

^{129}Xe n.m.r. spectroscopic characterization of multiphase polypropylene copolymers

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The morphology of multiphase polypropylene copolymers, called impact polypropylenes, was studied by ^{129}Xe nuclear magnetic resonance (n.m.r.) spectroscopy. The impact polypropylenes studied were composed of polypropylene homopolymer and ethylene-propylene rubber (EPR). The xenon atom is non-polar and is soluble only in the non-crystalline regions of semicrystalline polymers. Differing resonances were obtained for the differing regions in the non-crystalline phase of the impact polypropylenes. It was shown that the weight percent of EPR could be determined from the peak intensity of the resonance of the EPR regions of the polymer. Further, the average particle size of the EPR particles was shown to be determinable from the peak separation of the resonances due to the EPR particles and the non-crystalline polypropylene homopolymer. The qualitative aspects of the ^{129}Xe n.m.r. spectra are discussed on the basis of the microstructure and average particle size of the EPR.

(Keywords: multiphase polypropylene copolymers; ^{129}Xe n.m.r. spectroscopy; polymer morphology)

INTRODUCTION

The physical and mechanical properties of polymeric systems are intimately connected with their solid-state morphology^{1,2}. Polymer systems containing more than one phase in the solid state which are of particular interest in this respect include polypropylene, polystyrene and nylon. One such system is polypropylene modified with rubber-like polymers, such as ethylene-propylene rubber (EPR) or ethylene-propylene diene monomer (EPDM). These systems are referred to commercially as impact polypropylene.

The morphology of multiphase† polymer systems is most often qualitatively and quantitatively characterized by microscopy. Since the morphological structures involved are predominantly of the order of a micrometre in size, this characterization is most often accomplished by electron microscopy techniques³. These techniques provide images that are rich in information; however, these techniques are difficult and laborious.

The fact that electron microscopic techniques are laborious constitutes an impediment to their use. There are few alternative techniques providing equivalent information that are not equally as laborious. Since the information available from electron microscopy is often essential for the characterization of multiphase polymer systems, a rapid and convenient alternative technique is highly desirable.

One such technique is ^{129}Xe nuclear magnetic resonance (n.m.r.) spectroscopy. The natural abundance of ^{129}Xe (26%) and its high magnetogyric ratio make this nucleus a sensitive n.m.r. probe of non-crystalline polymers. Xenon is a noble gas and van der Waals' forces provide the primary mode of interaction with its surroundings. Although the van der Waals' interactions are relatively weak, the high atomic number (large number of electrons) of xenon leads to a relatively large chemical shift and a large temperature dependence of the chemical shift.

The xenon atom is non-polar and is readily soluble in the non-crystalline region of semicrystalline polymers⁴. The particular usefulness of ^{129}Xe n.m.r. lies in its ability to distinguish between differing regions in a non-crystalline polymer at temperatures above the glass transition. Below the glass transition temperature of the polymer the technique does not work well because there is a loss in the sensitivity (due to the lower solubility of the xenon gas) and a loss in resolution due to an increase in the line-width of the ^{129}Xe resonance. Above the glass transition temperature the non-crystalline material can yield a narrow resonance (or multiple resonances)

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† The discussion in this paper makes use of the terms phase and region. The term phase is intended to refer to a homogeneous, physically distinct portion of matter in a non-homogeneous system. The crystalline and non-crystalline phases of a polymer are examples. The term region is sometimes used interchangeably with phase. However, it is used in the sense of a physical position within the polymer system, such as in the crystalline or non-crystalline regions. The term region can also refer to a physical position within a phase (or region) of the polymeric system. For example, the non-crystalline phase in impact polypropylenes contains two regions: the non-crystalline portion of the polypropylene homopolymer and the EPR, which is non-crystallizable

depending on the homogeneity (or heterogeneity) of the non-crystalline phase. These regions offer different environments to the xenon atom, resulting in chemical shift differences in the spectrum. Under quantitative conditions, the relative intensity of the n.m.r. peaks depends on the relative amounts of each region and the relative solubility of the xenon gas in each region of the polymer. The peak shape depends on the number of environments or the distribution in environments and the rate of exchange of xenon between the various non-crystalline environments in the sample.

In the case of impact polypropylene copolymers the xenon is not found in the crystalline (isotactic) polypropylene, but resides in the non-crystallizable polypropylene and ethylene-propylene copolymer (EPR) portions of the sample. The ¹²⁹Xe n.m.r. spectrum of an impact polypropylene (IPP2) is shown in Figure 1. The downfield resonance is due to non-crystalline

polypropylene and the upfield resonance to EPR in Figure 1.

EXPERIMENTAL

Materials

A series of 10 commercial impact polypropylene copolymers was used in this study. The properties of these polymers relevant to this study are given in Table 1. Other detailed structural data on one of these polymers (IPP7), which is typical of the others, is given elsewhere⁵.

