level was high, the significant splitting of the C-1 peak observed above the noise level should be ascribed to the tacticity effect (isotactic, heterotactic and syndiotactic) [20, 21] The observed data were explained based on the Alfrey-Mayo terminal model [22].

The relation between monomer sequence and reaction kinetics as described by the Alfrey-Mayo model is expressed as follows [23].

$$F_{SSS} = [1 - P_{(A/S)}]^2$$

$$F_{SSA} = F_{ASS} = 2[P_{(A/S)}(1 - P_{(A/S)})]$$

$$F_{ASA} = [P_{(A/S)}]^2$$

$$F_{AAA} = [1 - P_{(S/A)}]^2$$

$$F_{AAS} = F_{SAA} = 2[P_{(S/A)}(1 - P_{(S/A)})]$$

$$F_{SAS} = [P_{(S/A)}]^2$$

where F_{SSS} , F_{SSA} , F_{ASA} , F_{AAS} and F_{SAS} are normalised triad fractions of the respective triads indicated in the subscript (normalized to unity), $P_{(A/S)} = 1/(1 + r_{S/q})$ and $P_{(S/A)} = 1/(1 + r_{A.q})$ and $q = [A]/[S]$ monomer feed ratios, r_S and r_A are the respective terminal reactivity ratios of styrene and acrylonitrile. $P_{(S/A)}$ is the probability of the A-S unit that arises as a result of an A growing chain end adding S and $P_{(A/S)}$ is the probability of the S - A unit that arises as a result of an S growing chain end adding A.

r_S and r_A were obtained from the following treatment:

$$r_A = [S_f]/[A_f] \cdot [1/P_{(S/A)} - 1]$$

$$r_S = [A_f]/[S_f] \cdot [1/P_{(A/S)} - 1]$$

where S_f and A_f were the monomer feed concentrations of the styrene and acrylonitrile, respectively.

Table III. Average sequence lengths of styrene and acrylonitrile, run number, terminal model reactivity ratio and conditional probabilities $P_{(A/S)}$ and $P_{(S/A)}$ from $^{13}\text{C-NMR}$

Molar ratio	r_A	r_S	$P_{(S/A)}$	$P_{(A/S)}$	$\langle A \rangle^a$	N_A	N_S	R	$\langle S \rangle^b$
Sty: β -CD									
1 : 0	0.85	8.98	0.705	0.052	1.72	1.42	19.2	9.70	18.23
10 : 1	1.05	11.82	0.659	0.04	2.08	1.52	25.0	7.54	7.03
20 : 1	0.904	3.51	0.692	0.123	1.81	1.46	8.13	20.86	7.03
10 : 1 β -CD-polymer	1.06	3.42	0.658	0.126	2.09	1.52	7.94	21.14	6.99

^aBased on Equation (1); acrylonitrile sequence lengths.

^bBased on Equation (2); styrene sequence lengths.

Table IV. Calculated and observed^a values for the triad fractions of styrene and acrylonitrile centered triads in prepared SAN copolymers

Molar ratio Styrene: β -CD		Styrene centered			AN-centered		
		F_{SSS}	F_{SSA}	F_{ASA}	F_{AAA}	F_{AAS}	F_{SAS}
1 : 0	Obs	0.896	0.104	0.000	0.00	0.590	0.410
	Cal	0.899	0.099	0.002	0.08	0.420	0.500
10 : 1	Obs	0.923	0.080	0.00	0.00	0.683	0.317
	Cal	0.920	0.080	0.000	0.12	0.45	0.430
20 : 1	Obs	0.751	0.249	0.000	0.00	0.617	0.387
	Cal	0.769	0.216	0.015	0.08	0.430	0.490
10 : 1 β -CD-polymer	Obs	0.749	0.251	0.000	0.00	0.685	0.315
	Cal	0.765	0.230	0.050	0.12	0.450	0.430

^aObserved values were obtained from $^{13}\text{C-NMR}$ spectra and calculated values from the Alfrey Mayo terminal model [23].

Conditional probabilities $P_{(S/A)}$ and $P_{(A/S)}$ were determined as follows:

$$P_{(S/A)} = ([SAS] + [SAA])/2/([AAA] + [AAS] + [SAS])$$

$$P_{(A/S)} = ([ASA] + [SSA])/2/([SSS] + [SSA] + [SAS])$$

Terminal model reactivity ratios and the conditional probabilities for all the prepared copolymers are given in Table III.

