Characterization of poly(2,6-dimethyl-1,4-phenylene ether) by high resolution pyrolysis–gas chromatography (HR–Pyg.c.)

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Pyrograms of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) samples were obtained by on-line high resolution pyrolysis–gas chromatography (HR–Pyg.c.). Characteristic peaks on the pyrograms (up to trimers) were assigned by using gas chromatography–mass spectrometry (g.c.–m.s.) and retention time data. The analysis of a series of fractions of varying molecular weight from a given PPE sample suggested that HR–Pyg.c. would be a powerful technique for characterization of the end groups of PPE when ^{13}C-n.m.r. was used to take reference data for these end groups.

(Keywords: poly(2,6-dimethyl-1,4-phenylene ether); high resolution pyrolysis–gas chromatography; pyrolysis products assignments; ^{13}C-n.m.r.; end group analysis)

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE), which is primarily a moulding material, is prepared by the oxidative coupling of 2,6-dimethyl phenol[1,2]. It is rated among the superior engineering plastics and has played an important role in the field of polymer alloys because of its high temperature resistance.

Various techniques such as infrared spectroscopy[3–5], ^{13}C-n.m.r.[6], pyrolysis gas chromatography (Pyg.c.)[7], and mass spectroscopy (MS)[8,9] are available for the characterization of PPE. Among them, the earlier work by Jachowicz *et al.*[7] using off-line Pyg.c. with a packed separation column showed Pyg.c. to be a promising technique for studying the structure of PPE. Recently, the resolution and reproducibility of the pyrograms have been improved drastically by the use of highly specific on-line pyrolysis devices and a fused-silica capillary separation column[10,11]. This technique is highly sensitive and very useful for the characterization of microstructures within various polymers, such as the end groups of poly(methyl methacrylate)[12,13].

This paper describes the HR–Pyg.c. technique applied to the characterization of thermal degradation products of PPE as a function of molecular weight. The observed HR–Pyg.c. data for the end groups of PPE were compared with those obtained using ^{13}C-n.m.r.

EXPERIMENTAL

PPE samples

A PPE sample was obtained using a Mn-based catalytic system[2]. PPE samples with varying molecular weights were prepared from the parent PPE sample by fractionation. Fractionation of PPE was carried out using a solvent gradient technique at room temperature. The polymer fractions were precipitated from the benzene solution by adding methanol as a poor solvent, and the precipitates were filtered at different concentrations of methanol (23 and 79 vol%). Detailed conditions of the fractionation and the characteristics of the whole and fractionated PPEs are listed in *Table 1*. The molecular weights were determined on the basis of polystyrene standards by a Waters 150C liquid chromatograph equipped with three Shodex AD 80M/S columns in series at 140°C using ortho-dichlorobenzene as solvent.

HR–Pyg.c. measurements

A vertical microfurnace-type pyrolyser (Yanagi-moto GP-1018)[10] was directly coupled to a gas chromatograph (Hewlett-Packard 5890) equipped with a fused-silica capillary column (0.25 mm i.d. × 25 m) coated with 0.25 μm of immobilized poly(5% phenyl)-methylsiloxane. About 0.1 mg of the polymer sample was pyrolysed at 510°C under nitrogen carrier gas. The column temperature was programmed from 50°C at a rate of 5°C min^{-1}

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Table 1 Fractionation conditions and characteristics of the PPE fractions

Sample	PPE fractions			
Item	Whole	HMW[a]	MMW[b]	LMW[c]
Fractionation conditions (benzene/MeOH)	–	29% MeOH insoluble	29% MeOH soluble 79% MeOH insoluble	79% MeOH soluble
Wt%	100	69.5	29.8	0.7
$\bar{M}_n$ ($\times 10^{-4}$)	1.33	3.09	0.632	0.088
$\bar{M}_w$ ($\times 10^{-4}$)	4.81	6.37	1.12	0.132

[a] High molecular weight fraction
[b] Medium molecular weight fraction
[c] Low molecular weight fraction

