



## Effect of Temperature on Polystyrene Tacticity Through *Para* Aromatic Carbon Splitting in $^{13}\text{C}$ NMR Spectroscopy

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### ABSTRACT

Stereoregularity and microstructure of polystyrene (PS) were investigated by split *para* carbon of the benzene ring demonstrated by  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy. Polystyrene was synthesized via bulk thermal polymerizations at 50, 150 and 250°C at low conversions. Assignment of all the peaks of *para* carbon in a triad sequence was achieved. Bernoullian statistics was applied for three PS samples and by comparing the experimental and theoretical results it is found that with increasing polymerization temperature the probability of *meso* is augmented. Furthermore, with increasing NMR acquisition temperature from 20 to 65°C, triad sequences were converted to pentad sequences which follow 1st-order Markov statistics. Finally, it is shown that different deuterated solvents and their mixtures affect peak resolution and splitting of syndiotactic and isotactic sequences. To investigate the effect of deuterated solvent, deuterated benzene and tetrahydrofuran (THF- $d_8$ ) were also used and the spectra of polystyrene *para* aromatic carbon of benzene ring in these solvents were compared. There are three peak regions in  $\text{CDCl}_3$  at 20°C while, in THF- $d_8$ , syndiotactic region is almost separated and isotactic region overlaps with the atactic region, and in  $\text{C}_6\text{D}_6$  both syndiotactic and isotactic regions overlap. As a result, motions of *racemic* rich segments in THF- $d_8$  are higher than those of *meso* and conversely the mobility of *racemic* rich segments in  $\text{CDCl}_3$  is lower than that of *meso* rich segments. In summary, in THF- $d_8$  the upfield regions and in  $\text{CDCl}_3$  the downfield regions show better splitting.

### Key Words:

polystyrene;  
NMR;  
tacticity;  
*para* carbon;  
thermal polymerization.

### INTRODUCTION

In thermal initiated synthesis of polystyrene and high impact polystyrene process, polymerization is performed in several steps and reactors [1]. During these processes, polymerization begins at low temperature and with increasing conversion, temperature increases as well so that the difference would reach 150 to 200°C. In general, polystyrene chains take the form of

atactic structure by this method [2]. The most effective technique to study stereoregularity and tacticity, specifically in polystyrene is  $^{13}\text{C}$  NMR [3-7]. Due to a wide chemical shift window of  $^{13}\text{C}$  NMR compared with  $^1\text{H}$  NMR, splitting and accuracy are higher which would permit the quantitative and qualitative analysis of stereoregularity. Basically, a change in

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reaction temperature in different polymerization processes has different effects on stereoregularity and tacticity of a polymer product. For example, in coordination or ionic polymerization of styrene, temperature has a greater effect on stereoregularity in comparison with radical polymerization [8]. With reduction of reaction temperature in radical polymerization, difference in propagation energy for isotacticity and syndiotacticity becomes greater which decreases with temperature increase [9]. Generally, in radical polymerization at high temperature, polymer chains are synthesized in atactic form while at lower temperature the trend is towards syndio-tacticity of chains. The effect of temperature on stereoregularity varies for different polymers as methyl methacrylate is more susceptible than vinyl chloride [9]. There are a number of research works in which PS tacticity is investigated by  $^{13}\text{C}$  NMR. Quaternary carbon of benzene ring [10-15], methylene carbon [13-17] and methine carbon of PS was the target of these investigations. In another related research work the probability of *meso* has been reported [18]. Among them, Cheng et al. [15] have performed more in-depth investigation through nuclear magnetic resonance spectroscopy of one and two dimensional techniques and on triad sequences of PS methine carbons.

The aim of this research is to study the microstructure and stereoregularity of synthesized PS at different reaction temperatures through investigation of triad sequences of *para* carbon of benzene ring as an innovative pathway. Additionally, triad to pentad sequence transformation during NMR temperature variation and employing 1st-order Markovian and Bernoullian statistics for investigation of PS chains stereoregularity was studied. Finally, the effects of various deuterated solvents and their mixtures on resolution of PS *para* carbon were studied as another new aspect of the work.