Observed and calculated values for the triad sequences based on the Alfrey-Mayo model are shown in Table IV. The calculated (based on terminal model) and observed values for the styrene centered triad sequences were found to be in good agreement, except for those with AN centered triad sequences which showed some variation.

A knowledge of M_A , M_S , r_A and r_S enables a prediction to be made, not only of the average mole ratios, but also of the average number of sequences of monomer units per unit length of the polymer and the average sequence length of each polymer.

The run number, R , of the copolymer is defined as the average number of segments of either types per 100 monomer units

$$R = 200/\bar{N}_A + \bar{N}_S$$

where \bar{N}_A and \bar{N}_S are the number-average sequence lengths of A and S monomer units (being the reciprocal of the conditional probabilities [25] of $P_{(S/A)}$ and $P_{(A/S)}$ in the copolymers [24]) and are shown in Table III.

The average acrylonitrile sequence length can also be determined by the method of Stejskal and Schaefer [18] using the following treatment.

$$\langle A \rangle = 1 + (2R_1)^{-1} \quad (1)$$

$$\langle A \rangle = 1 + 2R_2, \quad (2)$$

where $R_1 = [SAS]/[SAA, AAS]$, $R_2 = [AAA]/[SAA, AAS]$

$$\langle A \rangle = \frac{1 + 2r_1r_2M_A/M_S}{[(M_A/M_S - 1)^2 + 4r_1r_2M_A/M_S]^{1/2} - (M_A/M_S - 1)}. \quad (3)$$

The reactivity ratio product r_1r_2 is taken to be 0.021 [20] for styrene acrylonitrile copolymer. Values of the acrylonitrile and styrene average sequence lengths obtained from comparison of triad concentrations as described above are given in Table IV.

Although the actual monomer feed ratio employed for all the copolymers was 67:33 (styrene:AN), the actual values based on ^{13}C -NMR data were different (Table II). Acrylonitrile incorporation in the copolymer was found to be affected, as the styrene: β -CD ratio increased. Thus, when the styrene: β -CD ratio was increased from 1:0 to 20:1, the acrylonitrile incorporation in the copolymer increased from 7 to 16.3 mole percent only (Table II).

The average acrylonitrile sequence length for the control SAN copolymer was found to be 1.72 (Table III) as per Equation (1) [18]. In the SAN copolymer prepared in the presence of 10:1 styrene: β -CD, and 10:1 styrene: β -CD-polymer, the average acrylonitrile sequence length increased to 2.08 and 2.09, respectively. When the molar ratio of styrene to β -CD increased to 20:1, the average acrylonitrile sequence length was found to be 1.81. Similarly, the average styrene sequence length decreased in the polymer prepared in the presence of β -CD and β -CD-polymer, compared to that in the control. Hence, the polymer prepared in the presence of β -CD and β -CD-polymer resulted in an increase in the average acrylonitrile sequence length and a decrease in the average styrene sequence length.

