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Stereochemical Assignment of ^{13}C NMR Spectra of Predominantly Syndiotactic Polystyrene

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ABSTRACT: In the present work, predominantly syndiotactic polystyrene samples were prepared with different catalysts and polymerization conditions and the obtained polymers were used for assignments of stereochemical structures of polystyrene. Assignment was carried out by comparison of ^{13}C NMR spectra of polystyrenes with different syndiotacticity and based on polymerization mechanism. Assignments were also compared with results in the previous work.

KEY WORDS Polystyrene / ^{13}C Nuclear Magnetic Resonance / Assignment /

The ^{13}C NMR spectrum of polystyrene was first reported by Johnson *et al.*[1] and the assignment of ^{13}C NMR spectrum of polystyrene has been carried out by many researchers.[2-6] However, there are still many controversies and the stereochemical structures of polystyrene are far from full understanding. The assignments of tetrad are different in ref 2—5.

Generally there are two methods for the assignment of ^{13}C NMR spectrum of polystyrene in previous work. First, assignment was made by calculating the intensity of resonances based on Bernoullian or Markovian statistics model and comparing calculated values with observed ones.[2-4] However it is difficult in this method to assign the peaks with similar intensity, especially weak resonances. Secondly, through comparing the ^{13}C NMR spectra of polystyrenes with different tacticity, assignment was also performed.[5] Nevertheless, most of the samples in previous work were atactic or isotactic-rich, and predominantly syndiotactic sample was rarely reported. This leads to ambiguous assignments of *racemic*-rich sequences. Moreover, since stereochemical structures of polymer are strongly dependent on the polymerization mechanism (active-site-controlled or chain-end-controlled), the types of stereochemical sequences in the polymer chain and relative ratios among them provide useful information for assignment.

In the present work, predominantly syndiotactic polystyrene samples prepared with different catalysts and polymerization conditions were used for the assignments of stereochemical structures of polystyrene. Assignment was carried out by comparing ^{13}C NMR spectra of polystyrenes with different syndiotacticity and based on polymerization mechanism.

EXPERIMENTAL

Preparation of Polystyrene Samples

Four polystyrene samples for ^{13}C NMR characterization were prepared with different catalysts and polymerization conditions (Table I). The cocatalyst was methylaluminoxane (MAO). The preparation of polymer-supported catalyst was described in elsewhere.[7]

^{13}C NMR Analysis

100.7 MHz for ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer at 370 K in pulsed Fourier transformation model. The polymer solutions were prepared by dissolving *ca.* 50 mg polymer at 130°C in 0.5 ml $C_6D_4Cl_2$. 1% hexamethyldisiloxane (HMDS) was added as the internal standard. The pulse angle was 90°, pulse repetition, 10 s, spectral width, 5000 Hz, number of scans, 2000, and data points, 32 K.

RESULTS AND DISCUSSION

From the whole ^{13}C NMR spectrum of polystyrene, the methylene region consists of a widely spreading band and is best resolved, while the resonances of other carbon atoms are not sufficiently resolved. In the present work, emphasis was placed on the assignment of methylene region. As reported earlier, in the ^{13}C NMR spectrum of polystyrene the methylene chemical shift sensitivity is basically tetrad.[4] Some hexad splittings may also be observed. Figure 1 shows the expanded ^{13}C NMR spectra of polystyrenes prepared with different catalysts and polymerization conditions. Stereochemical assignments of the methylene region are summarized in Table II.

Figure 1a is the expanded ^{13}C NMR spectrum of the methylene region of polystyrene prepared with $CpTiCl_3$–MAO homogeneous catalyst at Al/Ti ratio 600. Based on the ^{13}C NMR spectra of highly syndiotactic and isotactic polystyrene, peaks 8 and 12 are assigned to long *racemic* sequence (*rrrr* hexad) and long *meso* sequence (*mmm* tetrad) respectively. Previous work showed that the polymerization mechanism of $CpTiCl_3$–MAO ho-

Table I. Catalysts and polymerization conditions for the preparation of samples

Samples	Catalysts	Al/Ti ratio	Polym. temp	Polym. time
		mol mol^{-1}	°C	h
A	$CpTiCl_3$	600	50	5.0
B	$CpTiCl_3$	100	50	5.0
C	Supported-$CpTiCl_3$	600	50	5.0
D	Supported-$CpTiCl_3$	100	50	5.0