## EXPERIMENTAL

### Materials

Styrene from Merck containing 20 ppm 4-*t*-butyl pyrocatechol was used after removing the inhibitor through 3 times washing with 5 wt% aqueous solution of NaOH followed by distilled water for its

removal. Calcium chloride was used to remove remaining water and then styrene was distilled at 40°C under vacuum of 150 mbar. The middle fraction of the distillate was used for further experiments. Toluene from Merck and methanol with technical grade were used as solvent and non-solvent, respectively.

### Polymerization

To perform reaction at specific temperature and study the microstructure of the product, the concentration of reactants must be low enough to reach adequate temperature at the shortest delay. In this regard ampoule reactors allow temperature accomplishment of the ingredients less than one minute. Since the aim of this study is microstructural investigation of PS obtained by polymerization at different temperatures up to 250°C in which styrene has a vapour pressure of 8 bar, stainless steel ampoules with higher thermal conductivity were used with dimensions of 15 cm length, 0.8 cm internal diameter and 0.2 cm wall thickness equipped with Whitley pressure valve. For thermal polymerization, 0.5 g of purified styrene was injected to the ampoule and then it was deoxygenated via degassing process. These ampoules were immediately immersed in oil bath working at  $\pm 0.1^\circ\text{C}$  precision. At different time intervals ampoules were withdrawn from the bath followed by immediate cooling in liquid nitrogen to halt the polymerization. The contents of ampoules after cooling were first dissolved in toluene and then PS was precipitated by adding the solution to its 20-fold volume of methanol. The resulting PS samples were dried in vacuum oven at 40°C for 24 h to a constant weight for conversion measurements. Reactions were performed at 50, 150 and 250°C and the corresponding samples were assigned PS-50, PS-150 and PS-250. Table 1 represents PS polymerization parameters.

**Table 1.** Condition of styrene polymerization.

Sample	Temperature (°C)	Time (min)	Conversion (%)
PS-50	50	2880	2
PS-150	150	30	15
PS-250	250	1	20

### Characterization

NMR Spectroscopy was performed on a Bruker Avance 400 MHz. Polystyrene concentration of 50 mg/mL deuterated chloroform ( $\text{CDCl}_3$ ), benzene- $d_6$  and deuterated tetrahydrofuran ( $\text{THF-}d_8$ ) in 5 mm tubes were used. Acquisition parameters for  $^{13}\text{C}$  NMR included flip angle of 90, delay time of 2 s, acquisition time of 1.37 s and 20000 scans at temperatures from 20 to 65°C using power gate pulse programme. NMR Spectra were treated with XWIN-NMR software version 3.5.

## RESULTS AND DISCUSSION

### $^{13}\text{C}$ NMR Spectrum of Polystyrene

As mentioned earlier,  $^{13}\text{C}$  NMR spectrum has advantage over  $^1\text{H}$  NMR due to its wider chemical shift. Figure 1 shows PS-50 spectrum in which methine and methylene carbons of backbone appear at 40.1-40.3 ppm and 41.4-46.6 ppm, respectively. Carbons *para*, *meta*, *ortho* and *quaternary* of benzene ring of pendant groups appear at their respective order of 124.7-126.3 ppm, 126.6-127.3 ppm, 127.3-129.3 ppm and 145.2-146.5 ppm. Among them methylene carbon and quaternary carbon of benzene ring show wide chemical shift and maximum splitting which permits more detailed investigations on microstructure and stereoregularity of the polystyrene.

In the past, in some references there were reports

of non-splitting of *para* carbon due to the limited magnetic field of NMR instruments [19]. While nowadays, with stronger magnetic fields splitting is observed. One of the examples is methine carbon which is investigated by Cheng et al. [15]. *Para* carbon of PS benzene ring is among carbons which show splitting at stronger magnetic field. Figures 2a and 2b show expanded spectrum of this carbon for PS-50 and PS-250 between 124.7-126.3 ppm. As it is evident in Figure 2, these carbons show three regions of triad sequences for isotactic, atactic and syndiotactic from downfield to upfield, respectively. Syndiotactic (rr) a combination of peaks 1 and 2, atactic (mr) peak 3 and isotactic peak 4 can be considered. For integration of peaks and calculations based on triad sequences peaks 1 and 2 which are overlapped were taken as one peak relating to syndiotactic region.