N.m.r. analysis

The samples were placed in n.m.r. tubes fitted with Teflon rotary valves (i.e. J. Young valves, available from Wilmad, NJ) that allowed the sample to be sealed under pressure. The samples were then evacuated. Enough

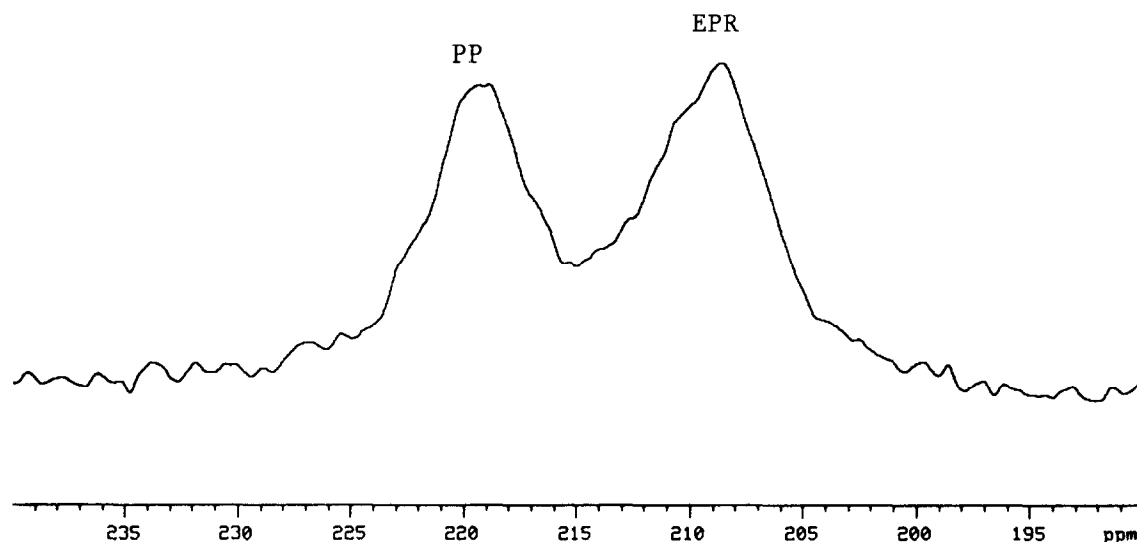


Figure 1 ¹²⁹Xe n.m.r. spectrum of an impact polypropylene sample (IPP2). The chemical shift is referenced relative to the xenon gas peak set to 0 ppm (no correction applied for pressure)

Table 1 ¹²⁹Xe n.m.r. characterization data of impact polypropylenes

Sample	Rubber ^a (wt%)	Particle diameter ^b \bar{d}_n (μm)	\bar{d}_w/\bar{d}_n	¹²⁹ Xe n.m.r.	
				EPR peak intensity ^c units	Deconvoluted peak separation (Hz)
IPP1	53	—	—	42.2	—
IPP2	45	—	—	24.8	—
IPP3	40	—	—	29.9	—
IPP4	34	—	—	24.1	—
IPP5	30	—	—	20.9	—
IPP6	15	—	—	4.9	—
IPP7	18	0.15 ± 0.01	0.93	9.6	749
IPP7	18	0.18 ± 0.01	0.94	8.2	820
IPP7	18	0.31 ± 0.02	1.00	8.9	927
IPP7	18	0.44 ± 0.02	1.00	8.1	941
IPP7	18	1.00 ± 0.16	1.10	7.6	941

^a See ref. 5

^b See ref. 7

^c Intensity units for IPP7 were obtained on deconvoluted spectra, those for IPP1–IPP6 were obtained directly from the spectrum

xenon gas was allowed to enter the tube such that the final pressure at room temperature was ~ 8 atm. Each sample tube was closed off under vacuum and allowed to equilibrate at room temperature for several hours before placing the tube in the spectrometer.

The ¹²⁹Xe n.m.r. spectra were obtained at 82.9 MHz on a narrow bore Varian Unity-300 spectrometer. Data were obtained using a 45° (11 μ s) observe pulse width and a recycle delay of 10 s with 1500 scans per sample. All plotting and integration parameters were kept constant for the analysis.

Quantitative comparisons were made under the same instrumental conditions on samples using the same number of scans in absolute intensity mode. Good resolution was obtained between peaks in the spectra of samples IPP1–IPP6. This permitted the integrals to be measured directly on spectra of these samples. These integral areas were correlated with the rubber concentration, as presented in the Results and Discussion section, and were an average of two to five trials. The relative standard deviation of the area measurements was $\sim 10\%$. Day-to-day instrument reproducibility was checked with the integration of an external standard (high rubber content sealed sample). The chemical shift data were referenced to an external standard. This standard was a sealed sample of linear low-density polyethylene (LLDPE) (9 mol% butene copolymer). At 25°C the peak due to xenon absorbed in the non-crystalline phase of this LLDPE sample was determined to be 199.8 ppm downfield from the free xenon gas peak (no correction was made for pressure). The free xenon gas peak was used as secondary reference for all chemical shifts.