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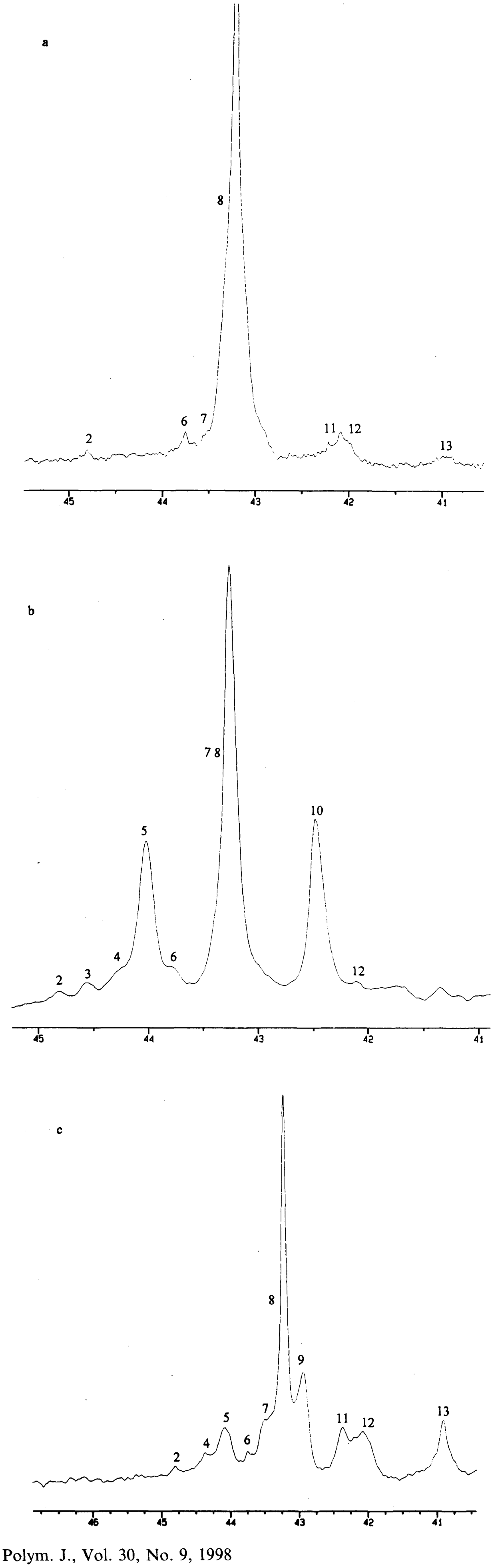


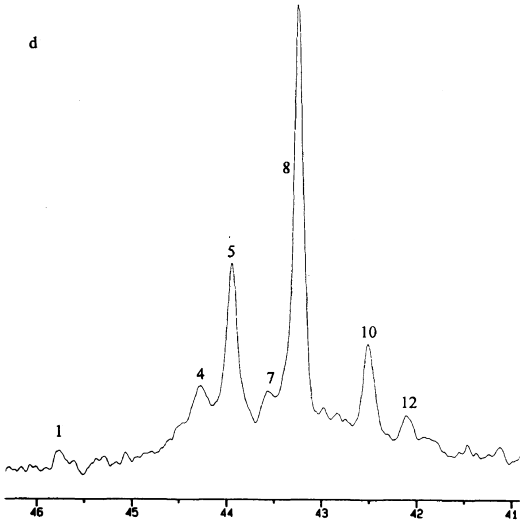


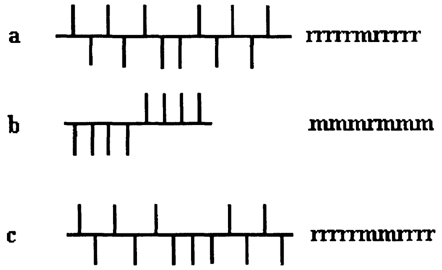
Figure 1. Expanded ^{13}C NMR spectra of the methylene region of (a) sample A, (b) sample C, (c) sample B, and (d) sample D.