As it is seen in Figure 2, *para* carbon of benzene ring has low complexity and splitting and triad sequences are produced. On the other hand, quaternary carbon of benzene ring and methylene show higher splitting and complexity giving rise to pentad and hexad sequences [18]. Physical state, temperature, molecular weight of PS and type of deuterated solvent are effective on clarity of the sequences [20]. Table 2 presents microstructure and their chemical shifts of triad-pentad sequences. As it may be observed in Table 2, sequences are logically related to magnetic field so that by moving to higher or lower magnetic field the respective *racemic* or *meso* sequences are visible. At lower fields, PS-250 is

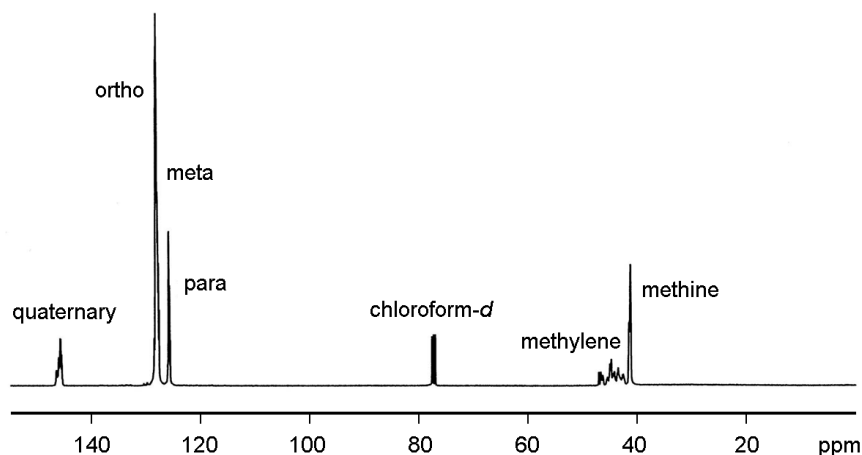


Figure 1. Expanded proton decoupled  $^{13}\text{C}$  NMR spectrum of PS-50 in chloroform- $d$  at 20°C.

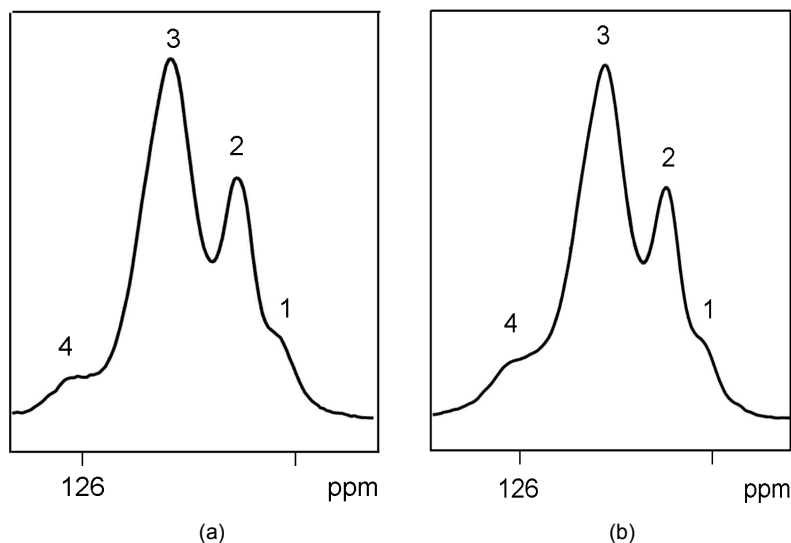


Figure 2. Para aromatic <sup>13</sup>C NMR spectrum of polystyrene in chloroform-d at 20°C: (a) PS-50 and (b) PS-250.

