β-Cyclodextrin Mediated Synthesis of Syndiotactic-rich Polystyrene

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Abstract. Stereoregular polystyrene (PS) was prepared using various molar equivalents of β-cyclodextrin (β-CD) by polymerising styrene in the presence of β-CD. Stereoregular (isotactic, atactic and syndiotactic) distributions of the prepared polystyrene polymers were determined from terminal model Bernoullian statistics using ^{13}C NMR data. Inclusion complexation of styrene by β-cyclodextrin was detected by UV-Visible spectroscopy, which gave a binding constant value of 31606 ± 3350 M^{-1} for the 1 : 1 complex. With an increase in the styrene : β-CD ratios, the proportion of syndiotactic polymers increased. The glass transition temperature (T_g) of the polymer also increased along with melting temperature (T_m) at higher styrene : β-CD ratios. In addition, the molecular weight of the polymers prepared decreased with increase in the β-CD concentration.

Key words: β-CD, syndiotactic rich, ^{13}C NMR, crystallanity, stereoregularity

1. Introduction

The preparation of stereoregular polymers with controlled molecular weights are the emerging challenge for polymer chemists as the properties of polymers depend mainly on their stereoregularity and molecular weight. Generally, the two component catalytic systems (Ziegler–Natta catalyst) and their modifications are normally used for the preparation of stereoregular olefinic polymers [1]. Several methods have been described for the polymerization of styrene [2] and when used these at times resulted in divergent stereoregularities [3, 4].

Stereoregularity was affected by polymerization conditions like catalyst, solvent and temperature [5]. The polymerization of styrene using sodium naphthalene as catalyst resulted in 66–68% syndiotactic dyads independent of solvent and temperature. However, potassium and cesium naphthalenes as catalysts produced PS with different stereoregularities, ranging from syndiotactic rich to isotactic rich configurations, depending on the solvent and temperature [6]. Usually, polymerization of styrene using free radical initiators resulted in atactic [7] as well as syndiotactic rich polystyrene [8, 9].

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Inclusion complexation involving clathrates changes the physical and chemical nature of the included guest monomers [10] and also affects the propagation step of the polymer reaction, leading to polymers with controlled stereoregularity [11, 12] and molecular weights.

Although numerous studies have been dedicated to inclusion polymerization using several host molecules [13–15], less attention has been focused on the unimolecular host β-cyclodextrin (β-CD). β-Cyclodextrin was used for the first time in the field of inclusion polymerization by Maceijewski *et al.* [16].

The reports on inclusion polymerization involving styrene are very limited. In fact, there has been only one report on the synthesis of non-cross linked poly-4-vinylstyrene and of stereoregular poly-4-bromostyrene inside *tris*-(2,3-naphthalenedioxy)cyclotriphosphazene (TNP) [10]. However, no work has been carried out on the polymerization of styrene inside the β-CD cavity. The present investigation deals with studies on β-CD mediated polymerization of styrene monomer through the free radical polymerization of an emulsion containing β-CD and styrene and the results of the investigation are reported in this paper.

2. Materials and Methods

2.1. A TYPICAL REACTION

A typical procedure employed for the polymerization of styrene was as follows. A mixture of styrene (0.15–0.2 mole) and β-CD (catalyst depending on molar ratio), was stirred for half an hour to form an inclusion complex. Potassium persulfate (5–25 mg) as an initiator, sodium lauryl sulphate (50–300 mg) as an emulsifying agent and sodium hydrogen phosphate (5–30 mg) as buffer, in 36 mL of water were added to the mixture. The mixture was stirred at 60–80 °C for 6 h under nitrogen. After polymerization was completed, the polymer was isolated by adding 2–5% aluminium sulphate solution. The precipitate formed was filtered, washed with hot water and dried in vacuum. Apart from β-CD, a water insoluble polymer of β-CD prepared with epichlorohydrin was also employed for polymerisation of styrene in the presence of this polymer.

2.2. VISCOSITY AVERAGE MOLECULAR WEIGHT

Viscosity average molecular weights ($\bar{M}_v$) of the polystyrene polymers were determined using an Ostwald viscometer at room temperature. Four different concentrations were used for each polymer with at least three efflux periods recorded at each concentration. Benzene was used as a solvent for viscosity measurements. From the intrinsic viscosities, molecular weights of the styrene polymers were calculated using Mark–Houwink equation

$$(\eta) = K \cdot \bar{M}_v^a.$$

The K and a values used for the prepared PS polymers were 11.5 and 0.73 for atactic PS and 11.5 and 0.74 for isotactic PS in benzene [17]. The average value of both atactic and isotactic polymers was taken as the viscosity average molecular weight.

