High resolution solid state ^{13}C n.m.r. of butadiene grafted polypropylene

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^{1}H dipolar decoupled ^{13}C n.m.r. experiments with the aid of the magic angle spinning technique have been used to determine the graft content and the isomer content of the polybutadiene grafts in a graft copolymer with isotactic polypropylene.

Keywords Solid state nuclear magnetic resonance; ^{13}C n.m.r.; magic angle spinning n.m.r.; polypropylene; graft copolymer

INTRODUCTION

Infra-red spectroscopy proved to be unsuitable for the estimation of isomer content in polybutadiene, poly BD, segments of poly(propylene-g-butadiene), PP-g-BD, samples[1]. Although the absorptions due to polyBD graft are easily observed, they are generally too close to absorption peaks of the PP backbone to make quantitative analysis a feasible proposition. The polymers are insoluble and do not readily gel, hence conventional solution n.m.r. techniques cannot be used.

Here we consider the application of the high resolution solid state techniques of cross-polarization (*CP*), ^{1}H dipolar decoupling (*DD*) and magic angle spinning (*MAS*) to this problem. In particular, we are interested in what components of this polymer system are being observed using the *CP/MAS* and *DD/MAS* techniques and different conditions, and hence, what reliable quantitative information can be obtained. The *CP* technique relies on the presence of strong ^{1}H–^{13}C dipolar coupling to enable transfer of polarization from the more highly polarized and abundant ^{1}H to ^{13}C resulting in enhanced ^{13}C sensitivity. In addition experiment efficiency is further improved by the substitution of the typically shorter ^{1}H T_1's for the ^{13}C T_1's as the determining factor of the rate at which the experiment can be repeated. Unfortunatly, such experiments may not produce quantitatively interpretable spectra due to a number of factors including differences in ^{1}H $T_{1\rho}$'s and variations of the strength of ^{1}H–^{13}C dipolar coupling within a sample. The latter is of particular relevance in the study of semi-crystalline polymers above their T_g due to the presence of regions of both high and low molecular mobility. Dipolar coupling will be greatly reduced in the amorphous regions resulting in reduced response in the *CP* experiment. An alternative for obtaining quantitative data is to perform single pulse experiments with high power ^{1}H dipolar decoupling using sufficiently long pulse repetition delays to allow for the long ^{13}C T_1's in the relatively immobile crystalline regions. For example, the ^{13}C T_1's in the rigid regions of polyethylene have been found to be greater than 1000s making experiments somewhat impractical[2]. The use of short pulse delays will essentially yield spectra of the mobile, amorphous regions due to the enhanced ^{13}C relaxation rates. An exception to this exists where groups in rigid regions exhibit internal motion and hence have reduced T_1's. The methyl group is a typical example and this has proved particularly useful in this work on PP-g-BD. We have measured the T_1's of a number of the carbon atoms in PP-g-BD by pulse sequence used by VanderHart[2] and have studied the spectrum obtained in *CP* and DD experiments. The results suggest that the latter experiment can provide quantitative results.

Previous work on the ^{13}C n.m.r. spectrum of isotactic polypropylene in the solid state, using the *CP* technique, by Bunn *et al.* has shown that significant spectral differences are observed according to the thermal history of the sample[3]. For example, signal splitting was clearly observed for the methyl and methylene carbons in the spectrum of a highly annealed sample due to crystallographic inequivalent intermolecular effects. However, these differences are restricted to shifts of less than 1 ppm and do not interfere with assignments. There has been no previous reported work on ^{13}C n.m.r. spectra of polybutadiene in the solid state.

EXPERIMENTAL

Sample

A detailed description of the preparation of the sample will be described elsewhere[1]. Briefly, it was made by the post gamma-irradiation technique in which annealed (5 h at 418 K) isotactic PP film (density 911 kg m^{-3}; d.s.c. crystallinity: 54%) was irradiated to 7.5 Mrad *in vacuo* at 195 K; grafted by exposure to BD gas at 318 K and finally annealed at 413 K for 1 h before opening to the atmosphere. Mass increase showed the sample contained 57.1 mass %, with respect to *total* polymer, of polyBD. Its gel content (insoluble in boiling xylene) was 81.6%.

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N.m.r. experiments

^{13}C spectra were obtained at 75.46 MHz on a Bruker CXP-300 spectrometer, using a Bruker DR/*MAS* probe. R_f field strengths of 10 and 40 G for ^1H and ^{13}C respectively were used for both *CP* and single pulse ^1H *DD* experiments. A contact time of 1 ms, acquisition time of 67 ms and a recycle time of 5 s were used for *CP* experiments. Single pulse experiments were performed with ^1H decoupling applied during the acquisition period of 67 ms. The rolled films were inserted into boron nitride/Kel-F rotors along with a small amount of KBr. Samples were spun at 2.5–3.5 kHz with the magic angle accurately set and spinning stability checked by observing the ^{79}Br resonance of KBr. Chemical shifts were referenced externally to TMS using a small amount of added adamantane.

