Polybutadiene Content and Microstructure in High Impact Polystyrene

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SYNOPSIS

The polybutadiene (PB) content and its microstructure in different grades of high impact polystyrene (HIPS) has been studied by various spectroscopic techniques. PB is characterized by deformation bands in FTIR spectroscopy at 994, 967, 912, and 729 cm^{-1}. FT-Raman was used for higher constant resolution over the range of wave numbers. It provides reasonable signal to noise ratios in near IR excited Raman. Proton and ^{13}C-NMR spectroscopy was utilized for the determination of polybutadiene content in HIPS and tacticity, and reactivity ratios. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The improvement of impact resistance of polystyrene (PS) is generally ensured by polybutadiene (PB) introduced before the free radical polymerization of styrene. The PB nodules are then compatibilized by grafting of styrene units. This blend of PS and PB is termed as high impact PS [HIPS] where the PB content is in the range of 3–8 mol %. The property improvement[1] is due to the chemical interaction between the growing PS chain and the rubber, chemical crosslinking of the rubber, and occlusion of the cocontinuous polymer phase inside the rubber particles, which increases the effective volume of the rubber phase.

Many methods[2-4] are in use for the characterization of PB. However, because of its low content and microstructure distribution (*cis*-1,4, *trans*-1,4, and vinyl-1,2) in the blends (HIPS), several complementary techniques are required for its analysis. This article describes the advantages and limitations of ^{1}H- and ^{13}C-NMR, IR and Fourier transform (FT)-Raman spectroscopies for the determination of both the content and microstructure of PB present in commercially available HIPS.

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EXPERIMENTAL

Materials

Commercial samples of HIPS from Elf-Atochem-France (HIPS I and II) and from Polychem, India (HIPS III and IV) were compared with a commercial PS from Elf-Atochem-France and with a PB containing all of the three microstructures (PB) from Aldrich-Europe. A few samples were extracted with methanol to ensure that additives were not interfering with the analysis.

Analysis

All the materials were pressed in an electrically heated laboratory press at 180°C for 2 min to get 100-μm films suitable for the IR analysis. For Raman analysis, because of the heat accumulation in 100-μm thick samples, a continuous IR emission was perturbating the spectral baseline. To avoid this problem, analysis were performed on thicker samples (>200 μm). FTIR and Raman spectra were obtained from Nicolet instruments impact 400 (100 scans, DTGS detection) and Raman 910 (100 scans; laser, 1064 nm, 10 Å), respectively.

NMR spectra were obtained on polymer samples dissolved or swollen (concentration ca. 40 mg/mL) in $CDCl_3$ (25° and 50°C), C_6D_6 (25°C), and *o*-di-

chlorobenzene-D_4 (25° and 110°C), with a Bruker AC 400 instrument at 400 MHz with trimethysilane (TMS) or solvent as internal reference. The best resolution was obtained with $CDCl_3$ sampling at 25°C. The conditions were as follows:

1. ^{1}H-NMR: repetition time 3 s, 90° pulse, accumulation of ca. 300 scans.
2. ^{13}C-NMR:

   (a) Quantitative: delay time 30 s, 300 scans.
   (b) J-Mod: this technique,[5] based on the modulation of the coupling constant, allows the differentiation of primary and tertiary carbons from secondary and quaternary ones; delay time 1.5 s, 8000 scans.
   (c) Distortionless enhancement by polarization transfer (DEPT) pulse sequence is an improvement of insensitive nuclei enhancement by polarization transfer (INEPT). The sequence is as follow:

