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CONFORMATION OF ETHYLENE/PROPYLENE COPOLYMERS (RANDOM OR BLOCK) AS SEEN BY ^{13}C NMR, IR AND THERMAL METHODS *

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ABSTRACT

Selected random and block ethylene/propylene (E/P) copolymers have been investigated thoroughly using ^{13}C NMR, IR, DSC and dynamic mechanical analysis (DMA). The ethylene content in the range 1–6% in random E/P copolymers can be quantified with good agreement by NMR relative intensity of PEP triad, by IR band intensity of the isolated ethylene units, and by DSC melting peak depression. The toughened polypropylenes containing E/P blocks show the expected "run" sequence of five or more methylene groups of intense PEE and EEE triads sequence in NMR and in IR bands. The glassy–rubbery transitions of the two-phase-structure block E/P copolymers are clearly demonstrated by DMA damping signals.

INTRODUCTION

Analyses of ethylene/propylene (E/P) copolymers were the subject of much work in the 1960s [1–7]. The review by Tosi and Ciampelli [8] is the best among several review articles on the spectroscopic analysis of these systems that appeared in the 1970s. Newer instrumentation has regenerated analytical interest in these systems. The composition of tailored E/P copolymers, both copolymers and blends, can be understood only by using multiple analytical methods. Historically, the copolymer compositions have been determined by IR spectroscopy with use of a tracer technique for calibration. More recently, ^{13}C nuclear magnetic resonance has been used successfully to characterize these materials. For example, Paxson and Randall [9] used NMR to measure the ethylene content of random P/E copolymers and calibrated an IR method using these as standards.

There is always a demand for faster and more affordable techniques, such as IR and thermal methods, for routine analysis. DTA/DSC has been used

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[5,6] to distinguish sequential and diblock E/P copolymers (ethylene content above 9 wt.%) and physical blends of polyethylene (PE) and polypropylene (PP) by their crystallization peaks. The randomness in these block copolymers was reported to be minor. DTA [6] is of no use for a random copolymer (presumably made from a mixture of ~ 50 : 50 ethylene and propylene gases in the presence of aluminum alkyl plus vanadium oxychloride), because there is no crystallinity. Random copolymers, made from the mixed gases in the presence of aluminum alkyl and titanium chlorides, exhibit some crystallinity, but there is no correlation to the ethylene content.

Gill et al. [10] found that the impact properties of ethylene modified polypropylenes are related to the intensity of polyethylene damping signal at −110 °C in dynamic mechanical analysis (DMA). Several other authors [11,12] observed the ethylene propylene (EP) rubber phase by DSC and by optical and electron micrographs in PP/elastomer and PP/EP blends.

The purpose of this paper is to demonstrate the utility of multiple methods in elucidation of the compositions of the E/P and P/E copolymers that are not covered in the literature.

EXPERIMENTAL

A group of random P/E copolymers with ethylene content varying from 1% to 6% were selected. The ethylene contents of these samples were determined from the ^{13}C NMR signal intensity of triads. Calibration curves were then established for IR band intensities and DSC melting peak positions. A group of block P/E copolymers and some blends with ethylene content of 6% to 70% were also selected. The ethylene contents were again determined by ^{13}C NMR. The ethylene contents in isolated form PEP and in a “run” EE were calculated from IR band intensities.

All selected examples were analyzed by DSC and DMA for their melting, crystallization and damping characteristics which will be grouped separately for the discussion of morphological significance.

^{13}C nuclear magnetic resonance spectroscopy

The samples were prepared as a 10% (w/v) solution in 1,2,4-trichlorobenzene (TCB). The samples were run at two different magnetic field strengths, 7.05 T and 9.4 T, and the data were compared. The 7.05 T and 9.4 T instruments were Bruker AM-300 wide bore and Varian VXR-400 narrow bore spectrometers respectively. The ^{13}C data were taken quantitatively, using suppressed Overhauser techniques. The samples were run unlocked at either 120 °C or 140 °C, depending on the appearance of the Fourier transformed spectra, i.e. whether or not optimal line width at half height was achieved on TCB. The data were acquired using a ^{13}C 90° pulse angle, the pulse repetition rate was 30 s or more, and an average of 2400 scans were stored in 32000 data points using a spectral window of either 12000 or 20000 Hz, depending on the magnetic field strength. Zero-filling was used with the 9.4 T. Spectra were referenced to the most upfield TCB peak at 127 ppm.