2.3. SPECTROSCOPY

^{13}C NMR spectra were recorded on a Bruker WH 270 MHz instrument (67.5 MHz for carbon) fitted with a Spectrospin magnet operating at 20 °C and Aspect 2000 computer. For each spectrum, about 3000 scans were accumulated. CDCl$_3$ was used for the preparation of samples. The signals were referenced to CDCl$_3$ at 78.0 ± 0.1 ppm. Proton noise decoupled spectra were obtained. A region between 0–250 ppm was scanned for the signals. A delay of 3.0 seconds was employed between the pulses.

A Shimadzu UV-240 instrument operating at 20 ± 1 °C was used for carrying out Ultraviolet-Visible spectroscopic experiments. Styrene monomer dissolved in 9 : 1 water : ethanol (1.092×10^{-4} M) was used. A stock solution of β-CD (9.985×10^{-4} M) dissolved in the above mentioned styrene solution was used for the addition of β-CD in increasing amounts. Spectra were recorded between 190–400 nm.

2.4. DIFFERENTIAL SCANNING CALORIMETRY

Differential Scanning Calorimetric studies were carried out on a Rheometric Scientific, UK instrument (DSC PLUS) provided with version 5.42 software and was calibrated against indium, tin and lead. The PS polymer samples used weighed approximately 1 to 10 mg. The equipment operated in the temperature range 30 to 400 °C with a 0.01 mcal/s sensitivity and a heating rate of 20 °C/min was employed.

3. Results and Discussion

3.1. NMR STUDIES

The viscosity average molecular weights of the prepared PS polymers are given in Table I. The molecular weights of the polymers prepared in the presence of β-CD were lower than that of the control. However, with increase in the styrene : β-CD ratio, the molecular weights of the polymers increased.

270 MHz ^{1}H NMR spectra of the PS polymers so prepared were recorded at both room temperature and 100 °C in DMSO-d$_6$. However, the spectra were quite complex, and did not give any information on the stereochemistry of the polymers.

Although the stereoregularity of most vinyl polymers can be measured relatively easily by ^{1}H NMR spectroscopy [18], this was not the case with PS or many of its homologues [19]. The ortho-aromatic proton resonances of PS contain ste-

Table I. Viscosity average molecular weights ($\bar{M}_v$) of PS polymers[a]

Molar ratio of styrene : β-CD	Viscosity average molecular weights
Control	1.37×10^5
5 : 1	3.19×10^4
10 : 1	8.49×10^4
20 : 1	1.02×10^5
10 : 1	9.0×10^4
Styrene : β-CD-polymer[b]	

[a] Error in molecular weight measurements arising from the viscosity determination will be of the order $\pm 5\%$.

[b] A water insoluble polymer formed by the reaction between β-CD and epichlorohydrin which was also used as an additive during polymerisation.

reosequence information, which is not yet fully understood [20].

Hence, ^{13}C NMR spectra of the polystyrene polymers prepared were recorded at 67.5 MHz in CDCl$_3$ at room temperature to determine the stereoregularity distribution. The quaternary aromatic carbon resonance (C-1) of polystyrene polymer [21] has been reported to be sensitive to triad, pentad and heptad stereosequence effects. Figure 1 shows the quaternary carbon spectra of polystyrene prepared by free radical polymerization. The aromatic C-1 signal at 145.1 to 146.1 ppm consists of three main peaks, corresponding to isotactic (145.1 ppm), atactic (145.8 ppm) and syndiotactic (146.1 ppm) triads of the polymer [22] irrespective of whether or not β-CD is employed. Although, the noise level was high, the major peaks could be distinctly recognised. Further splittings observed in the major peaks could also be due to splittings of some triad absorption into pentad and heptad signals [23].

Stereoregularities in the prepared polystyrene polymers were found to conform to Bernoullian or terminal model statistics using the following relationship. The proportion of the area of the signals were determined by the cut and weigh method, corresponding to the three major peaks, namely syndiotactic, atactic and isotactic.