Table II. Assignment of ^{13}C NMR spectra of the methylene region of polystyrene

Peak No.	Assignment		Chemical shift
	Tetrads	Hexads	ppm
1		*mrmrr*	45.8
2	*rmr*	*rrmrr*	44.8
3		*mrmrm*	44.5
4		*mrmmr* + *rrmmm*	44.3
5	*rmm*	*rrmmr*	44.0
6		*mrmmm*	43.7
7		*rrrrm*	43.5
8	*rrr*	*rrrrr*	43.2
9		*mrrrm*	42.9
10	*rrm*	*rrrmm*	42.5
11		*rrrmr*	42.3
12	*mmm*		42.1
13	*mrm*		40.9

mogeneous catalyst for syndiospecific polymerization of styrene is chain-end-controlled.[8,9] Thus the structures like that in Schemes 1a, b may be generated. In structure (a), four hexads *rrrrr*, *rrrrm*, *rrrmr*, *rrmrr* can be observed and the ratio of hexad [*rrrrm*] : [*rrrmr*] : [*rrmrr*] is 2 : 2 : 1.[10] Structure (b) produces four hexads *mmmmm*, *mmmmr*, *mmmrm*, *mmrmm*, and the area ratio of [*mmmmr*] : [*mmmrm*] : [*mmrmm*] is 2 : 2 : 1. However, due to low content of *meso* unit, only tetrads *mmm* and *mrm* are observed. Therefore, seven peaks attributed to five hexads and two tetrads are resolved in Figure 1a.

Figure 1b is the expanded ^{13}C NMR spectrum of the methylene region of sample C prepared with a polymer-supported catalyst at Al/Ti ratio 600. This polymer is predominantly syndiotactic, because three major peaks are observed and the intensity of other peaks is very weak in Figure 1b. This indicates a simple structure of this polymer. It is also observed that the relative intensity of peaks 5 and 10 is close to 1 : 1. From above facts, the structure of this polymer sample and polym-



Scheme 1. Possible structural defects in polystyrene chains.

erization mechanism of supported catalyst can thus be inferred.[10] The polymerization mechanism is active-site-controlled and sample C has the structure shown in Scheme 1c, since only in such a polymer structure the absorption of four hexads *rrrrr*, *rrrrm*, *rrrmm*, and *rrmmr* is very strong and the area ratio of [*rrrmm*] : [*rrmmr*] is 1 : 1. Thus peaks 5 and 10 are assigned to *rrmr* and *rrrmm* hexads respectively. Due to the lower syndiotacticity of this sample, the other two minor peaks at 44.5 ppm (peak 3) and 44.3 ppm (peak 4) in Figure 1b are assigned the splittings of *rmr* and *rmm* respectively, *i.e.*, *mrmrm* and *mrmmr* + *rrmmm*.

Figures 1c and d are the expanded ^{13}C NMR spectra of polystyrene prepared with $CpTiCl_3$–MAO and polymer-supported catalyst at Al/Ti = 100. These two samples possess even lower syndiotacticity. In these two spectra, splittings of *rrr* tetrad can be observed more obviously. Peak 9 at 42.9 ppm is assigned to the other hexad (*mrrrm*) splitting of *rrr* tetrad because it is very close to *rrrrr* hexad. A new peak appearing at 45.8 ppm in Figure 1d (peak 1) is attributed to *mrmrr* hexad, another splitting of *rmr* tetrad.

The assignments in Table II are similar to those of Kawamura to some extent,[5] but (1) the major difference lies in the order of *rrr* and *rmm* tetrads. In Kawamura's assignments *rrr* tetrad is in a lower field than *rrm* tetrad, whereas the order is reversed in Table II. The assignments of tetrads in Inoue's work were the same as that in the present work.[2] (2) The sequences of some hexad splittings in *rmr*, *rmm*, and *rrr* tetrads differ. In ref 5 hexad splittings were assigned in the order of *m*xxx*m*, *m*xxx*r*, *r*xxx*r* from lower field to higher field, but in the present work the hexad splittings are assigned according to the sequence of *m*xxx*r*, *r*xxx*r*, *m*xxx*m* from lower field to higher field, since the strongest hexad splittings *r*xxx*r* is found between the hexad splittings of *m*xxx*r* and *m*xxx*m*.

The hexad splittings of *mmm* and *mrm* tetrads and part of hexad splitting of *rrm* tetrad cannot be resolved in Figure 1, because the polystyrene samples used for assignment are predominantly syndiotactic and content of the *meso* unit is relatively lower.

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