IR spectroscopy

The IR band for isolated ethylene in PEP units is for three CH_2 units (two from ethylene and one from propylene polymerized in a head-to-tail configuration). It is due to a rocking motion and appears at 732.5 cm^{-1}. If there are ethylene runs of 5 units, or more, as would be true if there were some block copolymer or blended ethylene homopolymers present, there will be a band at 720 cm^{-1}; if the ethylene component is at all crystalline, a band will also be present at 730 cm^{-1}. To avoid interference from these bands, we did two things. First, we subtracted a spectrum of polyethylene from the sample spectrum, using the 720 cm^{-1} band (which will appear as a shoulder) as a guide for the subtraction. Second, we measured the 732.5 cm^{-1} $(CH_2)_3$ band not at its peak, but at 738 cm^{-1}. By thus moving farther from the overlap of the bands we diminished any error that remains from incorrect subtraction of the interference.

The following procedure was used. A film of thickness ca. 8 mil was pressed between polytetrafluoroethylene as a release film. A press temperature of about 175 ° C was used and the film was then cooled in the press. The spectrum was run on an IR spectrometer capable of interactive spectral subtraction. (We used a Nicolet 20SX at 2 cm^{-1} resolution, Happ-Genzel apodization.) The baseline was drawn as a tangent from the minima at about 760 cm^{-1} and 690 cm^{-1}. To calculate the amount of ethylene in runs longer than $(CH_2)_3$ the absorbance was measured at 720 cm^{-1} after correcting for interference from the 732.5 cm^{-1} band. This was done by assuming it to be symmetrical. Therefore, its absorbance was measured above the baseline at 745 cm^{-1}. The amount of ethylene in runs longer than three CH_2 units was calculated using as the factor for the 720 cm^{-1} band the value 0.005 absorbance units per mil for 1% ethylene (Fig. 1).

If the amount of ethylene in runs was calculated to be less than 0.5%, the isolated ethylene was then calculated from the absorbance at 738 cm^{-1} and the factor 0.0036. However, if the ethylene in runs was greater than 0.5%, there could be enough interference at 738 cm^{-1} to require spectral subtraction. The spectrum of a low-density ethylene homopolymer was used and the subtraction ratio was adjusted until the absorbance at 720 cm^{-1} was about the same height above the baseline as a 745 cm^{-1}. The calculation was then carried out at 738 cm^{-1} (Fig. 2). If the ethylene in runs was greater than 2%, the same procedure was followed, but because some crystallinity could be

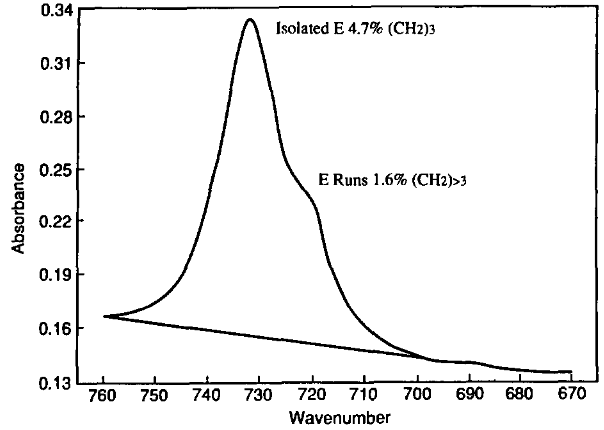

Fig. 1. IR absorption band of random P/E copolymer 1-16.

present the factor for the 720 cm^{-1} band was possibly somewhat greater than 0.005, and the spectral subtraction did not necessarily compensate as well for the interference.

Differential scanning calorimetry

A Du Pont 910 DSC in conjunction with a 1090 thermal analyzer was used for the analyses of melting and crystallization transitions. The temperature scale was standardized using the melting points of indium and mercury (156.6 °C and −38.9 °C); the calorimetric scale was calibrated using the heat of fusion of indium ($\Delta H = 28.42$ J g^{-1}). A sample (10 mg) was heated in an aluminum pan at 10 °C min^{-1} until melting, held for 3 min and then cooled at 10 °C min^{-1} back to ambient temperature. The peak positions were taken to be the melting and crystallization points.

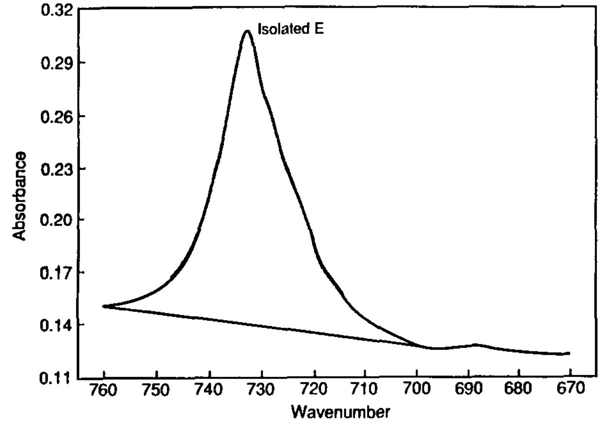

Fig. 2. Subtracted IR band of a P/E copolymer using spectrum of LDPE as reference.