The peak separations in the ¹²⁹Xe spectra for sample IPP7 were determined using the deconvolution software provided by the instrument manufacturer. Two resonances were used in the fitted spectra. The software allows each resonance to be fit as a Gaussian, Lorentzian or a combination of both line shapes. The spectra were processed with 25 Hz of line broadening and a digital resolution of 1.5 Hz per data point. A 3000 Hz spectral window was used for the deconvolution procedure. The frequency, line-width, peak height and Gaussian fraction of both resonances were optimized in the fit. The Gaussian fraction for each peak was less than or equal to 0.5 for all samples. The frequency difference between the peaks was determined from the fitted spectra.

The chemical microstructure of the EPR portion of samples IPP8, IPP9 and IPP10 was compared by solution ¹³C n.m.r.⁶, for the fractionated samples. The fractionated samples were prepared by dissolving in xylene at 85°C for 90 min. The sample was allowed to cool to room temperature and filtered. The soluble portion (EPR) of the sample was precipitated using acetone, filtered and dried.

¹³C solution n.m.r. results for the EPR rubber fractions were measured on samples dissolved in a 1,2,4-trichlorobenzene/benzene-d₆ (4 : 1) solution (0.3 g/2 ml solvent) at 125°C. The results were obtained on a Varian Unity-300 spectrometer using a 90° observe pulse, 15 s recycle time, and a 2 s acquisition time. The triads were calculated according to the procedure described by Randall⁶. The microstructural differences of the EPR are discussed later in terms of total ethylene content, randomness of the sequencing as reflected in the

differences in PEP/EPE ratio, the amount of total ethylene represented in EEE triads, and the amount of total propylene represented in PPP triads. These four parameters reflect changes in the overall composition of the EPRs.

Electron microscopy

Particle sizes were determined by electron microscopy as previously described⁷. The samples were microtomed at -100°C (liquid N₂ cooled) in a Reichert FC4E ultramicrotome, etched with n-heptane at 60°C in a sonic bath for 20 min and ion-coated with gold. The photomicrographs were obtained on a JEOL 1200 EX electron microscope. The area of the particles was determined directly from the electron photomicrographs using an image analyser. Using the area of the particles (assumed to be circular), the particle diameters (\bar{d}_n , \bar{d}_w , \bar{d}_z) and diameter distributions were calculated⁷.

RESULTS AND DISCUSSION

A number of studies, including the initial experiments by Stengle and Williamson⁴, have indicated that ¹²⁹Xe n.m.r. may be a useful technique in studying non-crystalline regions of polymers^{8–11}. The method involves bringing xenon gas in contact with the polymer at ~ 8 atm and allowing the gas to diffuse into the sample. The xenon gas atoms are too large to be incorporated into the PP crystal lattice and as a result the xenon gas only probes the non-crystalline regions of the sample⁴.

The chemical shift of the absorbed xenon gas is then determined by the local environment surrounding the xenon atoms. In systems which are closely related, the chemical shift is determined by the density or free volume of the amorphous material in the polymer. In samples containing two non-crystalline regions of different structure or density, such as impact polypropylene, two xenon n.m.r. signals are observed (assuming the size of the domains is large enough and the diffusion or exchange between the two regions is slow on the n.m.r. time scale).

Under quantitative conditions the integrated area under each resonance is proportional to the relative solubility of the gas in each region and the volume fraction of each particular region. The detailed relationship between the observed n.m.r. spectrum and the phase morphology may be described by the theory of chemically exchanging systems¹². In the slow exchange limit the xenon atom remains in a particular environment for a time which is long relative to the n.m.r. time scale, and the observed chemical shifts will be exactly equal to that observed for the corresponding pure bulk phases. This situation occurs when the particles are larger than some critical limit. Therefore, in the case of a two-phase system with large domains of each phase, the maximum separation between the resonances will be observed corresponding to the chemical shift of each pure phase. For domains smaller than the critical limit, xenon will diffuse more rapidly between the domains and the separation between the resonances will decrease and broaden. In the limit for very small domains, the diffusion of the xenon between the domains is sufficiently fast to allow a xenon atom to move between the chemically distinct phases many times relative to the