Although, the data obtained from the triad sequence obeyed the Bernoullian testing model, namely

$$4(mm)(rr)/(mr)^2 = 1,$$

where m = meso and r = racemic, the calculated values did not correspond to the experimentally observed values. Hence, higher stereo-sequences were analyzed for the correspondence between the experimental and observed proportions of areas.
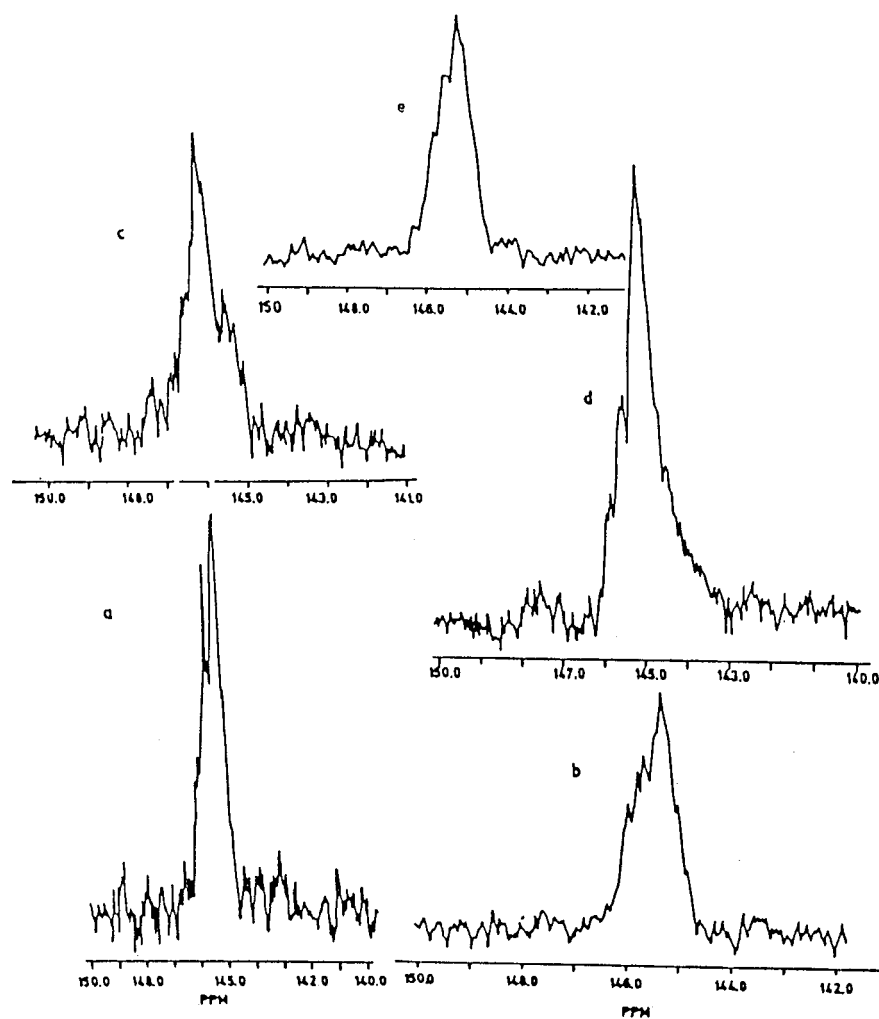
Figure 1. The quaternary carbon spectra (^{13}C-NMR) of PS polymers: (a) PS prepared with 5 : 1 styrene : β-CD; (b) PS prepared with 10 : 1 styrene : β-CD; (c) PS prepared with 20 : 1 styrene : β-CD; (d) PS prepared with 10 : 1 styrene : β-CD-polymer; (e) PS prepared without β-CD (control).

For a tetrad sequence, the probabilities are

$$
\begin{aligned}
(mmm) &= P_m^3 \\
(mmr) &= 2P_m^2(1 - P_m) \\
(rmr) &= P_m(1 - P_m)^2 \\
(mrm) &= P_m^2(1 - P_m) \\
(rrm) &= 2P_m(1 - P_m)^2 \\
(rrr) &= (1 - P_m)^3.
\end{aligned}
$$

Table II. β-CD mediated stereoregularity in PS polymers

Molar ratio of styrene : β-CD	Ratio of tacticities in %		
	Isotactic	Atactic	Syndiotactic
1 : 0	13	22	65
	(16)[a]	(28)	(56)
5 : 1	10	20	70
	(12)	(30)	(58)
10 : 1	9	18	73
	(11)	(20)	(69)
20 : 1	7	16	77
	(16)	(13)	(71)
10 : 1	3	10	87
β-CD-polymer	(10)	(13)	(77)

[a] Observed values obtained from the proportion of the peaks are shown in parentheses.

The triad sequences calculated from the tetrad sequences are

$$(mm) = (mmm) + 1/2(mmr)$$
$$(mr) = (mrr) + 2(mrm)$$
$$(rr) = 1/2(rrm) + (rrr).$$

Further for a pentad sequence, the probabilities and triad fractions calculated from pentad sequence distribution can be shown similarly.

The ratios of tacticities calculated based on Bernoullian statistics for the prepared PS polymers are given in Table II. The observed values from pentad sequences were in close agreement with the calculated ones. The values obtained for pentad sequences also obeyed the Bernoullian testing model. Hence, it can be concluded that the pentad sequence was sufficient to explain the observed data and the stereosequence.