Dynamic mechanical analysis

A Du Pont 983 DMA in conjunction with a 9900 thermal analyzer was used for determination of the size and location of damping signals (either the loss moduli in MPa or the analog mV) on the temperature scale, which was standardized with loss peaks of polycarbonate and Elvax (152 ° C and − 25 ° C) at 3° C min^{-1} scanning rate. Hotpressed sample sheets (5–10 mil thick) were cut into strips 12mm wide. The DMA was used in its resonant mode with an oscillation amplitude of 0.6 mm and a sample flex area of about 1.5 mm (L) × 12 mm (W) × 0.2 mm (T). Low temperature was achieved with the aid of liquid nitrogen cooling accessory, controlled directly from the 9900 computer. In all cases the measurement starts at − 150 ° C and ends at 100–120 ° C.

RESULTS AND DISCUSSION

Random copolymers

Figure 3 shows the 75.4 MHz, quantitative ^{13}C NMR spectrum of random P/E copolymer, 1-1. The spectrum is characteristic of a copolymer of low ethylene content [9]. Chemical shift data and assignments follow those in the literature [13–16]. Greek letters are used to distinguish the various methylene carbons and designate the location of the nearest methine carbons [17]. The large peak at 46.5 ppm is due to the $-\alpha\alpha$-CH_2 of propylene, which is in runs of propylene (PP dyad). The smaller peak at ~ 37.9 ppm is due to a methylene which is $\alpha\gamma$ to a methine (an EP dyad). In some of the spectra,

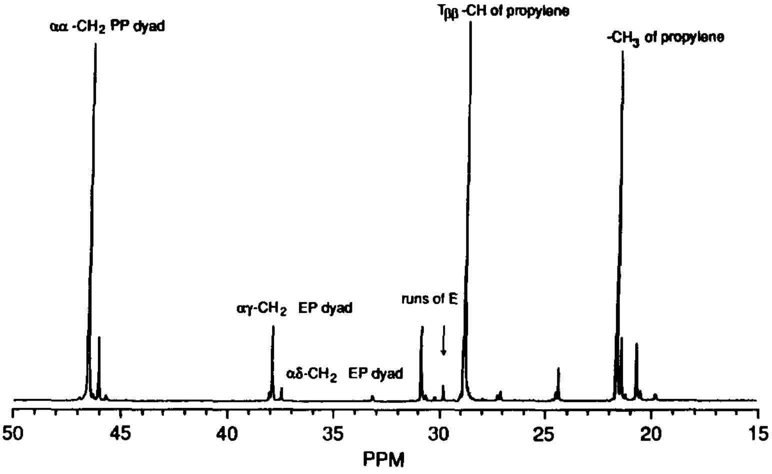

Fig. 3. Quantitative ^{13}C NMR spectrum of random P/E copolymer 1-1.

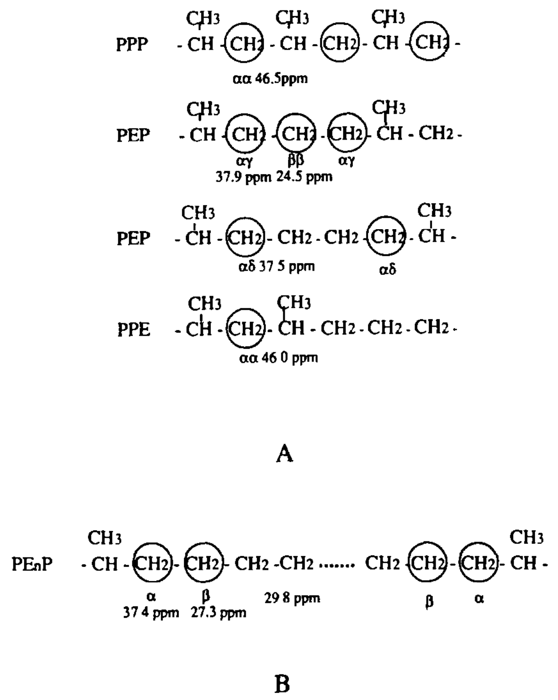

Fig. 4. Chemical shifts and sequence assignments of methylene carbons in ^{13}C NMR spectra of (A) random and (B) block P/E copolymers.

there is another small peak at ~ 37.5 ppm which is $\alpha\delta$ to a methine (also an EP dyad). These three peaks are used to determine the ethylene and propylene content [15]. The relationships are given below

$$\text{Propylene} = \text{PP} + \tfrac{1}{2}(\text{EP}) \qquad (1)$$

$$\text{Ethylene} = \text{EE} + \tfrac{1}{2}(\text{EP}) \qquad (2)$$

There is no evidence in of the ^{13}C spectra of the random copolymers of the presence of any long runs of ethylene (EE = $\delta\delta$-CH_2, $\beta\delta$-CH_2, $\gamma\delta$-CH_2).