Table 2. Para aromatic carbon chemical shift assignment of triad-pentad sequences for PS-50.

Peak number	Assignments	Chemical shift (ppm)
1	rrrr	125.531
2	mrrm + mrrr	125.618
3	mr	125.771
4	mm	126.003

richer in isotactic sequences than PS-50 while at higher magnetic field PS-50 is richer in racemic sequences than PS-250 which is clearly seen in Figure 2. In Table 3, data from normalized peak areas are shown for the three samples.

Data are obtained via integration performed by both the instrument and calculation routes by

Bernoullian statistics. Therefore, with these statistics, the probability of meso can be obtained for three samples as shown in Table 3. By increasing the temperature the probability of meso sequence increases and it approaches to ideal random ( $P_m = 0.5$ ) [19]. Another finding is that at all temperatures, racemic sequences are higher than meso and styrene radical polymerization has a general trend towards syndiotacticity. Reported  $P_m$  results are from 0.28 to 0.57 as shown in Table 4. The variation in  $P_m$  data is attributed to different peak assignment, type of carbon in calculations, NMR magnetic energy level and type of software for peak integration measurement. Average number of meso and racemic sequences [19] in PS-50 is calculated to be 1.564 and 2.769, respectively. In PS-250 these values are changed to 1.681 and 2.468 indicating that meso sequence number increases with polymerization temperature which is

Table 3. Triad sequences of para aromatic carbon, calculated and observed data for three PS samples.

Peak number	Triad sequence	PS-50 ( $P_m = 0.36$ )		PS-150 ( $P_m = 0.39$ )		PS-250 ( $P_m = 0.41$ )	
		Observed	Calculated <sup>a</sup>	Observed	Calculated <sup>a</sup>	Observed	Calculated <sup>a</sup>
1, 2	rr	0.3492	0.4096	0.3184	0.3721	0.3029	0.3481
3	mr	0.5800	0.4608	0.5797	0.4758	0.5822	0.4838
4	mm	0.0708	0.1296	0.1019	0.1521	0.1149	0.1681

<sup>(a)</sup> Bernoullian statistics equation

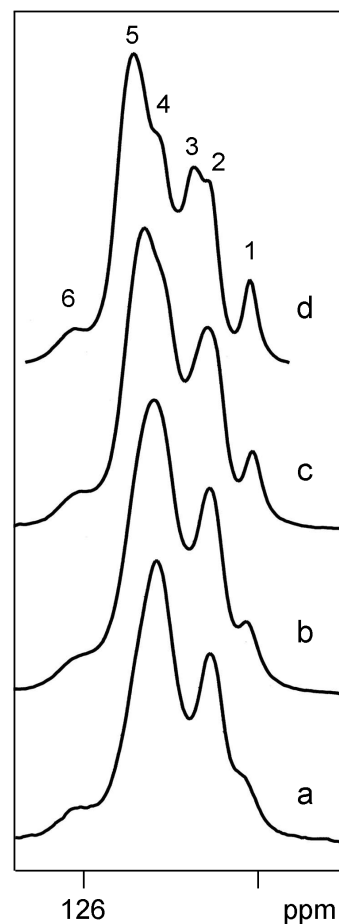
**Table 4.** Values of  $P_m$  for radical polymerization with relevant references.

Researchers	$P_m$	Ref.
Suparno	0.28	6
Matsuzaki	0.29	13
Inoue	0.31	2
Ziaee	0.38	16
Shepherd	0.45	15
Kawamura	0.46	7
Sato	0.46	4
Cheng	0.48	8
Randall	0.57	10

opposite to that of *racemic* isomer. The results are comparable with those of quaternary carbons of benzene ring and methylenes [18]. Besides, standard deviation of experimental results and Bernoullian statistics for all samples are calculated to be 0.0071, 0.0054 and 0.0049 from 50 to 250°C, respectively. Results show that with temperature increase, deviation from Bernoullian statistics is reduced.