From Table II, it can be seen that the stereosequence distribution of the polymers prepared was altered with a decrease in β-CD concentration. Polymerization carried out in the absence of β-CD gave 16% isotactic, 28% atactic and 56% syndiotactic polymers. When the molar ratio of styrene to β-CD was 5 : 1 the proportion of isotactic, atactic and syndiotactic polymers formed were 12, 30 and 58% respectively. But, whenever the molar ratios varied from 10 : 1 to 20 : 1, the ratios of isotactic, atactic and syndiotactic were 11 : 20 : 69 and 16 : 13 : 71, respectively. Thus, an increase in the styrene : β-CD ratio caused an increase in the percentage of syndiotacticity. In other words, an increase in the styrene: β-CD ratio caused a decrease in the proportion of both isotactic and atactic stereosequences. In the case of the polymer prepared in the presence of 10 : 1 β-CD-polymer, the proportions of

Table III. Determination of T_g, T_m, ΔH and ΔS of the prepared PS polymers

Molar ratio of	T_g (°C)		T_m	ΔH	ΔS
styrene : β-CD	1st	2nd	kJ/mol	entropy units	
Control[a]	92.9	108.2[a]	–	–	–
5 : 1	61.8	71.9	174.7	250 ± 20	1.43
10 : 1	76.2	95.7	201.1	989 ± 52	4.92
20 : 1	87.3	–	245.4	2339 ± 185	9.53
10 : 1	67.7	–	226.4	95 ± 6	0.406
β-CD-polymer					

[a] Since the control did not show satisfactory melting, the ΔH and ΔS values for the control are not shown.

isotactic, atactic and syndiotactic polymers formed were 10, 13 and 77%, respectively, indicating that the highest proportion of syndiotactic polymer was formed in the presence of 10 : 1 β-CD-polymer.

3.2. THERMAL CHARACTERISTIC OF POLYMERS

The glass transition temperatures (T_g) and melting temperatures (T_m) of the PS polymers were determined by DSC (Figure 2). All the samples were heated to 250 to 300 °C. Polystyrene prepared without β-CD (control) gave only two sharp endothermic peaks centered at 99.9 °C and 108.2 °C (Table III). These two peaks are due to the T_g of the polymer, although they were endothermic in nature. Such endothermic T_g peaks have been reported earlier [24]. Although, the melting temperature of the PS polymers was around 240° [25], the control polymer did not show any melting temperature above 200 °C. This may indicate lack of crystalline regions in the polymer. However, the PS polymer prepared with 10 : 1 styrene : β-CD showed two transitions at 76.2 °C and 95.4 °C, along with a melting temperature at 201.1 °C. Similarly, the 5 : 1 polymers also showed two peaks in the glass transition region and a melting temperature of 174.7 °C.

The polymer prepared in the presence of 20 : 1 styrene : β-CD and 10 : 1 styrene : β-CD-polymer showed only one transition at 87.3 °C and 67.7 °C along with melting temperatures of 245.4 °C and 226.4 °C, respectively. The two transitions observed in the glass transition region in the control, 5 : 1 and 10 : 1 polymers may be due to two types of stereosequences in the polymers, namely atactic and syndiotactic. Also, the absence of a melting temperature in the control probably showed the amorphous nature of the polymer. In the case of 20 : 1 (styrene : β-CD) and 10 : 1 (styrene : β-CD-polymer) polymers, the predominant syndiotactic sequences might have resulted in only one T_g.