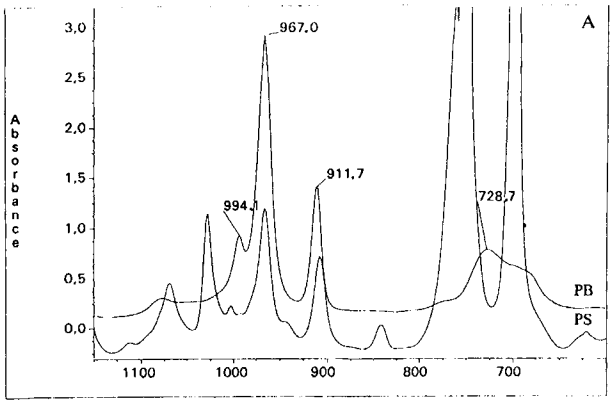

Figure 1 Deformation region of HIPS/FTIR spectra. (A) pure polybutadiene (PB) and polystyrene (PS). (B) PB spectra obtained by subtraction (HIPS-PS).

Table I Polystyrene Content (mol %) in HIPS from FTIR

HIPS I	HIPS II	HIPS III	HIPS IV
84	91	87	94

^{1}H (delay time) $(\pi/2)x$ τ

$(\pi)x$ τ $(\theta)y$ τ decouple

^{13}C

$(\pi)x$ τ $(\pi/2)x$ τ acquire

where $\tau = \frac{1}{2}J$, J being an average ^{1}H-^{13}C coupling constant setting to 135 Hz (we checked that the sequence is rather insensitive to this value if $120 < J < 200$ Hz). θ is the proton pulse of variable length ($\theta_1 = gB_1t_1$); in our experiments, $t_1 = 4.25$ μs ($\theta = 45°$). (Some experiments were performed with $\theta = 135°$ to differentiate secondary carbons.) The delay time of 5 s was longer as usual.[6] x, y referred to the rotating frame of the spectrometer. This technique usually allows the shortening of the delay time between two pulses and, consequently, reduces the acquisition time necessary to get quantitative data. The quaternary carbon atom of PS and the residual CH of $CDCl_3$ are not detected by this technique. In all ^{13}C experiments, sequences were obtained using a gate decoupling to avoid possible intensity distortions arising from nuclear Overhauser effect (NOE) factors.

RESULTS AND DISCUSSION

FTIR Spectroscopy

The main advantage of FTIR spectroscopy for polymer analysis is that it is nondestructive and is usable in the solid state. From the comparison of IR spectra of both PS and PB, it is obvious that PS can be identified by its medium band at 542 cm^{-1} and/or by its weak absorption bands at 1943, 1870, and 1803 cm^{-1} according to the sample thickness. PB is characterized[7,8] by the deformation bands present at 994 (vinyl-1,2), 967 (*trans*-1,4), 912 (vinyl-1,2), and 729 cm^{-1} (*cis*-1,4). A number of earlier articles emphasize the difficulty in quantifying the contribution of each structure because of the overlapping of the bands[9] and poor resolution of the *cis*-1,4 band.[10] To obviate this difficulty, Silas et al.[9] con-

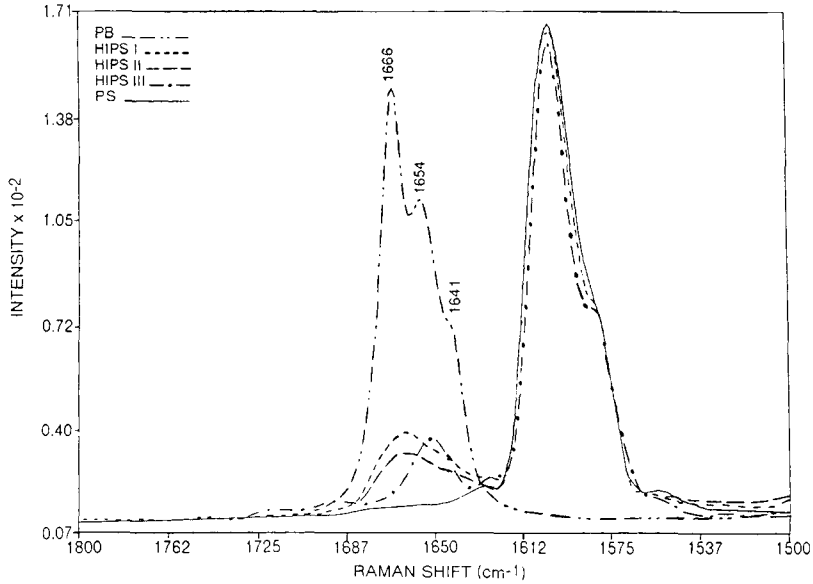

Figure 2 Comparison of Raman spectra of PB, HIPS, and PS.

