

N.m.r. analysis of polypropylene–maleic anhydride copolymer

Ramesh Rengarajan, Vetkav R. Parameswaran, Sunggyu Lee*
and Michael Vicic

Department of Chemical Engineering, The University of Akron, Akron, OH 44325, USA

and Peter L. Rinaldi

Department of Chemistry, The University of Akron, Akron, OH 44325, USA

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Polypropylene–maleic anhydride (PP–MA) copolymer was prepared by the solid phase graft copolymerization process. The grafted polymer was analysed by Fourier transform infrared spectroscopy, wet chemical methods, solid state ^{13}C n.m.r. analysis, and by liquid state ^{13}C n.m.r. spectroscopy. The solid state, 50 MHz, ^{13}C n.m.r. showed a distinct peak at 175 ppm indicating the presence of maleic anhydride functionality in the copolymer. These peaks were not detected in the liquid state ^{13}C n.m.r. spectra due to the presence of dipolar broadening. The structure of the PP–MA copolymer as determined by n.m.r. was in agreement with the proposed structure given by Minoura *et al.*¹ based on FTi.r. analysis. The extracted solution was analysed by g.c.–m.s. and it was found that unreacted maleic anhydride was extracted by the water. The presence of maleic anhydride in the copolymer was also confirmed by FTi.r.

(Keywords: polypropylene–maleic anhydride copolymer; FTi.r.; n.m.r. analysis; g.c.–m.s.)

INTRODUCTION

Nuclear magnetic resonance spectroscopy is one of the most valuable techniques to determine qualitatively and quantitatively the presence of graft in the copolymer. No studies have yet been reported on the n.m.r. analysis of the polypropylene–maleic anhydride (PP–MA) copolymer. Quantitative determination of the comonomer content has traditionally been done by wet chemical methods and by Fourier transform infra red spectroscopy. Though FTi.r. is a good qualitative tool, it cannot easily be used to quantify the graft comonomer content without proper standardization by other well recognized methods.

The solid phase graft copolymerization technique was used to graft reactive comonomers to polypropylene with the aid of an interfacial agent and a catalyst. The reaction was performed using a powdered polymer and at temperatures well below the melting point of the polymer. During the entire reaction the polymer remained a powder. This process offers several advantages such as low processing temperature and low operating pressure over conventional processes.

In this process the reactive monomer was sprayed on the heated, powdered polymer. A catalyst and a free radical initiator were added to the polymer. The reaction was performed in a nitrogen atmosphere. The polymer remained a free flowing powder during the reaction. The reacted polymer was extracted with water to remove the excess unreacted monomer from the reaction product.

The absence of reports in the scientific literature indicates that the grafting method being investigated has heretofore never been used to graft polymers. To prove the validity of this method, n.m.r. analysis was performed to determine if the comonomer was actually grafted to

the polypropylene or was adsorbed/absorbed to the polypropylene matrix. FTi.r. analysis was performed to qualitatively determine the comonomer in the copolymer.

EXPERIMENTAL

The reactor

A stainless steel reactor with a sigma-type twin blade variable speed agitator was used to perform the reaction. A sight glass was installed to monitor the colour shift during the reaction. A thermocouple was installed to monitor and control the reaction. Nitrogen was used initially to purge the reactor and maintain a nitrogen environment for the reaction. A teflon gasket was used to seal the opening. The reactor was heated electrically by a flexible heating tape and the temperature was controlled.

The ingredients

The homopolymer isotactic polypropylene was cryogenically ground to a powder (100% passing through a 200 mesh screen). Maleic anhydride was used as the reactive monomer. Maleic anhydride briquettes were also ground to a powder. Because maleic anhydride melts at 52°C (much below the reaction temperature) it was not necessary to powder it to any specific size range. Benzoyl peroxide was used as a free radical initiator. A novel catalyst RRGB-01 was used to enhance the graft level.

Polypropylene was added to the reactor and allowed to attain the reaction temperature. The additives were added into the reactor in a predetermined sequence. The reaction was performed for one hour.