Figure 3 shows the effect of the viscosity average molecular weight on T_g. Consistent with the increase in $\bar{M}_v$ observed with increase in the styrene : β-CD ratio,
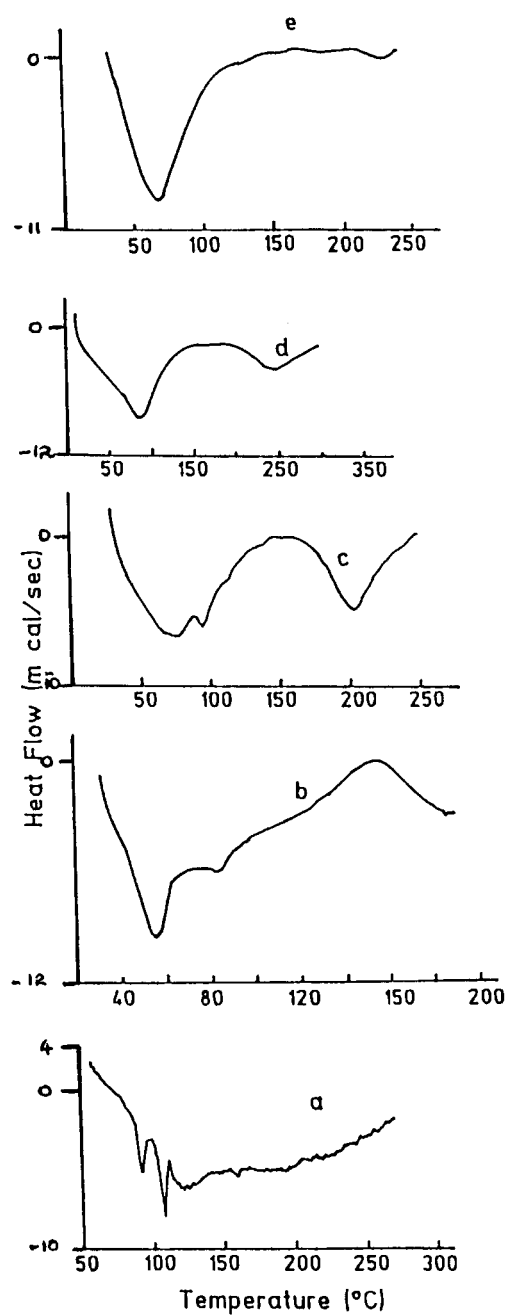
Figure 2. DSC thermogram for prepared PS polymers: (a) PS prepared without β-CD(control); (b) PS prepared with 5:1 styrene:β-CD; (c) PS prepared with 10:1 styrene:β-CD; (d) PS prepared with 20:1 styrene:β-CD; (e) PS prepared with 10:1 styrene:β-CD-polymer. A heating rate of 20 °C/min was employed for all the polymers. The scale in *x*-axis in each thermogram gives temperature in °C.
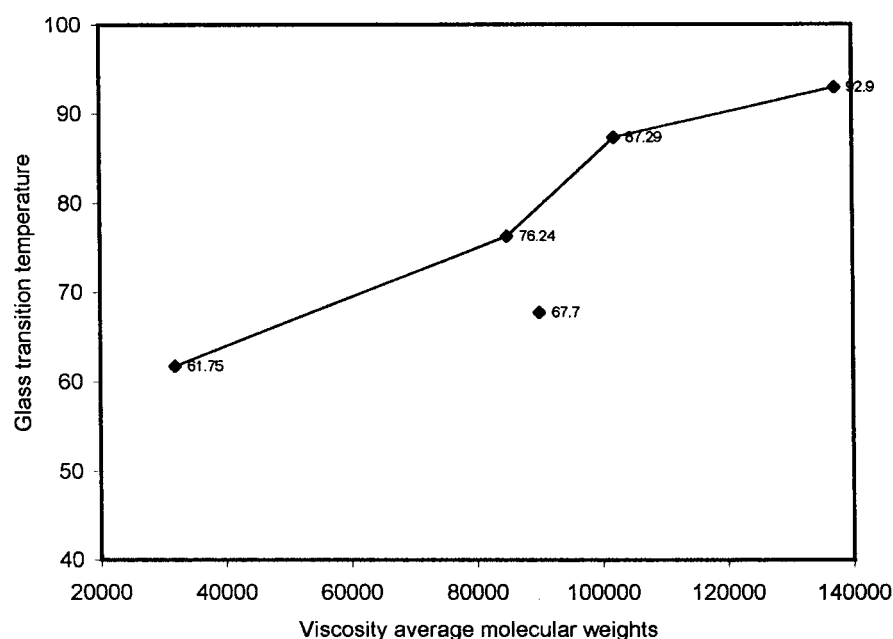
Figure 3. The effect of viscosity average molecular weights on the glass transition temperature (T_g) of the PS polymers.

a near linear relation (with slight asymptoticity) between molecular weight and T_g of the prepared polymers was observed, indicating that the molecular weight was responsible for the observed T_g [26]. The higher value of 108.2 °C observed in the control indicated not only a higher molecular weight, but also a higher proportion of isotacticity in the polymer prepared, when compared to the other polymers.

In the lower molecular weight polymers, the larger number of chain ends, will be effective in generating segmental motion. On the other hand, in the higher molecular weight polymers, the segments that are away from the chain ends restrict the mobility of the chain. Thus, the T_g values were lower for lower molecular weights (5 : 1 to 20 : 1) and increased with increased molecular weights [27].