sidered that each band resulted from the contribution of the three microstructures, Richardson and Sacher[10] proposed that the *cis*-1,4 content can be determined by subtracting the contribution of (*trans*-1,4 + vinyl-1,2) from the total concentration in PB.

The comparison of PS and PB spectra in the 1100–600 cm^{-1} region is shown in Figure 1(A); it can be seen that the band at 728.7 cm^{-1} overlaps with the strong bands of PS at 700 and 760 cm^{-1} and renders the quantification of the PB content by IR spectroscopy all the more difficult. However, the 542 cm^{-1} band (not shown) is typical of PS and it is possible to measure its absorption coefficient via a careful measurement of the sample thickness. The value obtained (ε 542 cm^{-1} = 19.8 mol, 1 cm) can be used via the Beer–Lambert law for the determination of PS content in HIPS (see Table I), but the accuracy of this method decreases for very low PB contents.

However, a precise subtraction of the PS contribution in HIPS is now possible with modern FTIR instruments. Figure 1(B) shows the PB spectra obtained by Omnic software (Nicolet) from subtraction of HIPS I, II, III, and IV-PS.

Microstructures of *trans*-1,4 and 1–2 are clearly revealed at 966.0, 912.7, and 995.2 cm^{-1}, respectively, but the *cis*-1,4 contribution cannot be evaluated; this fact is particularly dramatic for sample III for which, as we will see later, the *cis*-1,4 contribution is very high.

FT Raman Spectroscopy

Since the discovery of Raman effect in 1928, there have been a lot of improvements in all aspects of the instrumentation (source, collector, detector). Up to 1986, the developments were mainly the source (laser) and the detector (photomultiplicator), but the polymer analysis was often limited by fluorescence emission from impurities that made it difficult or even impossible to measure the Raman spectrum.[11] One typical advantage of FT-Raman developed in 1986 by Hirschfeld and Chase[12] is to reduce or to eliminate the fluorescence by the use of a near-IR excitation source [in our case, 1064 nm (9394 cm^{-1})]; other advantages are the same as for FTIR (high constant resolution over the range of wave numbers, accurate wave number calibration, etc.). Raman spectroscopy in this spectral region is virtually free from fluorescence interference and photochemical sample damage.

As shown in Figure 2, the PS and PB present in HIPS I, II, III, and IV can be differentiated by their 1600 and 1660 cm^{-1} band, respectively. The wide band around 1660 cm^{-1} for PB results in fact from the contribution of *trans*-1,4 (1666 cm^{-1}), *cis*-1,4 (1654 cm^{-1}), and vinyl (1641 cm^{-1}) microstructures; and some authors[13] claim that the relative content of each microstructure can be directly derived from the deconvolution of this band. The band shapes observed ensure that HIPS III is mainly *cis*-1,4 and that HIPS I, II, and IV contain appreciable quan-