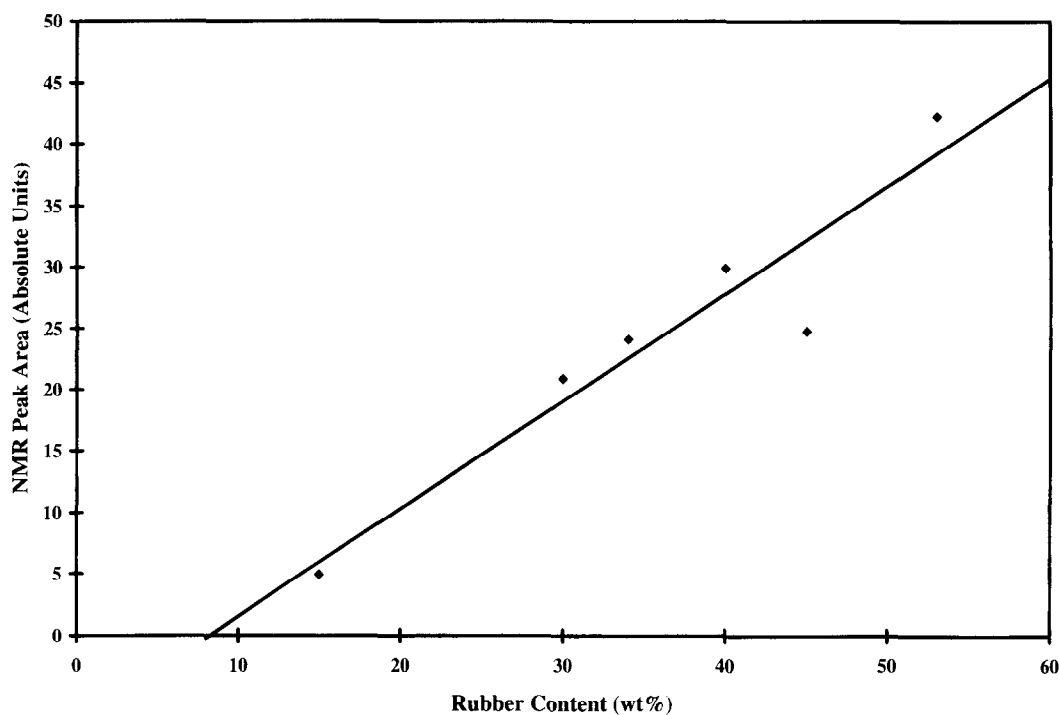


Figure 2 A correlation of the intensity of the EPR peak in the ¹²⁹Xe spectrum with the weight percent EPR determined by fractionation. The line is the linear least-squares fit to the data

n.m.r. time scale. In this case the resonances will collapse to a single chemical shift.

Two important characteristics of impact polypropylene samples which in part determine the final properties of these samples are the amount of EPR and the particle size of the rubber phase. The impact polypropylenes studied in this work are given in *Table 1*. The samples included in this study have a variation in (1) rubber content from 15 to 53%, and (2) rubber particle size (\bar{d}_n) from 0.15 to 1.00 μm .

Correlation of weight percent EPR and ¹²⁹Xe n.m.r. peak intensity

The data in *Table 1* may be used to correlate the ¹²⁹Xe n.m.r. method for the quantitative determination of weight percent EPR and the average particle size of the dispersed rubber particles in impact polypropylene resins or blends. *Figure 2* is a plot of absolute intensity units (area) under the EPR peak in the ¹²⁹Xe n.m.r. spectra of IPP1–IPP6 versus weight percent rubber (EPR) as obtained by fractionation⁵. This plot indicates that there is a good correlation of the intensity of the EPR peak obtained under these conditions with the amount of rubber in the sample.

In samples where polyethylene has been blended into the EPR portion of the sample or in samples containing rubbers of high ethylene content, it is possible to form PE crystallites within the rubber phase. These crystallites could lower both the diffusion of the gas into the EPR region, and the apparent solubility of the gas in the rubber portion of the sample as the xenon gas cannot penetrate the polyethylene crystalline phase. In this case there would be a decrease in the intensity of the resonance associated with the EPR/PE region of the sample.

Correlation of ¹²⁹Xe n.m.r. peak separation and particle size

The separation in the peak positions of the xenon gas dissolved in two non-crystalline phases such as the PP and EPR portions of the samples could be affected by many factors which include the microstructure of the non-crystalline phases, particle size, particle size distribution, the miscibility or partial miscibility of the two phases and relative solubility of the gas in each phase. For these reasons ¹²⁹Xe n.m.r. can provide a significant amount of qualitative information when comparing samples, and if a majority of these factors are held constant quantitative or semi-quantitative comparisons can be made.

In one experiment, a series of differing average EPR particle sizes was produced in the same impact polypropylene resin (IPP7) by the coarsening in the melt state of the EPR particles through Ostwald ripening⁷. *Figure 3* shows the ¹²⁹Xe n.m.r. spectra of the samples taken after ripening times of 5 s, 45 s and 8 min. The EPR particle radius increases as a function of time to the one-third power⁷. The particle size distributions are quite narrow in breadth as indicated by the \bar{d}_w/\bar{d}_n in *Table 1*. This is a result of the coarsening in the melt of solvent precipitated specimens⁷. With the larger particle sizes there is some narrowing in the resonance associated with the EPR phase as well as an increase in the separation of the peaks.