The melting temperatures of the polymers depend upon their crystallinity and hence their stereoregularity [28]. In the present study, polystyrene prepared in the absence of β-CD (control) did not show any melting temperature, clearly indicating the amorphous nature of the polymer, whereas polymers prepared in the presence of β-CD (at all the concentrations) showed distinct melting temperatures. The melting endotherm for the 5 : 1 (styrene : β-CD) polymer started at 155.5 °C and ended at 218 °C, with a melting point of 174.7 °C. In the case of the polymers prepared in the presence of 10 : 1 and 20 : 1 (styrene : β-CD) polymers, the melting endotherms started at 173.4 °C and 212.9 °C and ended at 237.3 °C and 296.7 °C, with a melting temperature of 201.1 and 245.4 °C, respectively. Thus, an increase in the styrene : β-CD ratio showed a rise in T_m of the polymers consistent with

the increase in syndiotacticity or total stereoregularity leading to an increase in the crystallinity and hence an increase in the melting temperature. This was observed in all cases, with the exception of the polymer prepared in the presence of the $10:1$ styrene : β-CD-polymer, which gave a melting temperature at 226.4 °C. Even though the stereoregularity of the polymer was high (77% syndiotacticity), the melting temperature of the polymer was less than that prepared in the presence of $20:1$ styrene : β-CD. However, its molecular weight ($10:1$ β-CD-polymer) was less (9.0×10^4) than that of the former ($20:1$ styrene : β-CD), which may explain the observed T_m that was lower than dictated by its syndiotactic proportion.

The enthalpy (ΔH) and entropy (ΔS) values of the melting endotherm peaks of the polymers were determined from the specific heat values obtained (Table III) from the thermograms.

The entropy (ΔS) was determined from the relation

$$\Delta S = \Delta H / T,$$

where T is the melting temperature of the polymer in °K

However, both the ΔH and ΔS values increased for the polymers prepared with a styrene : β-CD ratio of $5:1$ to $20:1$, probably due to an increase in the stereoregularity of these polymers. However, the ΔH and ΔS values of the $10:1$ (styrene : β-CD-polymer) were less than those of the other polymers.

3.3. STRUCTURAL STUDIES BY ULTRAVIOLET-VISIBLE SPECTROSCOPY

In order to determine the extent of complexation of styrene by β-CD, UV-visible spectroscopic studies were carried out. Styrene exhibited $\lambda_{\max}$ at 248 nm ($\epsilon = 3547$) in ethanol (Figure 4). Addition of increasing amounts of β-CD (9.985×10^{-4} M) to styrene (1.092×10^{-4} M) resulted in a decrease in the $\lambda_{\max}$ value from 248 nm to 243 nm. Absorption values also decreased correspondingly. A plot of ΔA versus [β-CD]/[Styrene] indicated formation of a $1:1$ complex between styrene and β-CD (Figure 5).

The binding constant value was determined both by the double reciprocal plot method (Figure 6) and the Scatchard analysis method [29]. A plot of $1/\Delta A$ against $1/[\beta$-CD] gave a straight line with slope equal to $1/\Delta A_{AB}.K$, where ΔA_{AB} was the difference in absorption between free styrene and its β-CD complex and K was the binding constant value for the $1:1$ complex. A binding constant value of $31,818 \pm 2900$ m^{-1} was obtained for the $1:1$ complex.

A Scatchard plot was constructed by plotting $\Delta A/(\Delta A_{\max} - \Delta A).[\beta$-CD] (corresponding to $\bar{\nu}/Sf$ – the ratio of fraction bound to free substrate) against $\Delta A/\Delta A_{\max}.\rho$ (corresponding to $\bar{\nu}$ fraction bound). The slope of the curve close
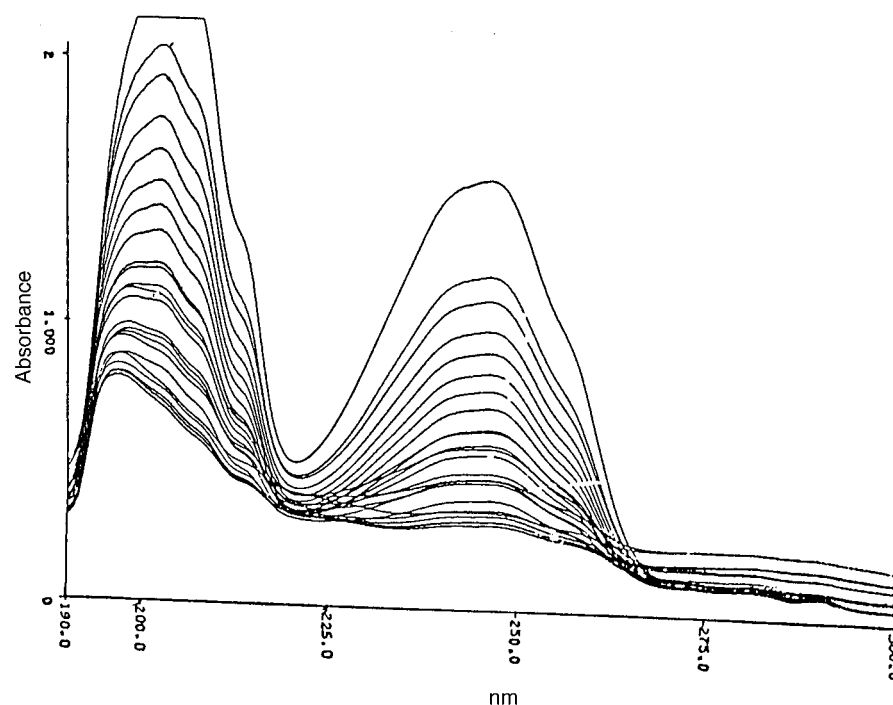
Figure 4. Ultraviolet-visible spectra showing the effect of gradual addition of β-CD to styrene in 90:10 (water:alcohol). [β-CD] = 9.985 $\times$ 10^{-4} M; [Styrene] = 1.092 $\times$ 10^{-4} M. The upper trace corresponds to the free guest substrate and subsequent ones to those at different concentrations of the host molecule.