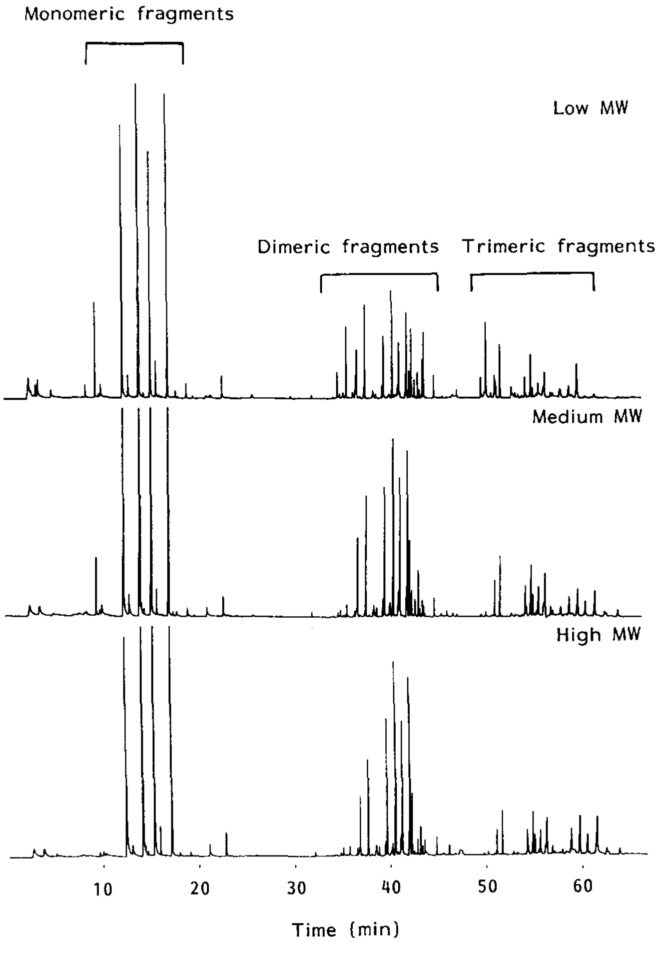


Figure 1 Pyrograms of PPE fractions with different molecular weights

up to 300°C. Peak assignments were mainly carried out by a directly coupled g.c.–m.s. (Shimazu QP-1000) instrument. The assignments were confirmed by retention data of the standard reagents for monomeric fragments. Retention data of the main monomeric fragments and the dimeric fragments with one and two hydroxy groups for dimeric and trimeric fragments, respectively, were also used to confirm assignments. For trimeric fragments, the pyrolysis products data of cresol/novolak resin were used in addition.