Analysis

A 10 g sample of the polymer was extracted with 100 ml

* To whom correspondence should be addressed

of water for 2 h at 100°C. The extracted solution was saved for evaluation by g.c.-m.s.

The extracted product was washed with water several times to remove all traces of unreacted maleic anhydride from the copolymer. The extracted and washed product was dried in a hot air oven and dried for 24 h. This sample was used for all analyses of graft level.

G.c.-m.s. analysis

The water that was used for the extraction of unreacted maleic anhydride was injected into a g.c.-m.s. to qualitatively determine the chemical species present in the solution. A computer based NBS library of g.c.-m.s. data was used for the search and species identification.

FTi.r. analysis

A 2 g sample was compression moulded to obtain a film of 100 μm thickness. The sample was analysed using a FTi.r. The presence of peaks at 1790 and 1865 cm^{-1} , that are characteristic of the carbonyl in the maleic anhydride, confirmed the presence of maleic anhydride in the copolymer.

N.m.r. analysis

The sample for liquid state ^{13}C n.m.r. analysis was dissolved in a mixture of 80% *ortho*-dichlorobenzene and 20% deuterated nitrobenzene. Liquid state n.m.r. spectra were obtained at 75 MHz using a ^{13}C Varian VXR-300 spectrometer with an 8 μs (30 degree) pulse and an acquisition time of 0.75 s. The spectral window was set at 20 kHz and 7500 transients were accumulated with Waltz-16 decoupling. The data were zero filled to 64 000 points and weighted with a 1 Hz exponential line broadening function before Fourier transformation.

Solid state ^{13}C n.m.r. spectra were obtained at 50 MHz with a Chemagnetics CMC-200 instrument using cross polarization and magic angle spinning (CP/MAS)². The acquisition parameters were as follows: 3.7 μs ^1H and ^{13}C pulse widths, 51 ms acquisition time, 5.5 kHz spin rate, 20 kHz spectral window, 1.0 ms contact time, 5.0 s relaxation delay, and 10 000 transients. The data were zero filled to 8000 points and weighted with a 5 Hz exponential line broadening function before Fourier transformation.

RESULTS AND DISCUSSION

N.m.r. analysis

Samples of homopolymer isotactic polypropylene and the polypropylene-maleic anhydride graft copolymer, were dissolved in a solution of *ortho*-dichlorobenzene and nitrobenzene- d_5 (80:20 v/v) and were analysed by the 75 MHz ^{13}C n.m.r. The spectra are shown in *Figures 1* and *2*, respectively. Maleic anhydride carbonyl signals, which are normally detected at 172–174 ppm were barely, if at all, detected in the copolymer sample (*Figure 2*). This may be attributed to the dipolar broadening of resonances near branch points that have restricted mobility.

When the solid state ^{13}C 50 MHz n.m.r. was used for the analysis, a peak was observed at 175 ppm as shown in *Figure 4*. This peak was not found in the homopolymer isotactic polypropylene feed stock used for grafting (*Figure 3*). Under the conditions used to obtain solid state CP/MAS spectra the dipolar broadening is removed by high power ^1H decoupling.

FTi.r.

FTi.r. spectra for the homopolymer isotactic polypropylene and the PP-MA copolymer are given in *Figures 5* and *6*, respectively. It is evident from *Figure 5* that there were no peaks at 1790 cm^{-1} and at 1865 cm^{-1} . Two distinct peaks are observed in *Figure 6* confirming the presence of maleic anhydride in the copolymer.

G.c.-m.s. analysis

The mass spectra obtained on the extracted solution were compared with the known spectra available in the file. It confirmed the presence of maleic anhydride in the solution in the form of maleic acid.