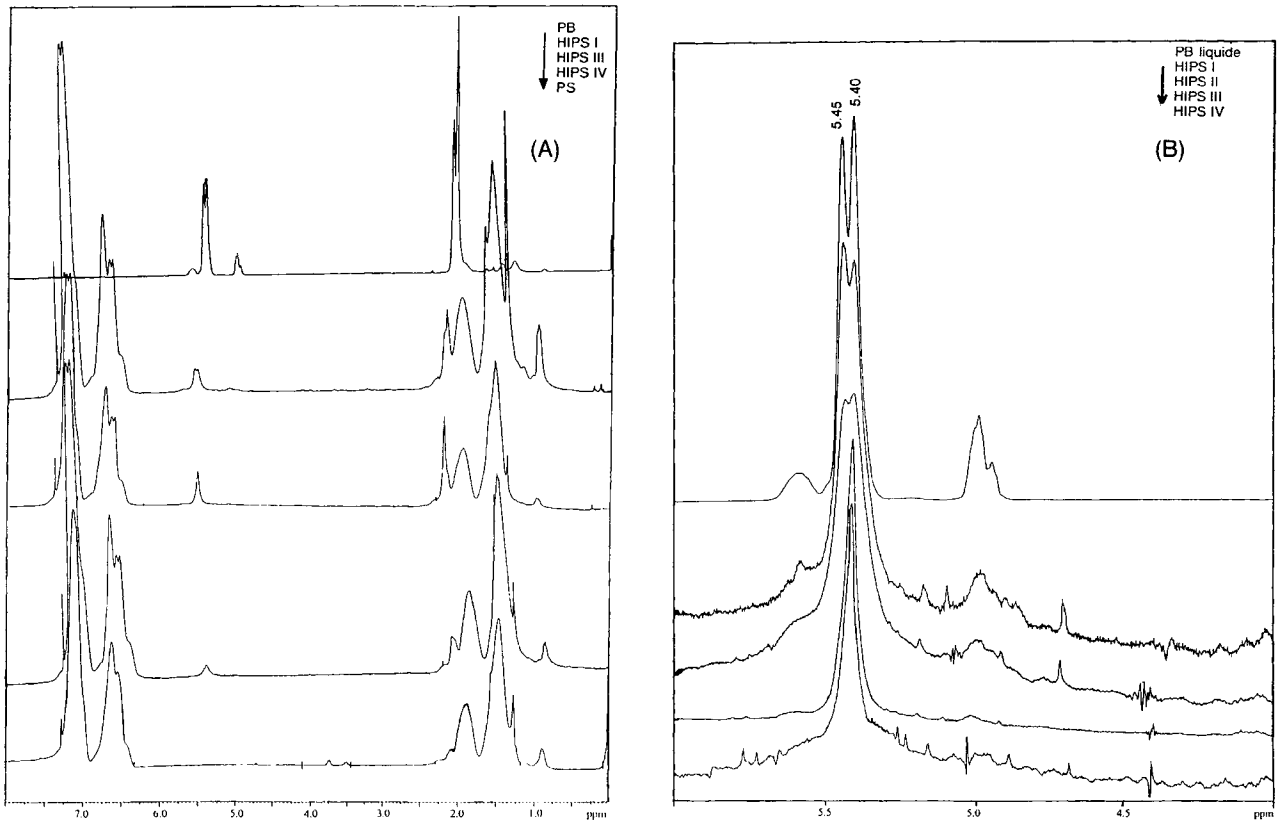

Figure 3 Proton NMR spectra of PB, HIPS, and PS (repetition time 3 s; scan number ca. 300). (A) Complete spectra (0–8 ppm). (B) Expanded olefinic region (4–6 ppm).

tities of *cis*- and *trans*-1,4 structures and a lower content in vinyl.

Proton NMR spectroscopy

^{1}H-NMR spectroscopy of PB has been extensively developed for the determination of microstructures,[14-17] tacticity (vinyl structures),[18] or for the determination of PB content in copolymers and consequently for the determination of reactivity ratios (r_1, r_2).[19-22] In the case of polymer blends, we can generally expect some simplifications compared to simple copolymers because of the absence of comonomer chemical linkages. In the particular case of HIPS, because of the synthetic method based on the polymerization of styrene in which PB is dissolved, we can expect to have some copolymerization between the residual double bonds of PB and styrene.