**Study of Temperature Effect on the Analysis of Para Carbon of Benzene Ring by NMR**

When temperature increases during NMR acquisition it is seen that resolution improves and the number of peaks increases. Figure 3 shows <sup>13</sup>C NMR spectra of *para* carbon of benzene ring of PS-50 obtained at temperatures of 20, 35, 50 and 65°C. As it is observed in Figure 3 the number of peaks arises from 4 to 6. Therefore, it can be admitted that at 65°C pentad sequences are observed which are not seen at lower



**Figure 3.** Para aromatic <sup>13</sup>C NMR spectrum of PS-50 in chloroform-d at (a) 20, (b) 35, (c) 50 and (d) 65°C.

temperature. As mentioned in ref. [19], triad and pentad sequences have 3 and 10 theoretical peaks, respectively. On the other hand, appearance of 6 peaks in *para* carbon of benzene ring can be attributed to splitting of some triads to pentad while

**Table 5.** Pentad sequences of *para* aromatic carbon, calculated and observed data for PS-50 and PS-250 samples at 65°C.

Peak number	Pentad sequence	Chemical shift (ppm)	PS-50			PS-250		
			Observed	Calculated <sup>a</sup>	Calculated <sup>b</sup>	Observed	Calculated <sup>a</sup>	Calculated <sup>b</sup>
1	mrrm	125.557	0.0756	0.0531	0.0721	0.0662	0.0585	0.0733
2	mrrr	125.657	0.1191	0.1887	0.1733	0.1033	0.1684	0.1497
3	rrrr	125.697	0.1548	0.1678	0.1042	0.1295	0.1212	0.0764
4	rmm	125.791	0.1623	0.1062	0.2133	0.1628	0.1170	0.2066
5	mmrr+mrrm+rmrr	125.851	0.4191	0.3546	0.3680	0.4217	0.3668	0.3777
6	mm	126.005	0.0691	0.1296	0.0691	0.1165	0.1681	0.1163

(<sup>a</sup>) Bernoullian and (<sup>b</sup>) 1st-order Markov statistics equations.

**Table 6.** Standard deviation between observed and calculated data for *para* aromatic carbon of PS-50 and PS-250.

Statistical model	$(\Sigma <d>^2 / n)$	
	PS-50	PS-250
Bernoullian	$2.8 \times 10^{-3}$	$2.0 \times 10^{-3}$
1st-order Markov	$1.8 \times 10^{-3}$	$1.5 \times 10^{-3}$

some others do not split. One of the reasons for this behaviour is peak intensity. With increasing NMR analysis temperature due to low intensity of isotactic (mm) region there is no splitting while in syndiotactic and atactic regions peaks are splitted. All peaks and suggestion for microstructure of pentad sequences with Bernoullian and 1st-order Markov statistics for 6 peaks are presented in Table 5.

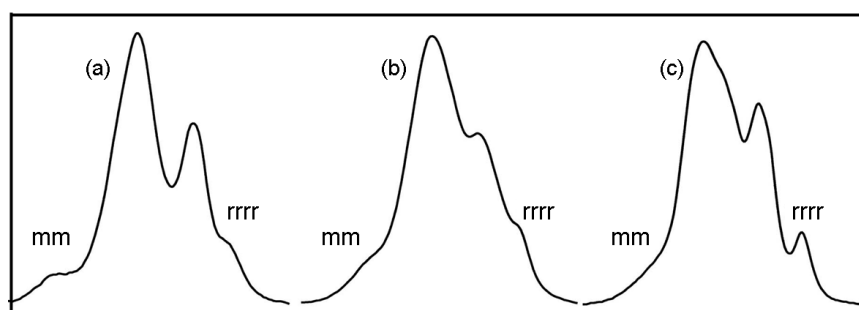
Table 5 includes results for verification of methods with experimental results and Table 6 shows standard deviation ( $\Sigma <d>^2 / n$ ) where  $<d>$  is difference between experimental and model, and  $n$  is number of data. As it can be seen in Table 6, PS chains propagation at high and low temperatures conform to Markov statistics. Although by increasing temperature chain tendency arises toward Bernoullian statistics but the overall preference is 1st-order Markov statistics.