Proposed structure based on n.m.r. analysis

Minoura¹ proposed the mechanism outlined in Scheme 1 for grafting of polypropylene with maleic anhydride. The solid state CP/MAS spectra of PP-MA copolymer confirmed the presence of structural units of type C in Scheme 1. Carbonyl resonances from carbon 4 are detected at 175 ppm. Signals from carbon 5 are expected to fall under the large PP resonance at ca. 20 ppm, and are not resolved. Additional olefin peaks from carbons

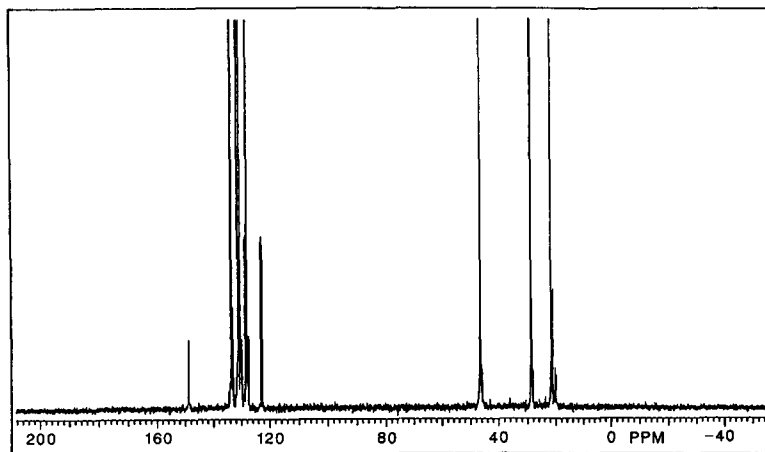


Figure 1 Liquid state 75 MHz ^{13}C n.m.r. spectrum of homopolymer isotactic polypropylene dissolved in a 80/20 (v/v) mixture of *o*-dichlorobenzene and nitrobenzene- d_5

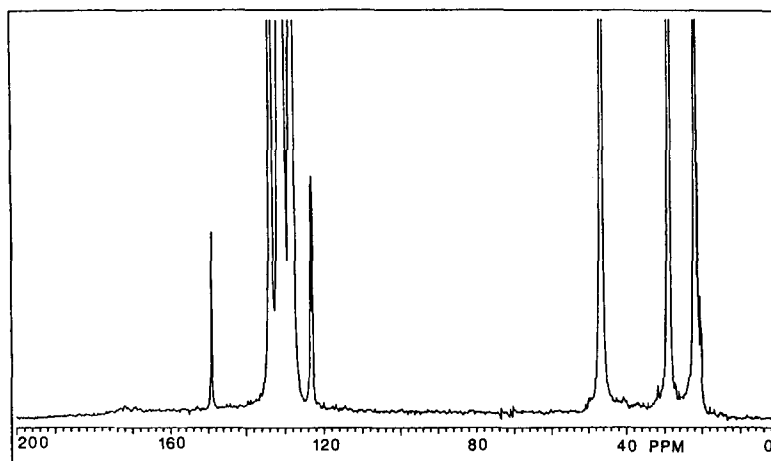


Figure 2 Liquid state 75 MHz ^{13}C n.m.r. spectrum of polypropylene-maleic anhydride copolymer dissolved in a 80/20 (v/v) mixture of *o*-dichlorobenzene and nitrobenzene- d_5