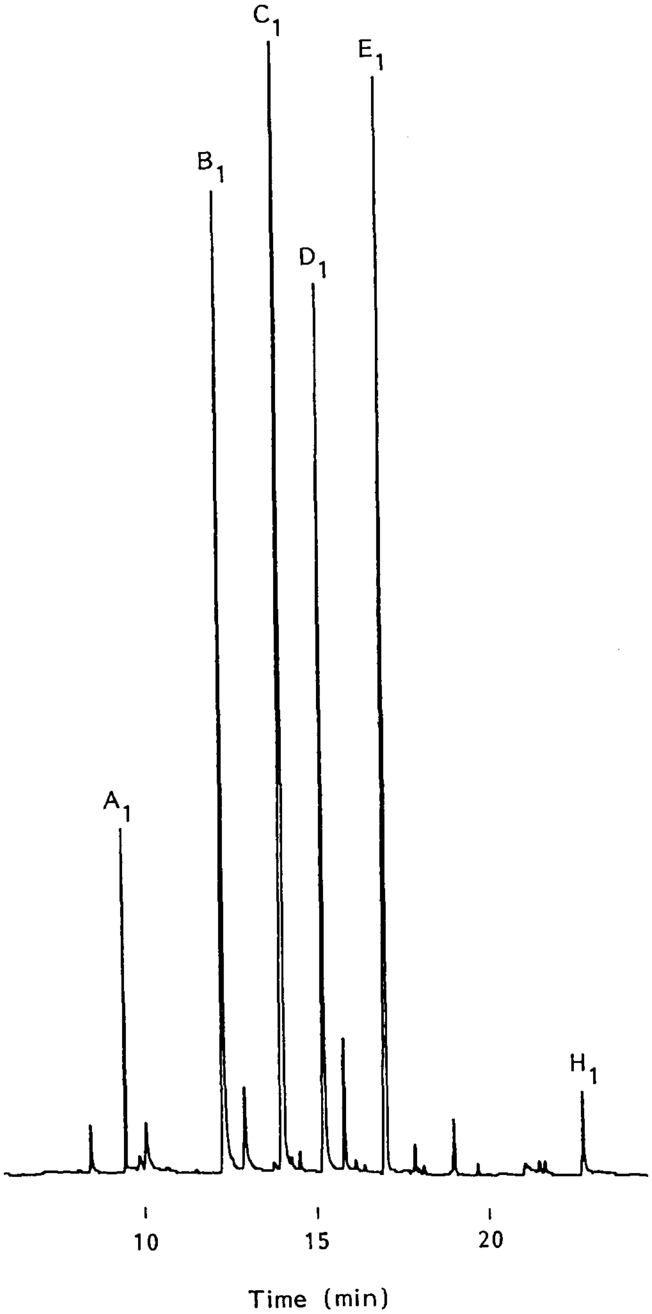
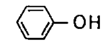
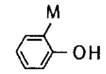
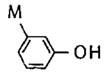
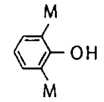
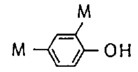
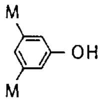
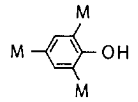
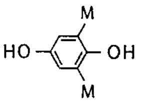


Figure 2 Expanded pyrogram of monomeric fragments for the lower molecular weight fraction of PPE

Table 2 Monomeric peak assignments of the PPE pyrogram

Peak	MW	Structure[a]
A_1	94	
B_1	108	
C_1	108	
D_1	122	
E_1	122	
F_1	122	
G_1	136	
H_1	138	

[a]M = methyl group

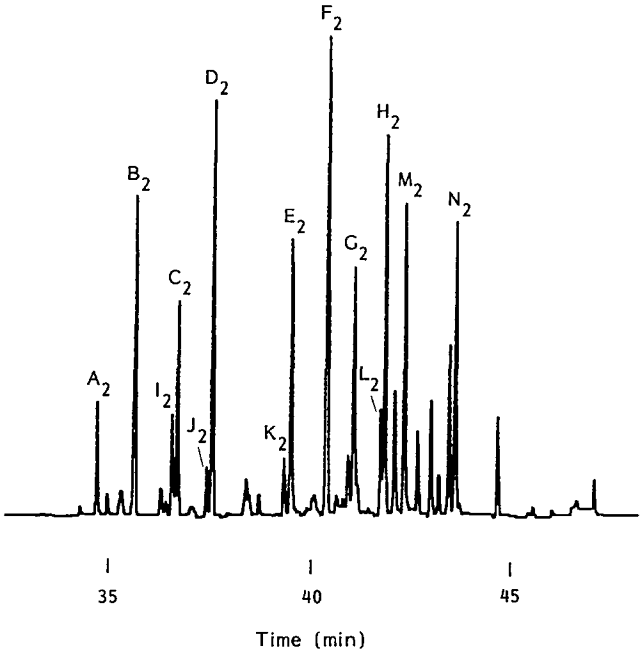
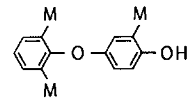
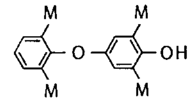
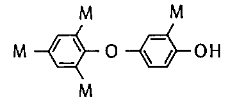
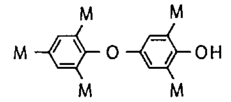
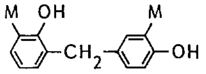
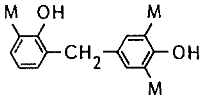
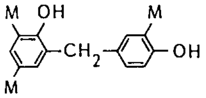
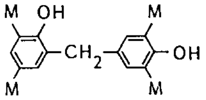
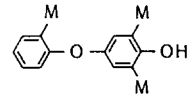
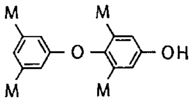
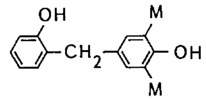
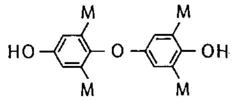