These data, obtained by deconvolution, were used to construct a plot of average particle diameter versus the peak separation of the non-crystalline polypropylene peak and the rubber peak in the ¹²⁹Xe n.m.r. spectra of these specimens (IPP7 in *Table 1*). This plot, given in *Figure 4*, is a correlation of particle size for the dispersed rubber particles in impact polypropylene resins and blends of polypropylene and EPR. Again, it is noted that

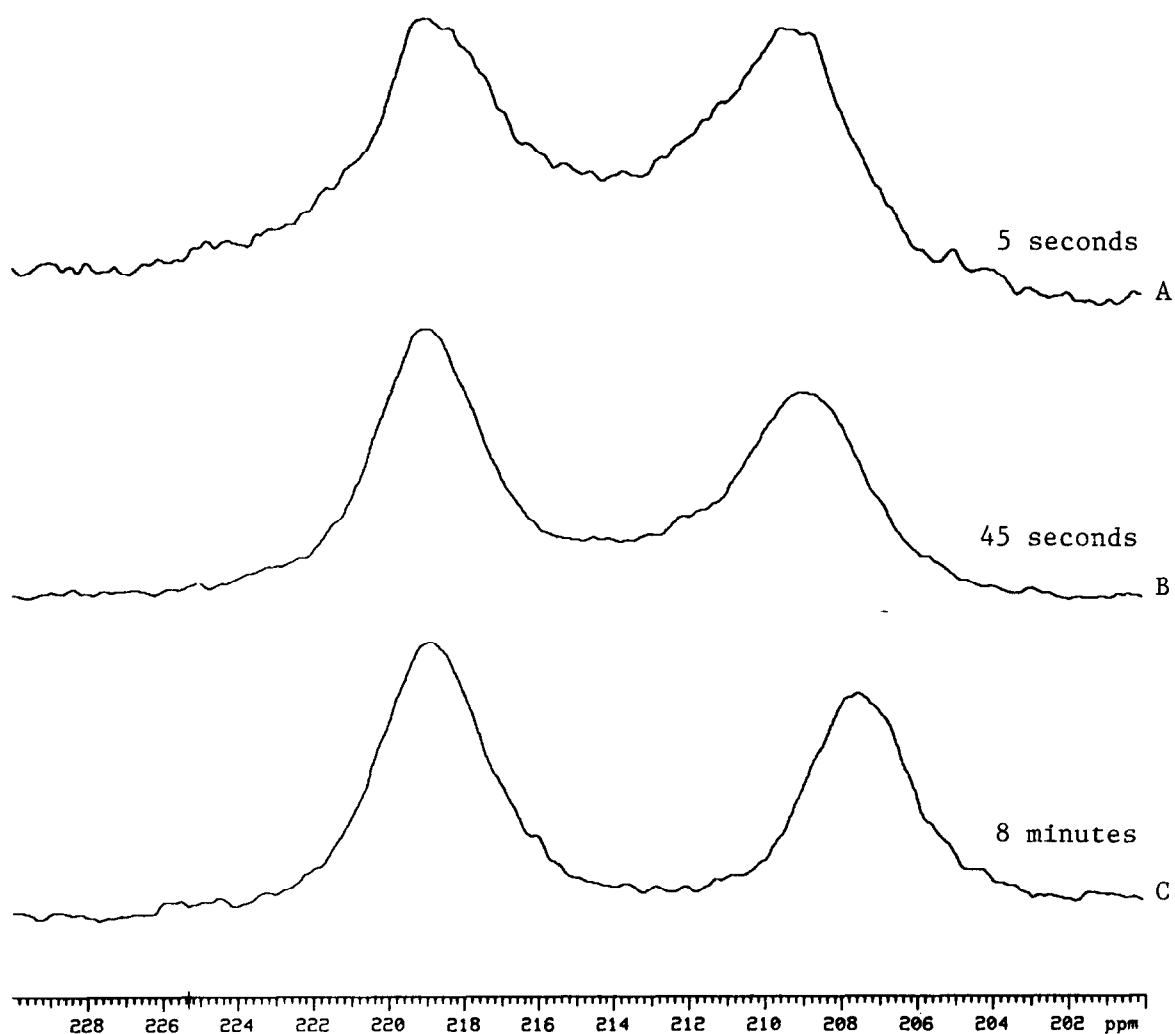


Figure 3 ^{129}Xe n.m.r. spectrum of sample IPP7 obtained after ripening in the melt state for 5 s, 45 s and 8 min