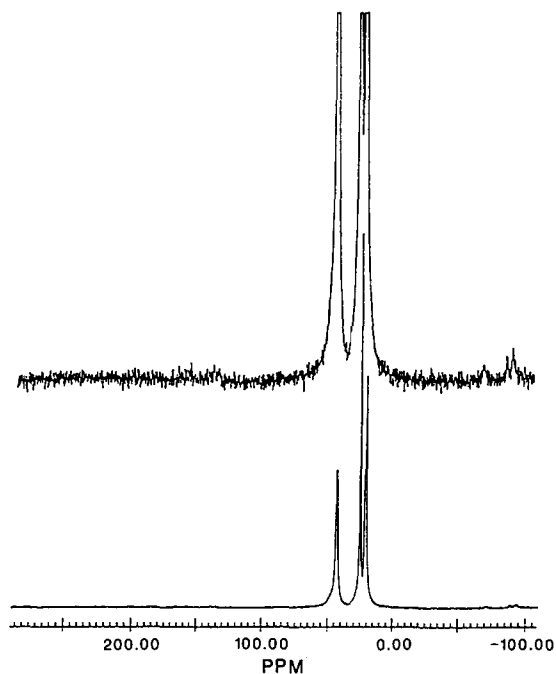
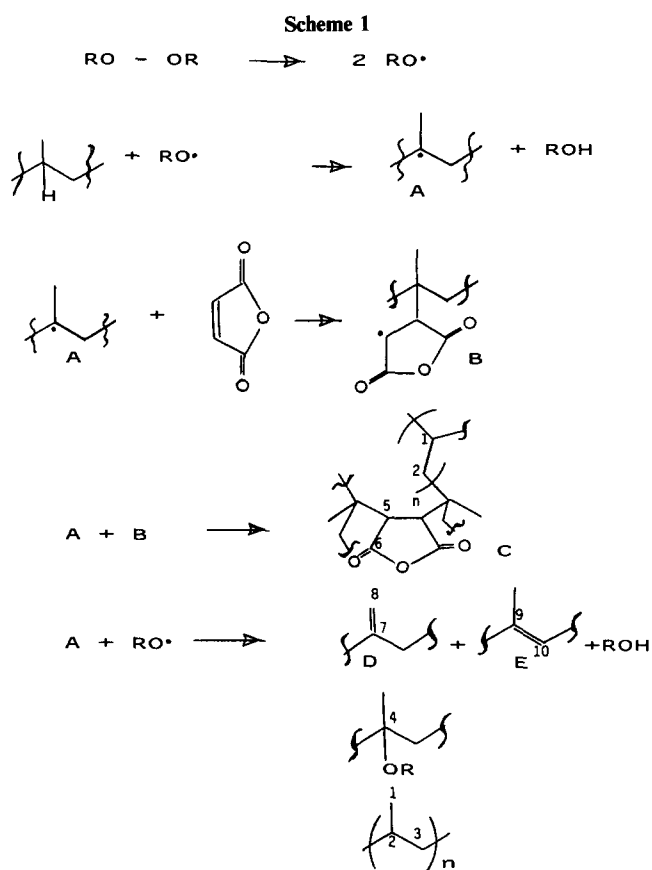


Figure 3 Solid state CP/MAS ^{13}C n.m.r. spectrum of homopolymer isotactic polypropylene. Magnification = 4.8 \times

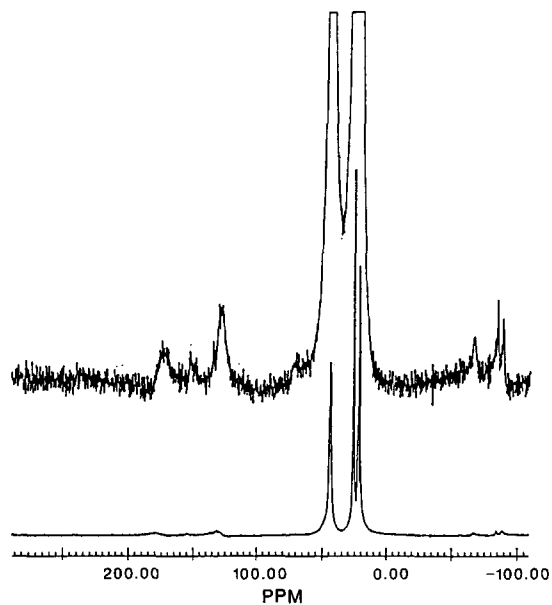


Figure 4 Solid state CP/MAS ^{13}C n.m.r. spectrum of polypropylene-maleic anhydride graft copolymer. Magnification = 4.8 \times