Figure 3 Expanded pyrogram of dimeric fragments for the lower molecular weight fraction of PPE

Table 3 Dimeric peak assignments of the PPE pyrogram

Peak	MW	Structure	Related end group
A_2[a]	228		Phenyl
B_2[a]	242		Phenolic Phenyl
C_2	242		
D_2	256		
E_2	228		
F_2	242		
G_2	242		
H_2	256		
I_2	228		
J_2	242		
K_2	228		
L_2	258		
M_2[a]	228	not assigned	Phenolic?
N_2	242	not assigned	

[a]Peaks used for end group analysis

^{13}*C-n.m.r. measurements*

^{13}C-n.m.r. spectra were obtained at room temperature using a JEOL-FX200 spectrometer at 50.10 MHz. About 10% (w/v) of the sample solution in $CDCl_3$ was measured using a 10 mm sample tube. A typical measurement was performed for 3–5 h for the lower molecular weight fractions and 40–50 h for the medium and higher molecular weight fractions. The chemical shifts were referenced internally to the major benzene ring carbon attached to methyl group taken as 132.57 ppm for Me_4Si. The spectral width was 10 kHz with 16 K data points. A pulse width of 45° (7 μs) and a pulse delay of 2 s were applied.

RESULTS AND DISCUSSION

Pyrograms of the PPE fractions

Figure 1 shows the pyrograms of the PPE fractions. As observed in *Figure 1*, the relative intensity of the peaks changes from fraction to fraction depending on the

Table 4 Trimeric peak assignments of the PPE pyrogram

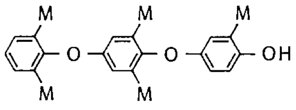
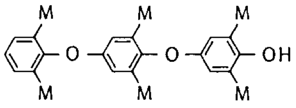
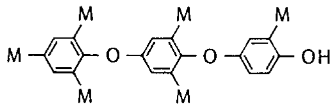
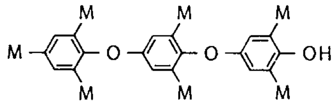
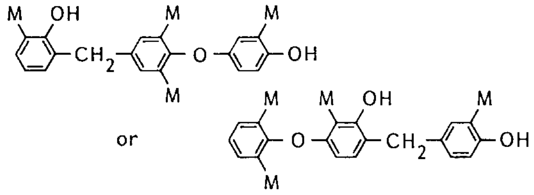
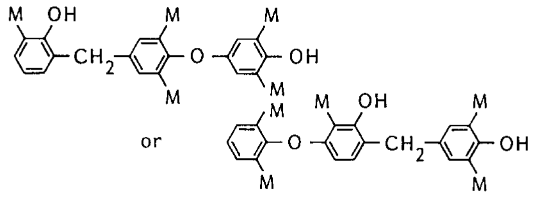
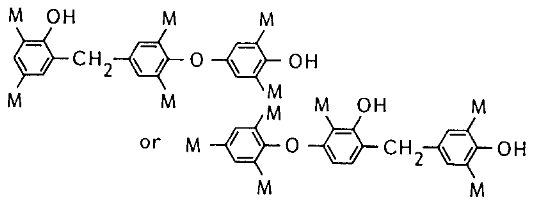
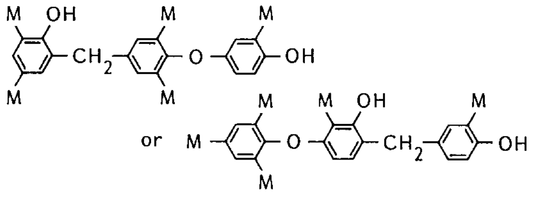
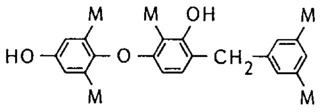
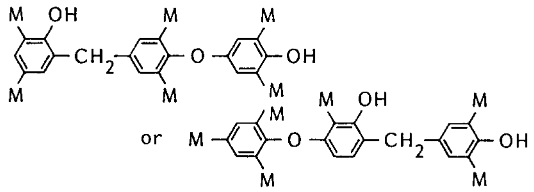
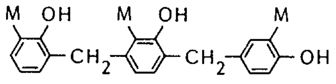
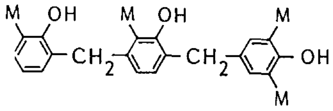
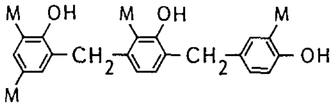
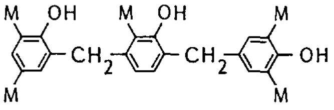
Peak	MW	Structure	Related end group
A_3[a]	348		Phenyl
B_3[a]	362		Phenolic Phenyl
C_3	362		
D_3	376		
E_3	348		
F_3	362		
G_3	376		
H_3	362		
I_3	362		
J_3	376		
K_3	348		