These PB/PS linkages ensure compatibilization of the blend, but their content is too low to be detected by ^{1}H-NMR. So we can assume that the ^{1}H-NMR spectrum is just a superposition of PB and PS homopolymers.

As shown in Figure 3 and Table II, PS and PB moieties can be differentiated from the aromatic (6.3–7.5 ppm) and the olefinic (4.8–5.6 ppm) regions, respectively.[23-28]

In addition, we can see that ^{1}H-NMR at 400 MHz ($CDCl_3$) has the potential to separate the olefinic resonance peaks of vinyl, *cis*-, and *trans*-1,4 protons. Attempts to further resolve the *cis* and *trans* protons by increasing the temperature (50°C in $CDCl_3$, 110°C in *o*-dichlorobenzene D_4) were not successful. This result is quite significant because the literature[26-28] recommends the evaluation of the *cis* and *trans* content only by ^{13}C-NMR because of the poor resolution of ^{1}H-NMR at lower magnetic fields.

The expanded 4–6 ppm region reported in Figure 3(B) for PB, PS, and HIPS I, III, and IV clearly shows that a full determination of PB (content and microstructure) can be done by proton NMR. However, the determination of the *cis*/*trans* content is not too accurate by this method.

Table II ^{1}H-NMR Chemical Shifts from PB and PS Homopolymers

Chemical Shifts (ppm)[a]	PB[25-28]	PS[23-25]
1.35	$C\underline{H}_2$ (1-2)	
1.50		CH_2
1.92		CH (aliphatics)
2.05	$C\underline{H}_2$ (*t*1-4)	
2.10	$C\underline{H}_2$ (*c*1-4)	
5.00	$C\underline{H}_2$=CH (1-2)	
5.40	$C\underline{H}$=$C\underline{H}$ (*c*1-4)	
5.45	$C\underline{H}$=$C\underline{H}$ (*t*1-4)	
5.60	CH_2=$C\underline{H}$ (*1*-2)	
6.55		CH (arom. *m, m', p*)
7.10		CH (arom. *o, o'*)

[a] This work.

Table IV ^{13}C-NMR Chemical Shifts from PB and PS Homopolymers

Chemical Shifts (ppm)[a]	PB[25-28]	PS[23-25]
25.0	CH_2 (1-2)	
27.4	$\underline{C}H_2$—CH= (*c*1-4)	
32.7	$\underline{C}H_2$—CH= (*t*1-4)	
40.4		CH (aliphatic)
44.0		CH_2 (aliphatic)
43.5	CH (1-2)	
114.0	$\underline{C}H_2$=CH (1-2)	
127.7		C (arom. *p*)
127.7-128		C (arom. *o, o', m, m'*)
129.2	CH=CH (*c*1-4)	
129.7	CH=CH (*t*1-4)	
142.7	CH_2=$\underline{C}H$ (1-2)	
145.4		C1 (aromatic)

[a] This work.

We can consider that the area of aromatic peaks corresponds to five protons of PS (the contribution of residual $CHCl_3$ at 7.27 ppm is negligible). The peak area at 5.0 and 5.6 ppm corresponds to one (=CH) or two (CH_2=) protons of vinyl; and the contribution of two protons (CH=CH) of both *cis* and *trans* microstructures can be deduced from the deconvolution of peaks at 5.40 and 5.45 ppm, respectively. Table III reports the results obtained from both ^{1}H- and ^{13}C-NMR.