to the ordinate gave a binding constant value of 31,395 $\pm$ 3800 M^{-1} for the 1:1 complex, where

ρ = [β-CD]/[styrene]
ΔA = Difference in absorption
ΔA_{max} = The maximum value of difference in absorption.

The average binding constant value obtained from both the methods was 31606 $\pm$ 3350 m^{-1}.

The PS polymer prepared in the presence of β-CD showed distinct differences in molecular weights, stereoregularities, T_g and T_m. Compared to the control, the syndiotacticities of the PS polymers increased with increase in the styrene:β-CD ratios. Although, the control exhibited 56% syndiotacticity, the polymer prepared with 10:1 styrene:β-CD polymer exhibited 77% syndiotacticity. Use of β-CD altered the stereoregularity by orienting the monomer molecules in a less sterically hindered orientation during polymerization, which can be achieved only by complexation of styrene by β-CD. Complexation equilibria examined by UV-Visible spectroscopy showed a 1:1 complex formed between β-CD and styrene with a binding constant value of 31606 $\pm$ 3350 m^{-1}. The high binding constant
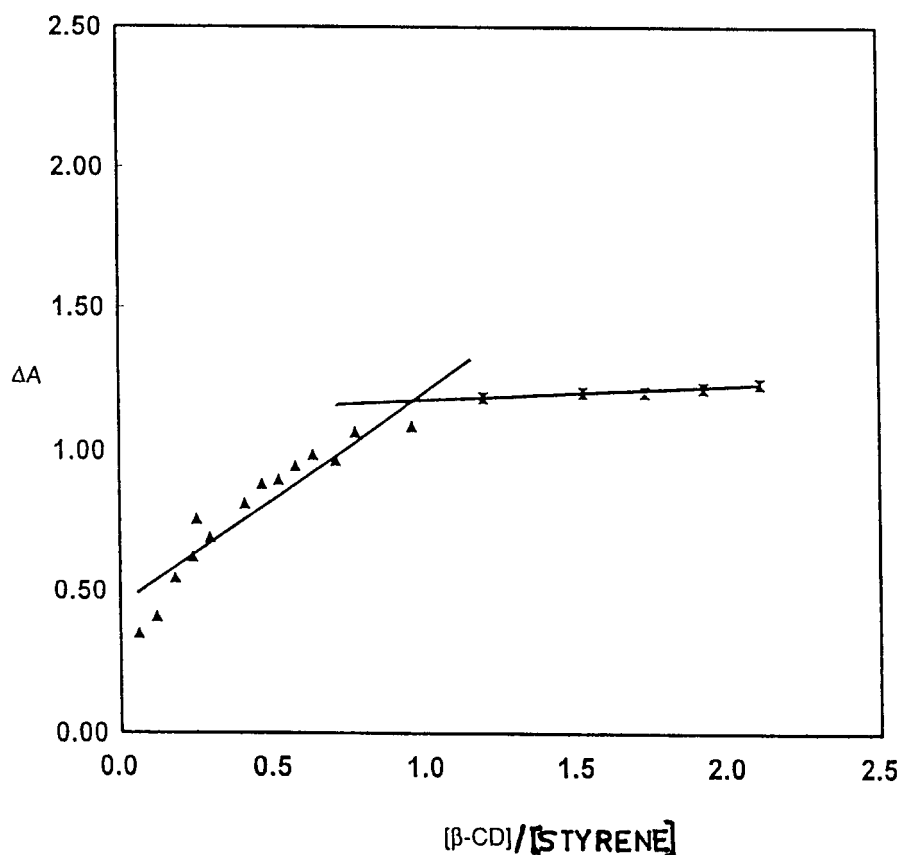
Figure 5. Determination of the stoichiometry of the β-CD-styrene inclusion complex in water : alcohol (90 : 10).