The next small peak at ~ 30.9 ppm is a methine which is $\beta\delta$ to another methine. The large peak at ~ 28.8 ppm is the methine in long runs of propylene (T$\beta\beta$ [15,16]). Paxson and Randall [9] use these two peaks to determine comonomer composition. They reason that these peaks give the best quantitative results, since the methine resonance is the least sensitive toward configurational differences. However, it would appear that at low ethylene contents (< 5 wt.%) configurational differences do not seem to affect quantitation of ethylene by use of the methylene resonances. The chemical shifts and sequence assignments of methylene carbons in ^{13}C NMR spectra are illustrated graphically in Fig. 4A. The ethylene contents of 16 random copolymers are calculated using eqns. (1) and (2) and are given in Table 1.

TABLE 1

Weight percent of ethylene in P/E random copolymers

^{13}C NMR [a]		IR			DSC	
Sample No.	Isolated E (wt.%)	Isolated E (wt.%)	EE (wt.%)	Sum (wt.%)	Weight%	T_m (°C)
1-1	0.4	0.4	0	0.4	0.4	162.9
1-2	0.9	0.9	0	1.0	0.7	160.9
1-3	1.5	1.5	0.1	1.6	1.3	156.2
1-4	2.0	2.1	0.2	2.3	2.2	148.4
1-5	2.3	2.4	0	2.4	2.5	146.4
1-6	1.4	1.1	0	1.1	1.1	157.2
1-7	2.1	2.2	0.2	2.4	2.3	148.2
1-8	2.6	2.8	0.2	3.0	2.7	145.0
1-9	3.9	3.6	0.5	4.1	3.6	137.2
1-10	1.5	1.6	0.3	1.9	1.6	153.5
1-11	0.3	0.4	0	0.4	0.3	162.3
1-12	4.0	4.2	0.6	4.8	3.7	136.5
1-13	3.5	3.2	0.4	3.6	2.9	143.1
1-14	3.4	3.3	0.4	3.7	3.3	139.5
1-15	4.1	3.4	0.5	3.9	3.3	139.8
1-16	5.4	4.7	1.6	6.3	5.3	123.8

[a] Calculated using eqs. (10) and (11) of ref. 13.

The IR method was calibrated based on the ethylene contents of the first five P/E random copolymers (1-1 to 1-5) determined by NMR. Confirmation of the NMR values was obtained in two ways. First, Paxson and

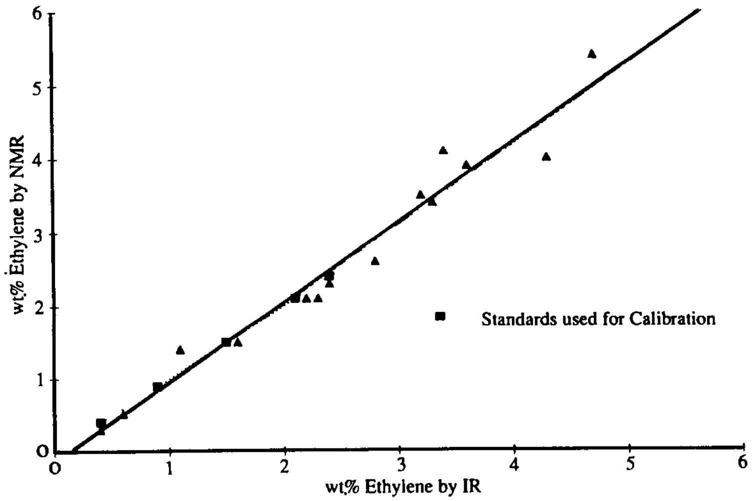

Fig. 5. Correlation of ethylene contents in the random copolymers between IR and NMR methods.

Randell [9] gave a calibration for the 932.5 cm^{-1} band for isolated ethylene units. Our factor for this band, given in the Experimental section, was 0.0036, but this is for a point on the side of the 738 cm^{-1} band. Measured at its 732.5 cm^{-1} maximum we find a value of 0.0066 absorbance per mil for 1% ethylene. Paxson and Randell's equation for the calculation has an intercept value. In our calibration against our NMR values the intercept is essentially zero. If, however, one calculates the absorbance for 1% ethylene using their slope and intercept and converts to our units (abs. mil^{-1}) we find a value of 0.0074, compared to our value of 0.0066. This indicates that our NMR values are in reasonable agreement with theirs for the similar polymers.