### Effect of Solvent Type on *Para* Carbon of Benzene Ring Spectrum

Most of PS NMR spectroscopy is performed on solutions made in  $\text{CDCl}_3$  which is suitable solvent for PS. To investigate the effect of solvent, deuterated

benzene and THF were also used and the spectra of PS *para* carbon of benzene ring in these solvents were compared. Figure 4 shows expanded spectra of *para* carbon of PS-50 obtained at 20°C in three deuterated solvents and constant concentration. As it was mentioned earlier and evident in Figure 4, this carbon has 4 peaks in  $\text{CDCl}_3$  which are assigned in Table 2. However, in THF (rrrr) peak is almost separated while (mm) overlaps with atactic region. In  $\text{C}_6\text{D}_6$  both syndiotactic and isotactic regions overlap. Based on NMR theories, line width has direct relation with relaxation time of magnetic nuclei in accordance with Heisenberg's uncertainty principle. Short relaxation time means high uncertainty which is seen as broad peaks in NMR [21]. In some instances peak broadening causes overlapping, the fact which is seen during investigation of polymer stereoregularity. If one can increase relaxation time of each sequence which in turn decreases the uncertainty, narrower peaks can be produced. Consequently, formerly overlapped peaks separate from each other leaving isolated peaks. Type of solvent influences the relaxation time through complex behaviour including, viscosity of solvent and polymer solution and their solubility parameters can be effective as well. Some solvent properties are shown in Table 7.

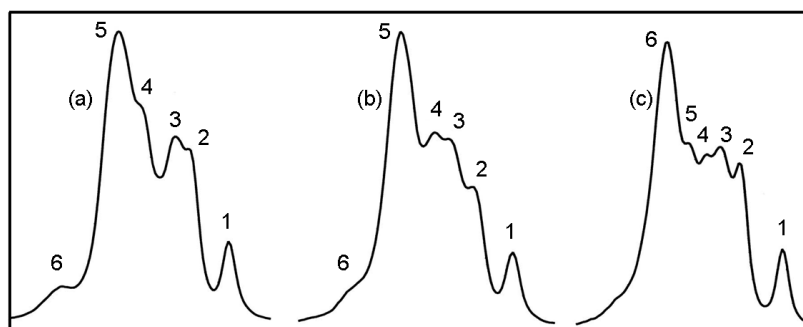
As it is given in Table 7,  $\text{C}_6\text{D}_6$  and hence its PS solution have higher viscosity, while all solvents have almost similar solubility parameters close to PS ( $9.1 (\text{cal}/\text{cm}^3)^{1/2}$ ) [23]. Therefore, higher  $\text{C}_6\text{D}_6$  viscosity causes lower relaxation time and thus broader peaks and higher overlapping are produced. Syndiotactic sequences of *para* carbon in THF and isotactic sequences in  $\text{CDCl}_3$  show better resolution. As a



**Figure 4.** *Para* aromatic  $^{13}\text{C}$  NMR spectrum of PS-50 at 20°C in (a) chloroform- $d_3$ , (b) benzene- $d_6$  and (c) tetrahydrofuran- $d_8$ .

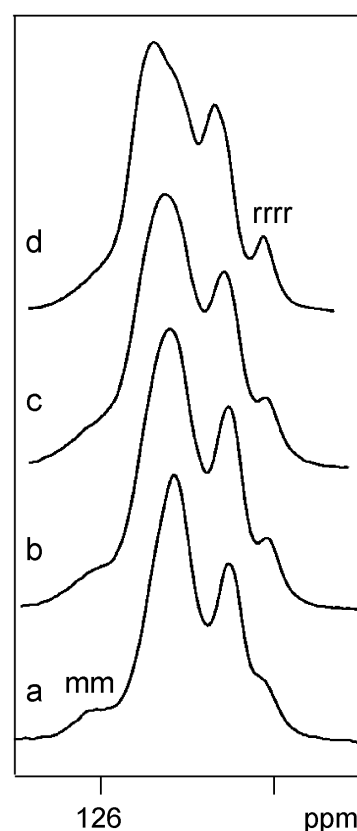
**Table 7.** Characteristic of solvents [22].