values indicated tight packing of the included guest monomers. The styrene : β-CD complexes being bulky were oriented in opposite directions during polymerization, leading to the enhanced syndiotacticity of the polymers prepared in the presence of β-CD. As such, the phenyl group of styrene being bulky was oriented in the opposite direction during polymerization, leading to 56% syndiotacticity in the control. A similar steric consideration was responsible for the lower molecular weight of the polymers prepared in the presence of β-CD, when compared to the control. Here also, the $\bar{M}_v$ increased as the β-CD content decreased, enforcing the role played by the bulky complexes during polymerization. The bulkier complexes with greater residency time of the included guest monomers favoured a slower reaction with greater probability of termination and greater propensity for steric hindrance, leading to lower molecular weight polymers with greater steric control in the presence of higher concentrations of β-CD. The enhancement of the residency time of the monomer on inclusion inside the β-CD cavity is already known [30].
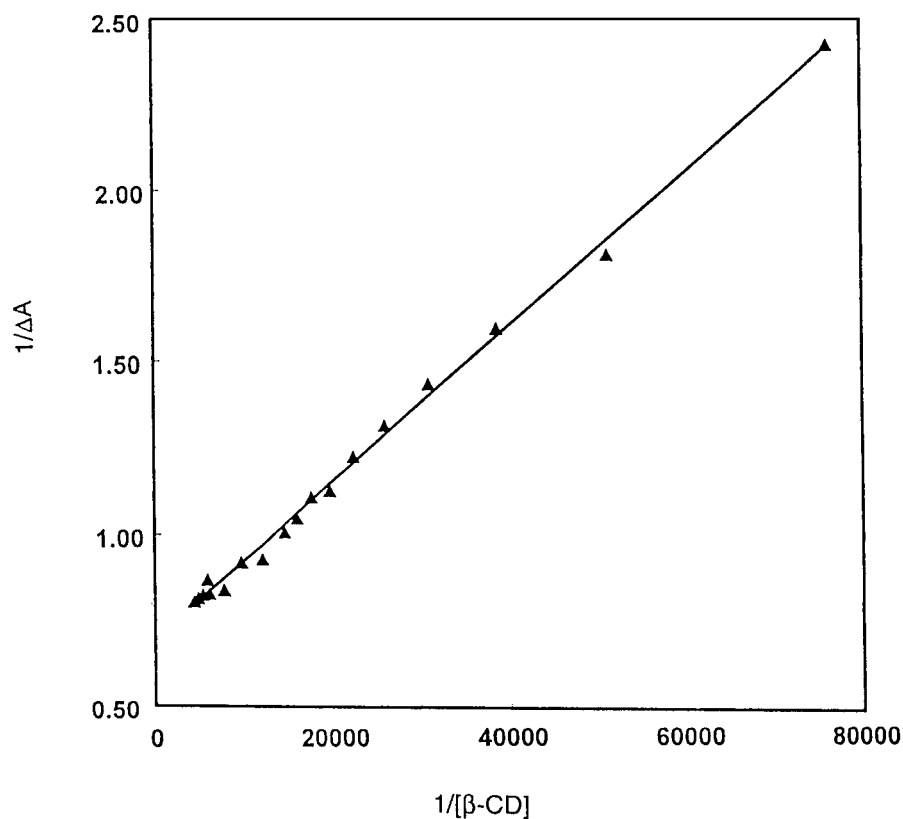
Figure 6. Determination of the binding constant value for the β-CD-styrene inclusion complex in water : alcohol (90 : 10) by the double reciprocal plot method. [β-CD] = 9.985 × 10^{-4} m; [Styrene] = 1.092 × 10^{-4} M.

The probable structure of the styrene : β-CD complex should be the one with the hydrophobic phenyl ring included inside the β-CD cavity and the vinyl portion, projecting outside at the wider end. This may explain not only the tight packing of the guest molecule inside the β-CD molecule, but also explain the steric interactions exerted in regulating the stereoregularity of the polymers during propagation. No indication of rotaxane formation was observed in NMR analysis which, if present, would show signals of β-CD in the polymer samples.

Acknowledgement

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