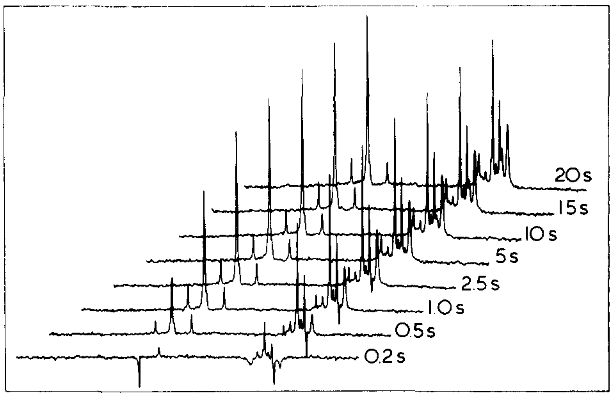

Figure 1 ^{13}C *MAS* n.m.r. spectrum f polypropylene-g-butadiene from a 180°-τ-90°-Aq-20s pulse sequence experiment with ^1H dipolar decoupling during acquisition. Values of τ noted

RESULTS AND DISCUSSION

For polyethylene, Earl and VanderHart[2] used an inversion–recovery sequence with a 10 s recycle delay to demonstrate that the carbons in amorphous or non-crystalline regions had spin lattice relaxation times of less than two seconds. *Figure 1* shows a similar series of 180°-τ-90°-Aq experiments using a recycle delay of 20 s and ^1H dipolar decoupling during acquisition and with τ varied from 0.2 s to 20 s. All peaks assigned to polyBD show negligible increase in intensity for τ values above 5 s indicating that T_1's are less than 1 s. Computed T_1 values for some resonances are given in *Table 1*, along with peak assignments and chemical shifts, and range from 0.1 to 0.5 s. Such short T_1's are indicative of relatively mobile carbons. Hence poly BD carbons should contribute fully to a single pulse experiment with a repetition rate of greater than 3 s and would be expected to make little contribution to a *CP* experiment. In contrast, the methine and methylence PP carbons must have T_1's much greater than 4 s as their intensity does not achieve a steady state up to a τ of 20 s. This is consistent with a far more rigid environment for these carbons relative to the BD carbons and it would be expected that these carbons contribute significantly in a *CP* experiment. The remaining PP carbon, the methyl, is a special case; although it is situated in the relatively immobile regions of the polymer struc-

Table 1 Spectral assignments and relative intensities of resonances in the n.m.r. spectra of polypropylene-g-butadiene

Chemical shift (ppm)			Peak area[d]			Assignment	
This work[a]	Lit[3–5] [b]	T_1's	CP	DD (10s)	DD (500s)	Group	Adjacent group
21.8	22.1 22.6	0.7	1.00	1.00	1.00	CH_3 (PP)	
26.3	24.9 26.8	*c*	0.97	0.33	0.79	*cis* CH_2 (1,4) CH (PP)	CH_2 (1,2-vinyl)
27.9	27.4	0.3	0.05	0.57	0.56	*cis* CH_2 (1,4)	*cis* or *trans* (1,4)
30.6	30.2	0.3	~0	0.08	0.09	*trans* CH_2 (1,4)	CH_2 (1,2-vinyl)
33.2	32.8	0.2	0.15	1.11	0.99	*trans* CH_2 (1,4) *cis* CH_2 (1,4)	*cis* or *trans* (1,4) CH (1,2-vinyl)
34.6	34.1		~0	0.15	0.17	CH_2 (1,2-vinyl)	*cis* or *trans* (1,4)
38.7	38.3	0.1	~0	0.08	0.09	*trans* CH_2 (1,4)	CH (1,2-vinyl)
44.0	43.5 45.2 44.2	*c*	0.80	0.39	0.63	CH (PP) CH (1,2-vinyl)	*cis* or *trans* (1,4)
114.9	~114	0.2	0.02	0.17	0.21	$\beta = CH_2$ (1,2-vinyl)	
128.7	~129					*cis* CH=CH (1,4)	1,2-vinyl ?
130.0	129.8	0.5	0.51	1.65	1.70	*cis* CH=CH (1,4)	*cis* or *trans* (1,4)
130.2	130.4					*trans* CH=CH (1,4)	*cis* or *trans* (1,4)
131.6	~132					*trans* CH=CH (1,4)	1,2-vinyl ?
142.6	~144	0.4	~0	0.18	0.16	$\alpha = CH-$ (1,2-vinyl)	

[a] To within ±0.1 ppm, peak maxima in the three experiments were the same
[b] Values from refs. 4 and 5 are for solution spectra
[c] Not fully relaxed
[d] Relative to PP methyl carbon

Table 2 Quantitative information from ^{13}C n.m.r. spectral resonance intensities of polypropylene-g-butadiene

Experiment	Mass % BD by			Isomer content by			
	Mass	n.m.r.[a]	n.m.r.[b]	n.m.r.[a]			n.m.r.[b]
				cis	*trans*	1,2-vinyl	1,2-vinyl
Dipolar decoupled 10s delay	57.1	57.9	56.2	30.1	55.6	14.3	17.4
Dipolar decoupled 500s delay	57.1	57.7	57.1	31.3	52.5	16.3	17.6

[a] Determined from saturated aliphatic region
[b] Determined from olefinic region

ture, it has a much shorter T_1 of 0.7 s as a result of the relatively unrestricted internal rotational motion. Hence, this carbon can be expected to contribute fully to single pulse spectra obtained with relatively short delays and perhaps exhibit slower cross-polarization than the methine and methylene PP carbons.