Table 4 *Continued*

Peak	MW	Structure	Related end group
L_3	362		
M_3	362		
N_3	376		

[a] Peaks used for end group analysis

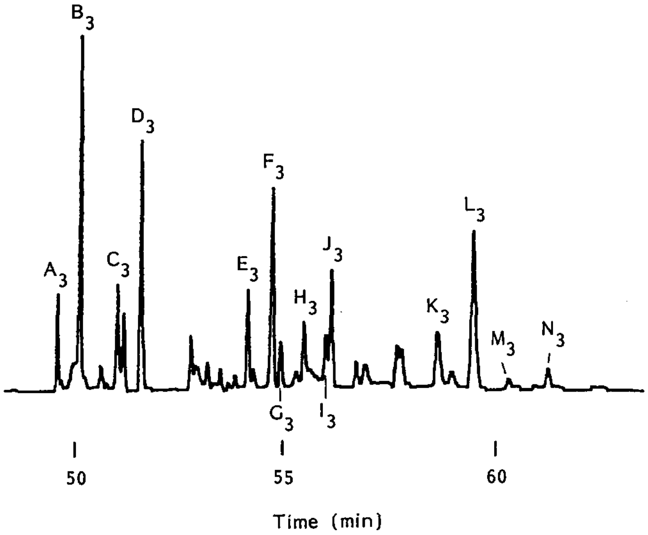
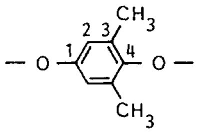
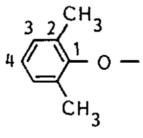
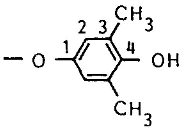


Figure 4 Expanded pyrogram of trimeric fragments for the lower molecular weight fraction of PPE

Table 5 Peak assignments of ^{13}C-n.m.r. spectrum of PPE

Structure	Carbon number	Chemical shifts (ppm from TMS)	Peak in *Figure 5*
	1	154.80	a
	2	114.52	j
	3	132.57	e
	4	145.53	d
	1	151.49	b
	2	131.52	f
	3	128.99	g
	4	124.95	h
	1	154.80	a
	2	114.10	k
	3	124.35	i
	4	146.41	c

molecular weight, although the majority of peaks is commonly observed in any pyrogram.

Figures 2–4 show the expanded pyrograms of monomeric, dimeric and trimeric fragments for the lower molecular weight fraction of PPE, respectively. The peaks are designated alphabetically with attached numbers that express the number of monomer units included in the degraded fragments. *Tables 2–4* summarize the structural assignments for those peaks corresponding to those in *Figures 2–4*.

Monomeric fragments. The pyrogram pattern and the assignments of the main peaks are similar to those described by Jachowicz *et al.*[7]. Furthermore, the higher resolution and sensitivity achieved using the fused-silica capillary column made it possible to detect and assign some additional minor peaks (F_1, G_1, H_1).