Second, we can derive an independent IR calibration from a model compound, 2,6-dimethylheptane. This is not a perfect model, the band being shifted to 734 cm^{-1} and, as is often the case, being somewhat sharper than the polymer band. The equation for calculating the calibration factor is

$$\text{IR factor (in abs. mil}^{-1}\text{ for 1\% ethylene)}$$
$$= \frac{(\text{absorbance of standard solution})(\text{density of polymer film})(0.254)}{(\text{liquid cell thickness in mm})(\text{standard solution concentration in g l}^{-1})} \qquad (3)$$

Equation (3) gave a factor for the "ethylene" content of dimethylheptane of 0.0069. When a correction was made for the difference in the band widths by multiplying the ratio of band areas, an adjusted band height calibration factor of 0.0057 abs. mil^{-1} for 1% ethylene was obtained. From the various IR factors, the percentages of isolated ethylene in sample 1-4 compare as given in Table 2. For the total of 16 random copolymers the agreement of ethylene contents between IR and NMR is excellent. The correlation can be seen in Fig. 5 and Table 1.

The random P/E copolymers of low ethylene content show melt depression and peak broadening from the propylene homopolymer (mp. 164° C), as shown in the composite DSC plot in Fig. 6. This depression is closely related to the ethylene content. Plotting ethylene contents of 16 random copolymers determined by our ^{13}C NMR against the melting peak positions

TABLE 2

Percentages of isolated ethylene in sample 1-4

Basis of calibration	Factor used	Percentage ethylene
Our NMR data	0.0066	2.1
IR data of Paxson and Randell	0.0074	1.9
2,6-dimethylheptane	0.0057	2.3

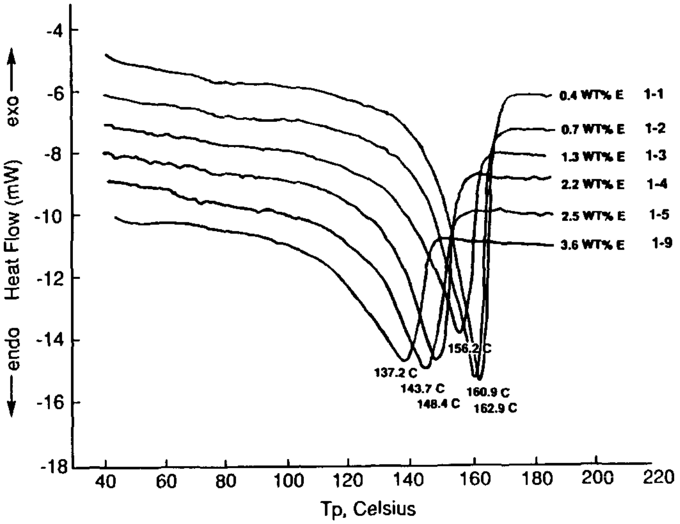

Fig. 6. Melt depression and peak broadening of random copolymers in DSC.

(Fig. 7), we found that the correlation is astonishingly linear

$$\text{wt.\% ethylene} = 22.0015 - 0.1325T_m \tag{4}$$

DSC is generally considered as an affordable instrument for routine analyses of ethylene contents in copolymers.

Table 1 summarizes our results of the ethylene contents of 16 random P/E copolymers measured by NMR, IR and DSC. The ethylene contents of random copolymers were determined by DSC melting peak depression using

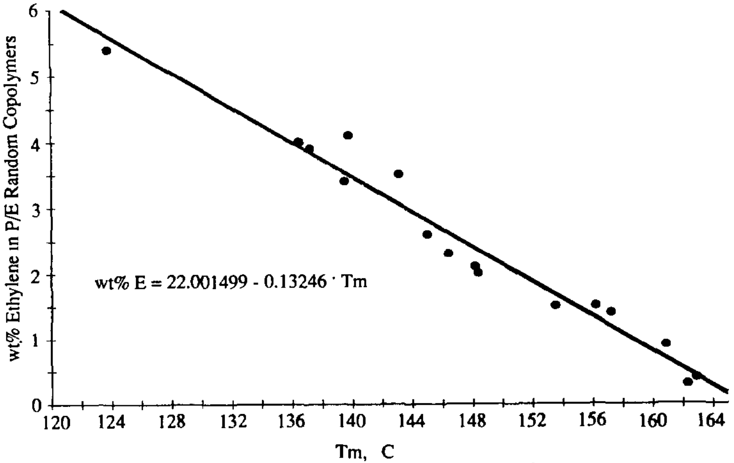

Fig. 7. Linear correlation of ethylene contents by ^{13}C NMR and melting peaks.