Solvent	Boiling point (°C)	Viscosity at 20°C (c.poise)	Solubility parameter (cal/cm <sup>3</sup> ) <sup>1/2</sup>
Chloroform	61	0.55	9.3
Benzene	81	0.65	9.2
Tetrahydrofuran	66	0.53	9.1

**Figure 5.** *Para* aromatic <sup>13</sup>C NMR spectrum of PS-50 at 65°C in (a) chloroform-*d*, (b) benzene-*d*<sub>6</sub> and (c) tetrahydrofuran-*d*<sub>8</sub>.

result motions of *racemic* rich segments in THF-*d*<sub>8</sub> are higher than those of *meso* and conversely the mobility of *racemic* rich segments in CDCl<sub>3</sub> is lower than that of *meso* rich segments. In summary, in THF upfield regions and in CDCl<sub>3</sub> downfield regions show better splitting. Another parameter which improves the resolution in NMR is acquisition temperature. Figure 5 shows the spectra of PS-50 *para* carbon at 65°C. It can be seen from Figure 5 that in THF-*d*<sub>8</sub> syndiotactic regions undergo higher splitting while isotactic region remained unchanged and almost invisible. However, in CDCl<sub>3</sub> syndiotactic regions which had overlapping at 25°C are completely splitted and isotactic regions show improved separation. As a consequence, it could be concluded that for calculation of *meso* probability ( $P_m$ ), CDCl<sub>3</sub> is the preferred solvent.

It could be interesting that NMR investigations perform on samples which are dissolved in a mixture of the two solvents. In this manner 30/70 and 70/30 solutions of CDCl<sub>3</sub> and THF-*d*<sub>8</sub> were prepared in order to achieve better observation on overlapping of isotactic and syndiotactic sequences. Figure 6 shows the spectra of *para* aromatic carbon ring in pure and mixture of solvents. As can be seen from Figure 6, by increasing THF-*d*<sub>8</sub>, isotactic (mm) sequences

**Figure 6.** *Para* aromatic <sup>13</sup>C NMR spectrum of PS-50 at 20°C in (a) CDCl<sub>3</sub>, (b) (70% CDCl<sub>3</sub>+30% THF-*d*<sub>8</sub>), (c) (30% CDCl<sub>3</sub>+70% THF-*d*<sub>8</sub>) and (d) THF-*d*<sub>8</sub>.

demonstrate more overlapping with atactic parts while syndiotactic sequences specifically (rrrr) ones show higher resolution and separation. It can be concluded that in THF- $d_8$  the mobility of syndiotactic segments in  $CDCl_3$  and isotactic segments in THF- $d_8$  are higher which cause longer relaxation times and better peak splitting.

## CONCLUSION

Thermal bulk polymerization of styrene was performed at 50, 150 and 250°C without any additives. Analysis of all triad sequences for *para* carbon of benzene ring was accomplished by  $^{13}C$  NMR and experimental data were compared with Bernoullian statistics. In all reaction temperatures 1st-order Markov fit slightly better with the experimental results and with increasing reaction temperature the discrepancy between experimental results and the model decreases indicating that propagation tends towards Bernoullian statistics. In all polymerization temperatures, *racemic* sequences are higher than *meso* sequences. Effect of solvent type and their mixtures and acquisition temperature were investigated and it was shown that higher NMR acquisition temperature produces improved splitting and isolation of peaks as 3 regions of triad is converted to 6 peaks of pentad sequences. Different solvents and their mixtures induce different splitting of the peaks so that syndiotactic and isotactic sequences show more splitting in THF- $d_8$  and  $CDCl_3$ , respectively.

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