^{13}C-NMR spectroscopy

^{13}C-NMR spectroscopy is known to be more suitable than ^{1}H-NMR for the determination of *cis* and *trans* contents of PB[26-28] because the resonances of methylene protons at 1.98 and 2.03 ppm or olefinic protons at 5.40 and 5.45 ppm are difficult to resolve even at high magnetic fields. Despite a lower sensitivity, the large range of ^{13}C chemical shifts enables a complete characterization of the resonances of all

Table III Quantitative Analysis of PB Contents by ^{1}H- and ^{13}C-NMR

		vinyl-1,2	*cis*-(1,4)	*trans*-(1,4)	*c* + *t*	PS
PB	^{13}C	14	38	48	86	—
	DEPT	14	35	51	86	—
	^{1}H	15	43[a]	42[a]	85	—
HIPS I[b]	^{13}C	—	11	8	19	81
	DEPT	—	3.2	3.2	6.4	93.6
	^{1}H	—	5[a]	5[a]	10	90
HIPS II	^{13}C	—	3	3	6	94
	DEPT	—	2.1	2.3	4.4	95.6
	^{1}H	—	4.5[a]	4.5[a]	9	91
HIPS III	^{13}C	—	11	—	11	89
	DEPT	—	9.5	—	9.5	90.5
	^{1}H	<1	8	—	8	>91
HIPS IV	^{13}C	—	4	1.5	5.5	94.5
	DEPT	—	2.3	<1	<3.3	>96.7
	^{1}H	<0.5	3	—	3	>96.5

[a] Approximate values.
[b] Results are slightly sample dependent.

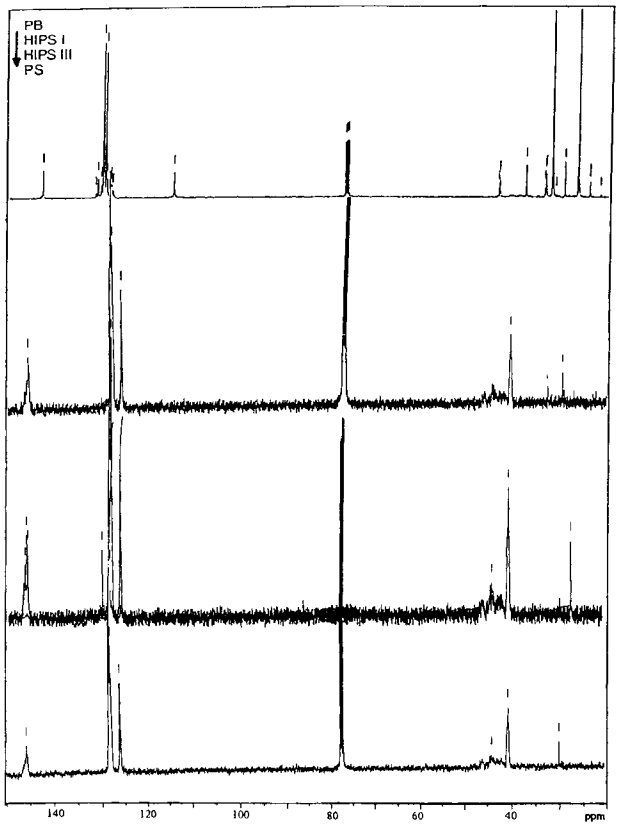

Figure 4 Comparison of quantitative ^{13}C-NMR spectra of PB, HIPS, and PS (delay time 30 s; scan number 300).

the carbons of PS and PB (Table IV); nevertheless, quantitative analysis is more difficult because of variations in relaxation times and Overhauser effects.[29]

As we can see in Figure 4, *cis* and *trans* PB microstructure can be identified in HIPS both in the aliphatic (27.4 and 32.8 ppm) and in the olefinic region (129.2 and 129.3 ppm). Vinyl microstructures are not present in any of the HIPS spectra. The unexpected peak at 29.7 ppm is also present in pure PS: it can be tentatively attributed to a head–head methylene linkage in pure PS. The J-mod and DEPT (135°) spectra performed on HIPS I were consistent with this assignment.