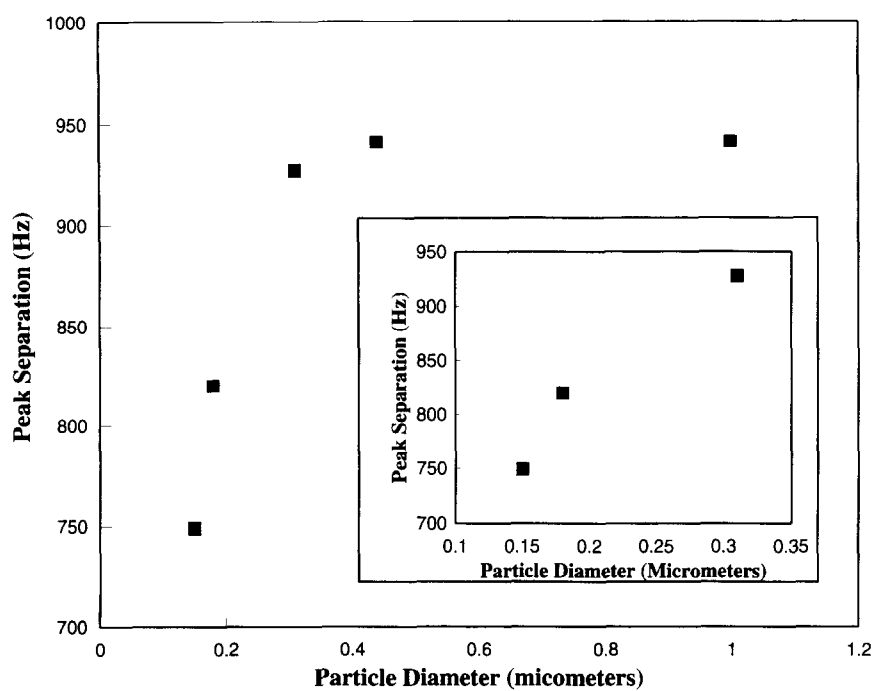


Figure 4 A correlation of ^{129}Xe n.m.r. method for the determination of rubber particle size. Deconvoluted peak separation between rubber peak and non-crystalline polypropylene peak in the n.m.r. spectrum versus the average particle diameter. The inset shows the useful correlation range of particle size and peak separation

Table 2 Characterization of EPR portion of samples IPP8, IPP9 and IPP10

	IPP8	IPP9	IPP10
Wt% EPR	24.0	22.2	23.4
<i>¹³C n.m.r. characterization of EPR fraction</i>			
mol% E	43.8	43.6	50.1
mol% EEE	18.6	22.1	25.0
mol% PPP	25.8	22.5	32.2
PEP/EPE	1.20	0.91	0.79
<i>Electron microscopy characterization of EPR particle sizes</i>			
\bar{d}_n (μm)	0.28	0.31	0.31
\bar{d}_w (μm)	0.31	0.45	0.34
\bar{d}_z (μm)	0.41	0.73	0.47

this correlation applies to EPRs with similar structure as that used to construct *Figure 4*.

Figure 4 shows that for large particle sizes of EPR the separation of the ¹²⁹Xe resonances due to non-crystalline PP and EPR reaches a maximum, as discussed above, and therefore the peak separation remains constant for particles larger than this maximum. This plateau in *Figure 4* occurs when the particle size reaches $\sim 0.31 \mu\text{m}$. *Figure 4* further shows that at room temperature (25°C) resolution of the peaks is not possible at particle sizes below $\sim 0.15 \mu\text{m}$. The inset in *Figure 4* indicates a useful correlation range for particle diameter and peak

separation in the xenon n.m.r. spectrum for particles between 0.15 and 0.31 μm in diameter.

The EPR peak areas in *Table 1* for the ripened IPP7 sample remain relatively constant independent of particle size. Therefore, these data would suggest that the correlation in *Figure 2* may also be independent of particle size when adequate resolution is obtained between the peaks in the spectrum.

The effects of temperature were not explored in terms of quantitatively measuring the particle sizes in these samples. Our initial studies indicate that lowering the temperature could slow the diffusion rate and allow particles of smaller dimensions to be measured. However, in these systems the glass transition temperature of amorphous PP phase is approximately -20°C which sets the lower limit for these particle size studies.

Detailed analysis of PP/EPR blends by ¹²⁹Xe n.m.r.

The application of ¹²⁹Xe n.m.r. to blends of EPR and PP was also studied. Three samples of *in situ* blends of similar EPR content (20–25 wt%) are described in *Table 2* and the corresponding spectra are shown in *Figure 5*. Spectrum A (IPP8) and B (IPP9) appear similar in that there is a good separation of the peaks, while in spectrum C (IPP10) the peak associated with the EPR portion of the sample is very broad and overlaps that for the non-crystalline PP part of the sample.