TABLE 3

Weight percent of ethylene in P/E block copolymers and blends

Sample No.	^{13}C NMR (wt.%)	IR		
		Isolated E (wt.%)	EE (wt.%)	Sum (wt.%)
2-1	10.6	1.4	6.9	8.3
2-2	12.1	1.6	9.0	10.6
2-3	6.4	1.6	4.2	5.8
2-4	71	8	56	64

the above calibration and by the IR calibration factor of 0.0036 using the 738 cm^{-1} band.

Block copolymers

Table 3 gives the ethylene contents for four block copolymers. For the samples which contain greater than 5 wt.% ethylene, there is a peak at 29.8 ppm indicating runs of ethylene (Fig. 4B) in ^{13}C NMR spectrum. These copolymers are often referred to as 'blocky' owing to the tendency of the ethylene segments which have polymerized together to form new domains. Figure 8 shows the 100 MHz quantitative ^{13}C spectrum of this type of copolymer (2-2). This obvious difference between Figs. 3 and 8, as well as

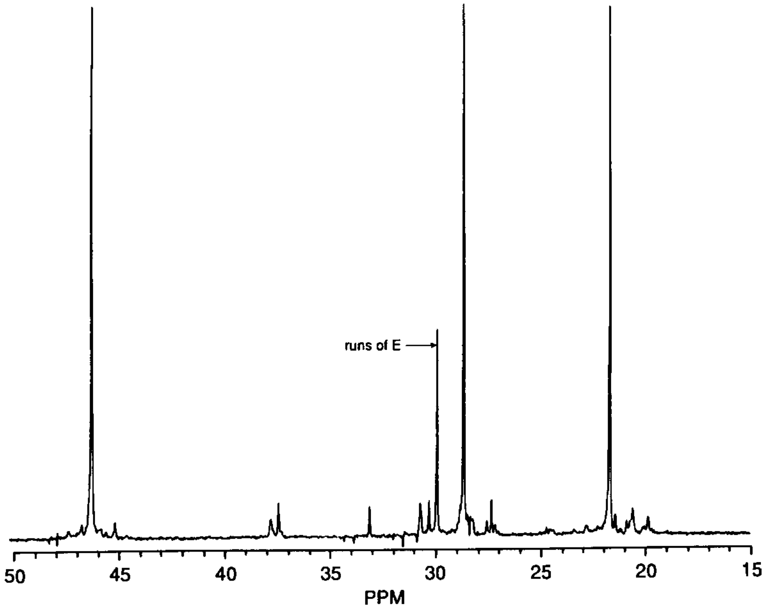

Fig. 8. Quantitative ^{13}C NMR spectrum of block P/E copolymer 2-2.

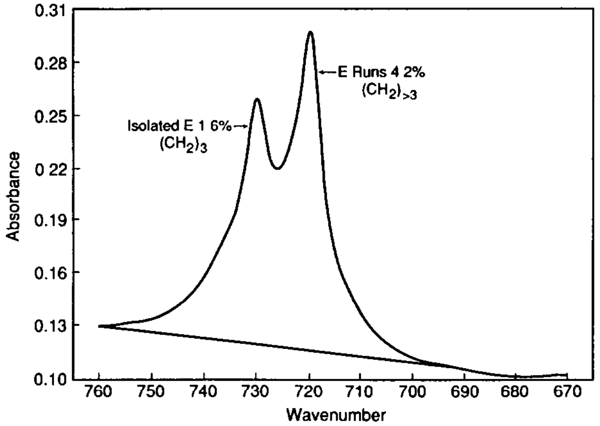

Fig. 9. IR absorption band of block P/E copolymer 2-3.

some subtle sequence distribution effects in the methylene and methyl regions, needs to be taken into account when quantitating the amount of ethylene. The IR spectrum of a block copolymer, sample 2-3, is shown in Fig. 9. Ethylene contents of these copolymers can be calculated using IR bands (details in Experimental section).