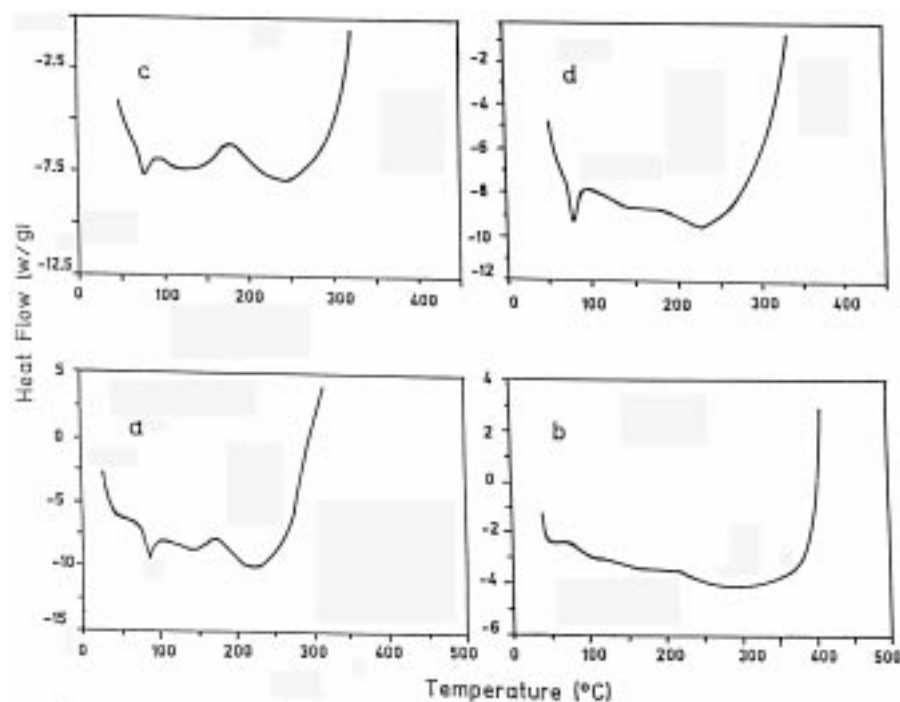


Figure 3. DSC thermograms of SAN polymers. (a) SAN prepared in the absence of β -CD; (b) Polymer prepared with 10 : 1 styrene : β -CD; (c) Polymer prepared with 20 : 1 styrene : β -CD; (d) Polymer prepared with 10 : 1 styrene : β -CD-polymer. A heating rate of 20°C/min was employed for all the polymers.

The concentrations of *AAS* and *SAS* triad sequences in the polymer prepared in the absence of β -CD and its derivative were found to be 0.59 and 0.41 (observed value), respectively (Table IV). In the copolymer prepared in the presence of 10 : 1 styrene : β -CD and 10 : 1 styrene : β -CD polymer, the *AAS* triad sequences increased to 0.683 and 0.685, respectively and the *SAS* triad sequences decreased to 0.317 and 0.315, respectively. When the molar ratio of β -CD to styrene was 20 : 1 the *AAS* and *SAS* triad sequences were 0.617 and 0.383 respectively. Hence, copolymers prepared in the presence of β -CD and its derivative increased the *AAS* and decreased the *SAS* triad sequences compared to that obtained from the control.

3.2. THERMAL CHARACTERISTICS OF THE SAN POLYMER (DSC)

The glass transition temperature (T_g) and melting temperature (T_m) of the prepared SAN copolymers were determined by DSC. Usually the T_g is affected by the sequential distribution of the monomeric units of the copolymer [26]. In the present work, all the samples were heated to 400 °C at the rate of 20 °C/min. The T_g and T_m of the SAN copolymers are given in Table V (Figure 3).

Table V. T_g and T_m values of the SAN copolymer prepared by inclusion copolymerization

Molar ratio Sty: β -CD	T_g ($^{\circ}$ C)		T_m ($^{\circ}$ C)	ΔH J/g	Exothermic starting temp ($^{\circ}$ C)
	1st	2nd			
1 : 0	78.1	129.1	220.6	265.1	257.8
10 : 1	89.7	131.0			373.3
20 : 1	104.5	–	241.1	277.0	294.3
10 : 1	130.7	–	237.0	204.5	280.0
β -CD polymer					

The copolymer prepared in the absence of β -CD gave two T_g peaks at 78.1 $^{\circ}$ C and 129.1 $^{\circ}$ C with one broad melting endotherm (T_m) at 220.6 $^{\circ}$ C ($\Delta H = 265.1$ J/g). The copolymer prepared in the presence of 10 : 1 styrene : β -CD gave again two T_g peaks at 89.7 and 131 $^{\circ}$ C. When the molar ratio was 20 : 1, the T_g and T_m values increased to 104.5 and 241.1 $^{\circ}$ C, respectively with a ΔH value of 277.0 J/g. The copolymer prepared in the presence of 10 : 1 styrene : β -CD-polymer exhibited T_g at 130.7 $^{\circ}$ C and T_m at 237 $^{\circ}$ C with a ΔH value of 204.55 J/g. The T_g of the prepared SAN copolymers were comparable with the T_g of the alternating and random copolymers reported in the literature [4, 27].

The T_g of the copolymers prepared in the presence of β -CD and its derivative were found to be higher than that of the control polymer. Also, the T_g of the copolymers increased with a decrease in the concentration of β -CD. The increase in T_g was mainly due to the increase in the acrylonitrile mole fraction in the copolymer. T_g decreases with increasing mole fraction of styrene in the copolymer [4, 26]. The T_g temperatures of the copolymers are not only affected by the comonomer content of the polymers, but also by the sequential distribution of the copolymers [28, 29]. Also, another interesting feature was the observation of two glass transition temperatures for the copolymers prepared in the control and that in the presence of 10 : 1 styrene : β -CD. From the four copolymers prepared, the above two copolymers produced less than 10 mole percent AN content (with increased styrene content) and a greater proportion of SSS triads (89.6% and 92.3%), when compared to the other copolymers prepared in the presence of β -CD (Table II). This again explains that the above two copolymers (namely the control and the one prepared with 10 : 1 styrene : β -CD) exhibit probably less ordered packing than the other two copolymers prepared in the presence of a lower β -CD concentration namely 20 : 1 and 10 : 1 styrene : β -CD (β -CD-polymer), which possess a probable alternating sequence of styrene content (high R for styrene, Table III).