Confirmation of the above ideas is provided by a study of the spectrum of PP-g-BD run under the three different experimental conditions shown in *Figure 2* which illustrates expansions of the olefinic carbon and saturated aliphatic carbon ranges respectively. A full assignment based on previous work[3-5] together with peak areas relative to that due to the PP methyl group in each spectrum is given in *Table 1.*

The dominance of PP carbon resonances seen in the *CP* spectrum (*Figure 2A*) confirm that PP constitutes the more rigid structural regions of the polymer. This is as expected since BD is unlikely to penetrate the crystalline core of the PP during the grafting experiment and will be associated with the flexible amorphous regions. The results of d.s.c. experiments are in agreement with this observation[1]. The resonance signals due to the carbon atoms of methyl, methylene and possibly methine units of PP are assymetric in agreement with the observations of Bunn *et al.*[3] on highly annealed isotactic α-monoclinic PP when account is taken of the lower degree of annealing applied to our sample. BD resonances contribute only slightly to the *CP* spectrum; those having longer T_1's, i.e. *cis/trans* methine, appear to contribute relatively more.

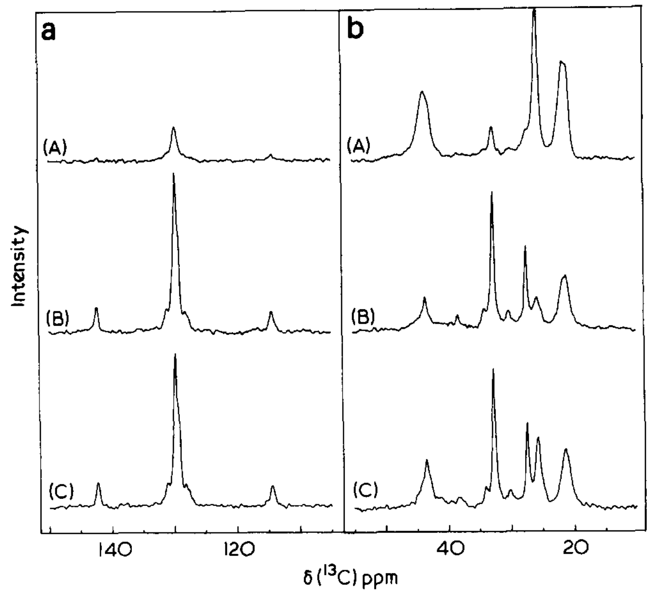

Figure 2 ^{13}C *MAS* n.m.r. spectrum of polypropylene-g-butadiene from cross polarization, (A), single pulse experiment with ^{1}H dipolar decoupling and pulse repetition delay time of 10 s, (B), and 500 s, (C). a: scale expansion of olefinic region; b: scale expansion of the saturated aliphatic region

A complete range of carbon resonances due to both PP and poly BD is clearly seen in the spectrum run under *DD* conditions. When the pulse repetition delay time is restricted to 10 s (*Figure 2B*) the methylene and methine carbon resonances of PP are considerably reduced in intensity as would be expected from the results of the 180°-τ-90°-Aq experiments. Even with a delay time of 500 s (*Figure 2C*) their peak areas are only 63 and 79% of the methyl carbon peak area respectively indicating that their T_1 values are very long. On the basis that all the polyBD carbons and the PP methyl carbons contribute totally to this resonance spectrum and based on the assignment given in *Table 1*, the mass per cent composition of the graft copolymer has been calculated both from the olefinic and saturated aliphatic regions. The values are compared with the known composition determined by mass increase at the preparation stage in *Table 2*. Good agreement is achieved suggesting that the assumptions are reasonable.

Peak areas were used to determine the isomer ratios in the polyBd grafts from both *DD* experiments. It was not possible to determine the *cis–trans* ratio from the olefinic region since peak resolution is not as good as in solution spectra[5]. A value for the 1,2-vinyl content however was possible. The saturated aliphatic region yields the *cis*, *trans* and 1,2-vinyl composition of the polyBD as shown in *Table 2*. Some of the resonances from which the latter is calculated are either hidden or adjoin larger resonances. This leads to an estimated precision of ± 10% for the 1,2-vinyl composition from the saturated aliphatic region and consistency with the value from the olefinic region.

In conclusion, intensity measurements on the *DD/MAS* experiments have given reasonably self consistent values of the graft content and the isomer ratios in a polypropylene-g-butadiene copolymer.

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