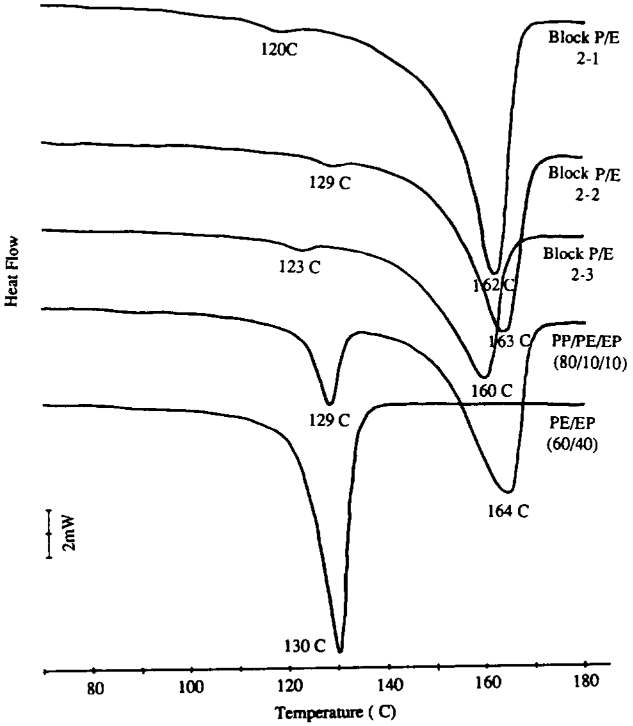

Fig. 10. Melting characteristics of P/E block copolymers and their blends in DSC.

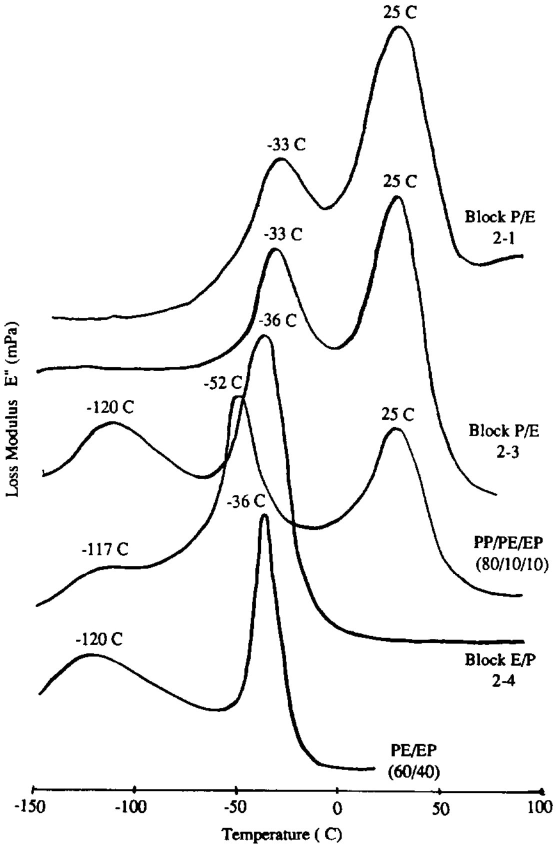

Fig. 11. Damping characteristics of P/E block copolymers and their blends in DMA.

The melting and damping characteristics of P/E block copolymers and their blends are compared in Figs. 10 and 11. Three polypropylene melting peaks in the copolymers are found to be lower than the expected 164° C in DSC scans. This is caused by the ethylene unit being randomly distributed in the polypropylene phase and is confirmed by the presence of the 732 cm^{-1} band in IR. The EP blocks in three copolymers can be vaguely seen in DSC by their small melting peaks at 120–130° C (due to the unreliable small degree of crystallinity of the EP domain). Whether the EP blocks in two blends (PP/PE/EP in 80/10/10 and PE/EP in 60/40) have any crystallinity is not clear, since the melting of EP blocks can be buried under the PE melting peak at 129–130° C. In Fig. 11 the unique large damping signals of the EP phase of the P/E block copolymers and their blends are detectable by DMA. These damping signals appear at -30° C to -50° C which are between the T_g value of polyethylene (-120° C) and polypropylene (25° C). This signal does not appear in DMA damping of PP/PE blends in Fig. 12. However, owing to the nature of spectroscopic methods, NMR and IR, the

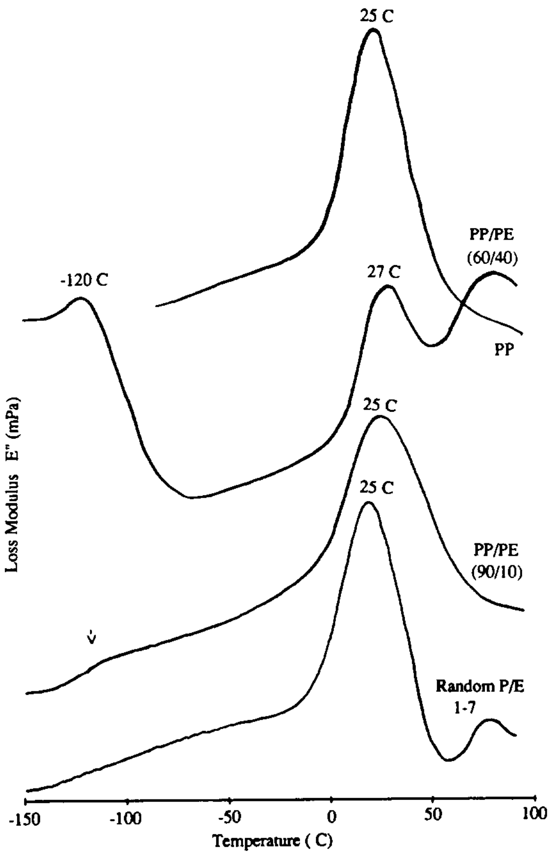

Fig. 12. Damping characteristics of polyethylene and polypropylene blends and P/E random copolymer in DMA.

source of ethylene "runs" is not distinguishable between the EP blocks in copolymers and polyethylene blends.