The T_m values of the copolymers prepared in the presence of styrene : β -CD (20 : 1) and styrene : β -CD-polymer (10 : 1) were higher than those of the control. These increased values were not only due to the higher acrylonitrile mole fraction

in the copolymer, but also due to the stereoregularity of the polymers. However, the contributions of the stereoregular distribution in the monomers could not be determined in the present work.

In the case of PS prepared in the presence of 20 : 1 styrene : β -CD and 10 : 1 styrene : β -CD polymers [30], greater syndiotacticity was found to be a predominant factor in the increase in the melting temperature of the polymer. The higher syndiotacticity of styrene units in the copolymer prepared may be a predominant factor here also (especially in the case of the polymer prepared in the presence of 20 : 1 styrene : β -CD and 10 : 1 styrene : β -CD polymer), probably resulting in an increase in T_m of the copolymers.

In all the above prepared SAN copolymers, a huge exothermic peak was observed after the immediate endothermic one (Figure 3). The starting points of the exothermic peaks were very much higher than those of the control. They represented the onset of degradation of the copolymers. Though TGA values have been used to determine the degradation temperature of the copolymers, only approximate degradation temperatures can be measured. From the above temperatures, the polymer prepared from the control started degrading earlier than the polymers prepared in the presence of β -CD and its derivative. $^1\text{H-NMR}$ spectra indicated the presence of β -CD in the copolymer. It may be present in the form of a rotaxane in the copolymer. The presence of β -CD in lower proportions may lead to better packing (reduced free volume) in terms of enhanced van der Waals and hydrogen bonding interactions (between acrylonitrile $-\text{C}\equiv\text{N}$ groups and β -CD hydroxyl groups) leading to an increase in degradation temperature of the copolymers prepared.

Like PAN [31] and PS [32] polymers, SAN copolymers prepared in the presence of β -CD and its derivative exhibited differential physico-chemical properties such as molecular weights, ^1H and ^{13}C -NMR characteristics and calorimetric properties from copolymers prepared in the absence of β -CD.

Although the molar feed ratios of styrene and AN employed were 67 : 33 the styrene and AN contents in the copolymers prepared were highly influenced by the presence of β -CD and its derivative. Earlier, from our inclusion studies of both the monomers inside the β -CD cavity [30, 31], styrene and AN were found to exhibit 1 : 1 stoichiometry with β -CD and the binding constant value of the styrene : β -CD complex [30] ($31, 607 \pm 3500 \text{ M}^{-1}$) was four times higher than that of the AN : β -CD [31] complex ($7242 \pm 360 \text{ M}^{-1}$). Although the β -CD proportions were always expressed as its molar ratios to styrene, with respect to AN, these values will be twice as high. For example, a 10 : 1 styrene : β -CD ratio with respect to styrene would amount to a 5 : 1 AN : β -CD ratio. Hence, the amount of β -CD available for AN will be greater than that available for styrene, although the binding constant value of the latter is four times greater than that of the former. Hence, the presence of β -CD at higher concentrations (i.e. at lower styrene : β -CD ratios) predominantly complexes styrene, enabling it to be incorporated into the copolymer efficiently, as the residence time of styrene inside the cavity is large. This is also reflected not only in the lower mole fraction of AN content in the copolymers but

also in the lower molecular weights estimated, as the chain termination reactions will be more favoured, in the styrene β -CD complexes rather than in the AN : β -CD complexes. As the β -CD concentration decreases, more AN gets incorporated, while at the same time the styrene incorporating ability of β -CD in the copolymer decreases.

This also leads to a higher proportion of SSS in the copolymer prepared in the presence of a higher concentration of β -CD than that prepared with lower concentrations of β -CD, which showed a smaller SSS content (Table II). The same behaviour is also reflected in the N_s values. ^{13}C -NMR data have been more useful than ^1H -NMR data in arriving at these details. The same behaviour has also been reflected by calorimetric studies, which have shown differential T_g , T_m and degradation characteristics.

The copolymer prepared in the presence of styrene : β -CD-polymer (10 : 1) showed slightly different properties to those observed for the copolymers prepared at all the other styrene : β -CD ratios. Although, the central ability of forming inclusion complexes of β -CD-polymer was not different from that of β -CD, the heterogeneity [32, 33] of the β -CD-polymer in the reaction itself (as it is insoluble) imposed a slight variation in the properties of the copolymers prepared.

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