Sato et al.[28] showed that ^{13}C-NMR quantitative determination of PB microstructures was possible because of similar values of NOE and relaxation times for aliphatic carbons; but the quantitative determination of PB content in HIPS needs to assume that at least one of the PS carbons (presumably the methine carbon) has similar NOE values and relaxation times to PB. The best accuracy can be obtained by using quantitative programs available in modern NMR instruments (see Experimental); but these sequences need long delay time to ensure the complete relaxation of the carbon nucleus and results in very long analysis times. An elegant alternative consists of the use of DEPT sequences[6,30,31] that provide complete quantitative ^{13}C spectra for all except quaternary carbon atoms. Mathematical treatment of the sequence leads to the conclusion that for CH_3, CH_2, and CH carbon atoms, the signal intensities have to be multiplied by the ratio $(3\sqrt{2})/4$, 1, and $\sqrt{2}$, respectively.

Figure 5 shows the spectra obtained by the two quantitative methods. The scan numbers (300), were identical but, because of the shorter delay time, the analysis duration was six times lower for DEPT. As we can see, DEPT sequences lead to a drastic increase of the signal to noise ratio; we can also observe the disappearance of both quaternary carbon of PS and solvent peaks.

For both methods, the PB contents and microstructures can be determined (i) from the aliphatic region by considering the peaks area at 25.4 (vinyl-1,2), 27.4 (*cis*-1,4), 32.7 (*trans*-1,4), and 40 ppm (PS) and/or (ii) from the olefinic region by using the peaks at 114.0 (vinyl-1,2), 129.2 (*cis*-1,4), and 129.7 ppm (*trans*-1,4) vs. aromatic carbon of PS

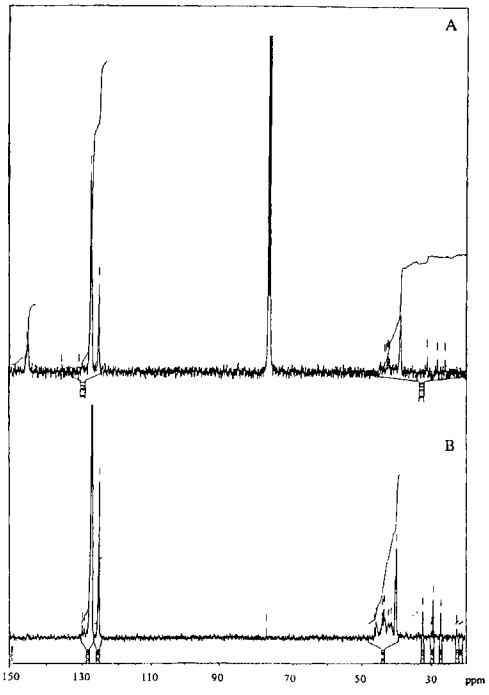

Figure 5 ^{13}C-NMR spectra of HIPS II. Comparison of quantitative (A) delay time 30 s, acquisition time 150 min and DEPT (B) delay time 5 s, $\theta = 45°$, acquisition time 25 min.

(127.7 ppm). Results from ^{13}C-, quantitative, and DEPT (PB aliphatic region), and ^{1}H-NMR analysis are reported in Table III.

CONCLUSION

All five methods give essentially the same trend with respect to PB content and microstructure: PB content in HIPS I > III > II > IV, with I and II essentially *cis* and *trans,* and III and IV mainly *cis.*

The vinyl (1,2) structures are well characterized by FTIR because relatively higher values for absorption coefficient, but Raman and ^{1}H-NMR confirm their low content, and no detection was possible by ^{13}C-NMR. Some important differences appear in the values for absolute concentration (Table III) probably because the measurement accuracy was not sufficient for such low PB contents (the relative experimental uncertainties were assumed to be 15% for FTIR and ^{13}C-NMR and 10% for proton and ^{13}C-DEPT NMR).

Except for HIPS I, DEPT and quantitative ^{13}C-NMR give similar results proving that DEPT is a very good technique for polymer characterization allowing fast analysis and good signal to noise ratio.

^{1}H-NMR could be a universal technique for determining both the rubber content and microstructure. However, even at 400 MHz, the resolution of *cis* and *trans* olefinic protons is still insufficient to ensure a quantitative estimation.

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