Figure 13 shows that the melting peaks of the PE and PP in either the homopolymers or the blends are characteristic of the two polymers themselves. The melting peak in random P/E copolymer (1-7) is substantially lowered and broadened compared with that of propylene homopolymers and PP/PE blends. The damping signals in Fig. 12, however, show little or no difference between the propylene homopolymer and random P/E copolymers, not even the PP/PE(90/10) blend.

Table 4 summarizes the morphological significance of P/E random, P/E block, and homo/block blends that have already been shown in Figs. 10–13. Randomness in a segment caused by a comonomer is indicated by melting depression and peak broadening of the segment. The presence of EP blocks in any copolymers is detectable by a small melting peak in the range 120–130° C (sometimes) in DSC and a large damping peak (always) in

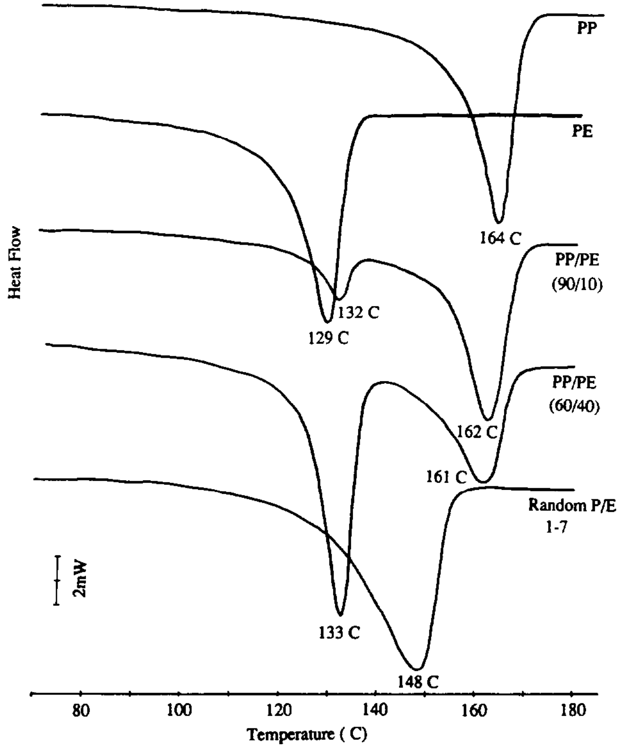

Fig. 13. Melting characteristics of polyethylene and polypropylene blends and P/E random copolymer in DSC.

DMA. The temperature of this small melting peak is unpredictable. We believe that it results from the degree of randomness in EP blocks. Multiple melting and crystallization peaks in DSC and multiple damping signals (usually the glass transitions) are due to the immiscibility of the phases.

CONCLUSION

The utility of multiple analytical methods is highlighted in this paper. Both IR and NMR spectroscopies are not specific to the difference between the copolymers and homopolymer blends. However, thermal methods can easily distinguish between the two. Spectroscopic methods are excellent for quantifying the ethylene content in copolymers.

TABLE 4

Melting, crystallization and damping characteristics

Sample No.	T_m (°C)	T_c (°C)	Damping max. (°C)		Significance
PP	164.0	116		25	Homopolymer
PE	128.9	114	−120		Homopolymer
PP/PE	133, 161	115, 118	−120,	27	Blend (60/40), immiscible phases
PP/PE	132, 162	115, 118		25	Blend (90/10), immiscible phases
1-7	148.2	99.9		25	Random (2.3 wt% E), melt depression
1-10	153.5	119.1		25	Random (1.6 wt% E), melt depression
2-1	120, 162	101, 123	−33,	25	Immiscible phases: PP and EP blocks, randomness
2-2	117, 166	98, 121	−33,	25	Immiscible phases: PP and EP blocks
2-3	121, 159	100, 109	−35,	25	Immiscible phases: PP and EP blocks, randomness
2-4	47, 126	17, 113	−120,	−36	Immiscible phases: PE and EP blocks, randomness
PP/PE/EP	129, 164	110, 115	−117,	−52, 25	Blend of homopolymers and EP blocks (80/10/10), immiscible phases
PE/EP	130	112	−120,	−36	Blend of homopolymer and EP blocks (60/40), immiscible phases

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