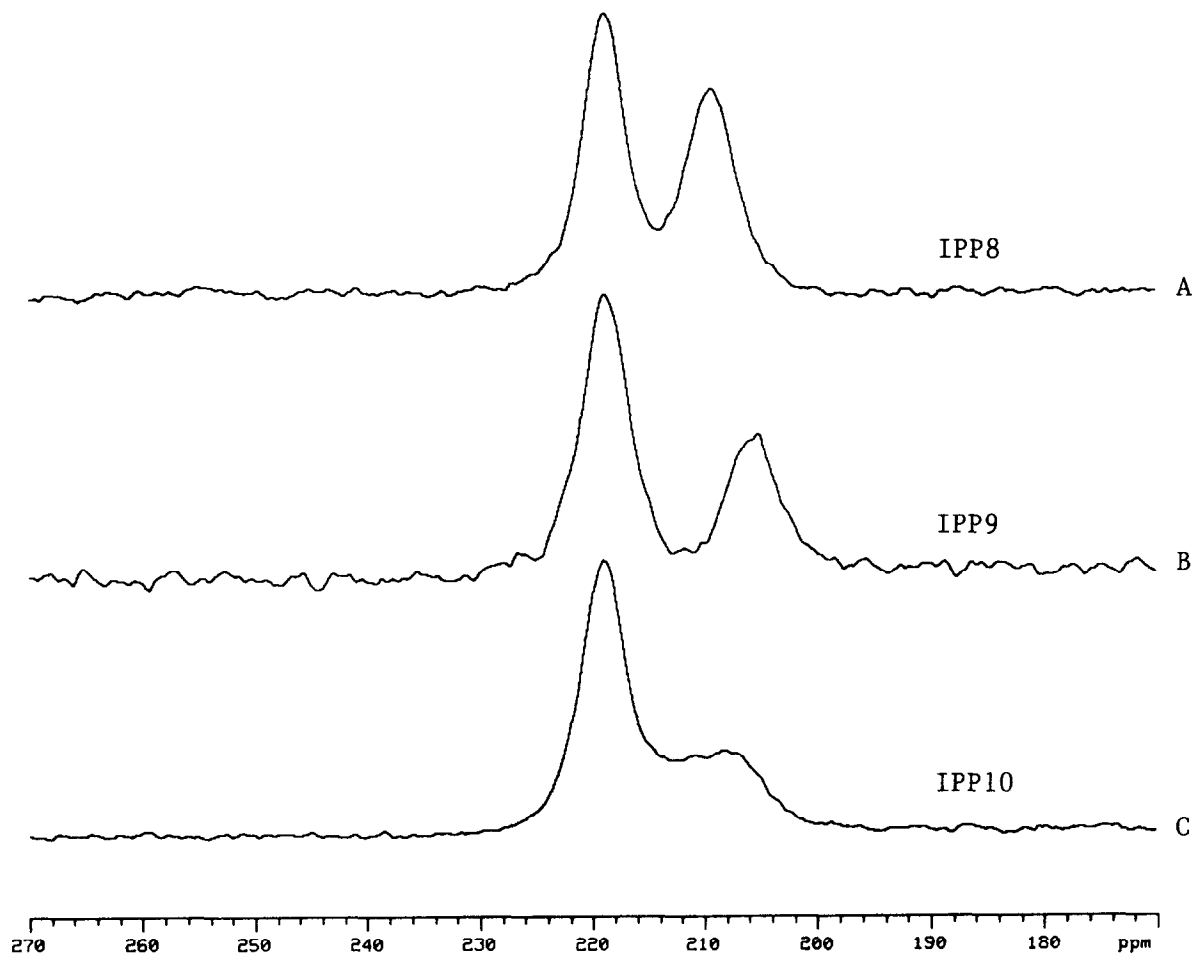


Figure 5 The ¹²⁹Xe n.m.r. spectra of three *in situ* blends (IPP8, IPP9, IPP10) with similar EPR contents. The differences in particle size, particle size distribution and microstructural differences in the EPR portions of the samples lead to qualitative differences in the spectra

The separation of the peaks is greater for IPP9 than for IPP8. This implies microstructural differences in the rubber and/or differences in the average particle size between IPP8 and IPP9. The average particle size \bar{d}_n for the samples is approximately the same (0.28 and 0.31 μm) but unlike the samples discussed above (Ostwald ripened samples) the particle size distributions of these samples are quite broad. The breadth of the particle size distribution as indicated by \bar{d}_z shows that IPP9 is skewed to larger particles (0.41 versus 0.73 μm). This change in particle size distribution for IPP9 could lead to a broader peak. The peak in the IPP9 spectrum due to EPR has shifted upfield but does not appear to be broader. This would suggest that the change in peak position is due to microstructural differences in the rubber and not to a change in particle size or particle size distribution at these levels of particle size polydispersity.