Table 1 Resonance assignments

Structure	ppm observed
1	16
2	35
3	53
4	70
5	not resolved
6	175
7, 8, 9, 10	130

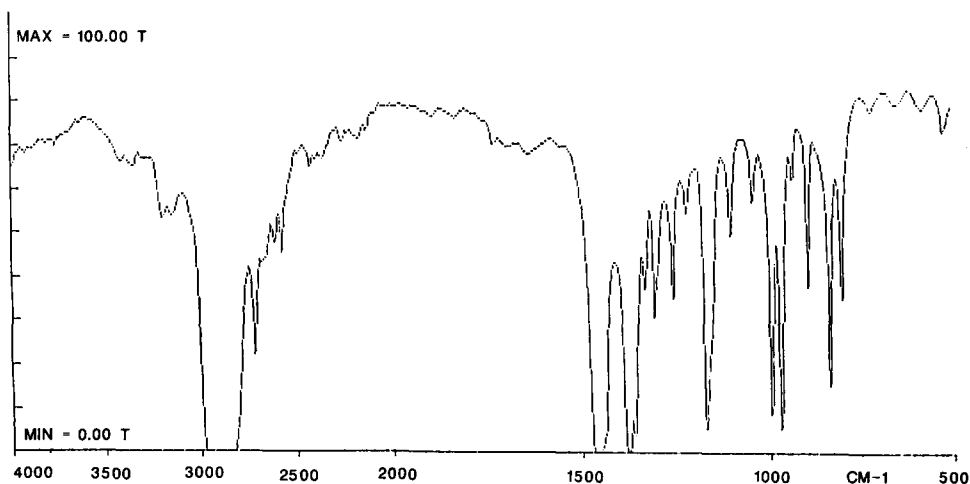


Figure 5 FTi.r. spectrum of homopolymer isotactic polypropylene

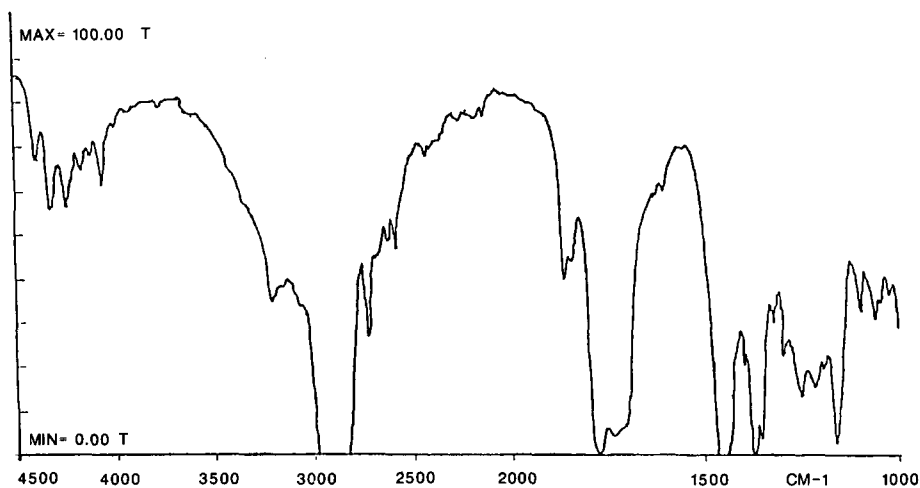


Figure 6 FTi.r. spectrum of polypropylene-maleic anhydride graft copolymer

7-10 confirmed the presence of structures D and E arising from free radical reaction termination steps. Resonance assignments are summarized in *Table 1*.

CONCLUSION

From the n.m.r. analysis it was clear that graft copolymers of polypropylene and maleic anhydride could be obtained by performing the reaction in the solid phase. This process did not require high processing temperatures and pressures. The product was free flowing and easily processable. Residual toluene in the copolymer showed

up as peaks between 122-148 ppm in the n.m.r. spectra. It was concluded that the peaks occurring between 172-174 ppm were those of the maleic anhydride functionality in the copolymer. It was clear that high efficiency could be achieved by this process.

REFERENCES

- 1 Minoura, Y., Ueda, M., Mizunuma, S. and Oba, M. *J. Appl. Polym. Sci.* 1969, **13**, 1625
- 2 Schaefer, J., Stejskal, E. O. and Buchdahl, R. *Macromolecules* 1975, **8**, 291