Although the EPRs of the IPP8 and IPP9 samples are nominally the same at an ethylene content of 44 mol%, some differences in the rubbers might be expected. For example, both differential scanning calorimetry (d.s.c.) and scanning electron microscopy (SEM) indicate the presence of crystalline polyethylene in IPP9, while there is no indication of any significant amount of crystalline polyethylene in IPP8. Solution ¹³C n.m.r. results of the fractionated samples indicate that the total ethylene content in the rubber portion is approximately the same for the IPP8 and IPP9 samples, but the amount of longer ethylene segments (EEE triads) is greatest in the IPP9 sample. This is consistent with the presence of more crystalline ethylene material in the IPP9 sample.

In a random distribution the PEP/EPE ratio for an EPR sample containing 44 mol% ethylene should equal 1.3. Although in these real systems a random distribution does not completely or adequately describe the sequencing in these samples, it is still important to note that the PEP/EPE ratio qualitatively indicates differences in the microstructure of the rubber. The PEP/EPE ratio is 1.2 for the IPP8 sample, suggesting a closer-to-random distribution of the ethylene and propylene units when compared with the IPP9 sample (PEP/EPE = 0.91).

Samples IPP8 and IPP10 ($\bar{d}_n = 0.31 \mu\text{m}$) have a similar EPR particle size and particle size distribution. The peak due to xenon dissolved in the EPR of IPP10 has shifted slightly to higher field and has become significantly broader. It is clear that the broadening of the resonance cannot be due to particle size distribution or the IPP9 sample would have the broadest peak associated with the EPR portion of the sample. Therefore, the broadening of the peak for IPP10 must be due to compositional heterogeneity of the rubber.

The ¹³C n.m.r. results on the extracted rubber indicate that the EPR portion of this sample (IPP10) has a higher ethylene content and consequently there is more linear ethylene (EEE triads) than seen in IPP8 or IPP9. The PEP/EPE ratio of IPP10 is 0.79 versus a predicted ratio of 1.0 for a totally random distribution. This result, like that of the IPP9 sample, indicates that the monomer units are not randomly distributed along the polymer chain. The EPR fraction of the IPP10 sample also has a significantly higher fraction of total propylene in PPP triads. Therefore, the xenon gas is in contact with a more heterogeneous local environment in the EPR portion of the IPP10 sample when compared with the other two samples. The EPR ranges from high propylene to high

ethylene content, which results in a peak that is very broad and cannot easily be resolved from that of the non-crystalline PP matrix.

D.s.c. and SEM confirm the presence of crystalline polyethylene in IPP10 at higher levels than are seen for samples IPP8 or IPP9. Crystalline ethylene is not penetrated by the xenon gas and as a result will not be detected in these experiments. Its presence can be related to the experimental results in one of two ways. First, crystalline polyethylene in the rubber portions of the samples reflects a more heterogeneous distribution of ethylene units in some of the chains or chain segments. A chain rich in ethylene content which does not completely crystallize should cause a shift upfield in the direction of non-crystalline PE (= 200–202 ppm for the non-crystalline region of LLDPEs under these conditions).

Second, if the EPR contains a significant amount of crystalline polyethylene then the EPR may exist only as a thin layer surrounding a PE core¹³. In this situation the impenetrable core could have an effect on the diffusion or exchange of the xenon gas between the non-crystalline sub-regions of the sample. This morphology has been observed by others in PP/EPR blends and is described in detail by other investigators¹³.

This 'core' effect was not examined in this study, but could be explored in the future by blending high density polyethylene (immiscible) and LLDPE (partially miscible) into an impact PP sample. The main difference between sample IPP9 and IPP10 exists in the overall heterogeneity of the EPR. Certainly, both contain significant amounts of EEE (of which some crystallizes), but sample IPP10 contains more propylene in PPP triads. This broad distribution in the overall composition of the rubber leads to the differences seen between samples IPP9 and IPP10.

CONCLUSIONS

It has been shown that ¹²⁹Xe n.m.r. spectroscopy provides a sensitive probe for the morphology of multiphase polymer systems. Specifically, in the case of impact polypropylene resins or blends of polypropylene and EPR, it was shown that a semi-quantitative determination of weight percent rubber (EPR) and average particle size of the dispersed rubber particles was determinable from the ¹²⁹Xe n.m.r. spectra of polymer samples containing similar EPR compositions.

The particle size correlation given above would be valid for systems with similar structure of the components; especially for similar structure of the EPR component. However, the method may be generalized to systems with differing component structures by recalibrating with polymer systems with the appropriate component structures.

The qualitative aspects of ¹²⁹Xe n.m.r. have been illustrated by comparing three samples of similar rubber content. Microstructural differences in the rubbers can be correlated with differences seen in the ¹²⁹Xe spectra of these samples.

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