Dimeric fragments. The main dimeric fragments with one and two hydroxy groups (A_2, B_2, C_2, D_2, E_2, F_2, G_2, H_2) are observed in *Figure 3*, showing similar intensity patterns and assignments to those obtained by Jachowicz *et al.*[7]. However, some additional minor peaks

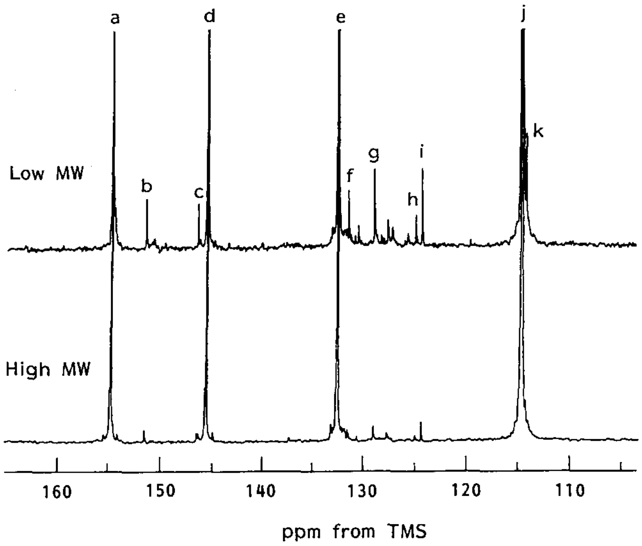


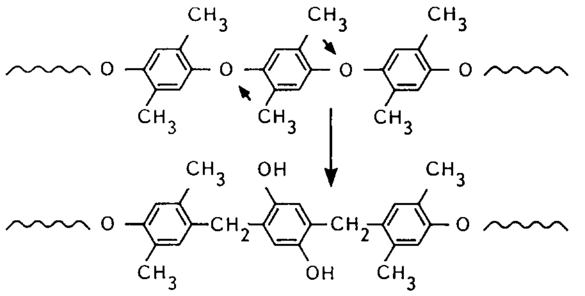
Figure 5 ^{13}C-n.m.r. spectra of lower and higher molecular weight fractions of PPE

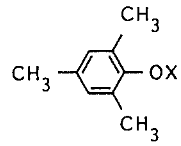
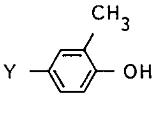
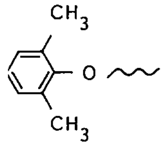
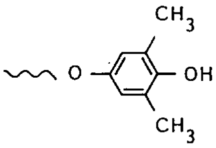
(I_2, J_2, K_2, L_2, M_2, N_2) were newly observed because of the higher resolution and sensitivity of the HR–Pyg.c. system.

Trimeric fragments. All the trimeric fragments were detected for the first time using the HR–Pyg.c. system.

Change of pyrogram for PPEs with varying molecular weight

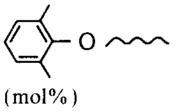
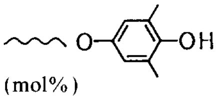
The fragment peaks that have a strong correlation with molecular weight are specified (with asterisks) in *Tables 3* and *4*. The correlation originated from the difference in end-group concentrations. As has been discussed by Jachowicz *et al.*[7,8], the formation of monomeric, dimeric and trimeric fragments is mainly associated with a Fries-type rearrangement.



The assignment of the peaks to each type of end group was carried out assuming that the elimination of the methyl group occurred only through a Fries-type rearrangement. This means that  and  products do not arise from  and  chain ends, respectively.

A quantitative analysis of end groups can be carried out by ^{13}C-n.m.r. *Figure 5* shows the ^{13}C-n.m.r. spectra of the lower molecular weight (LMW) and higher molecular weight (HMW) fractions of PPE. The peak assignments in *Table 5* were made using the results by White[6]. The quantitative results of the end groups in monomer unit mol% were obtained from the intensity ratios of the peaks of the benzene ring carbon signals attached to methyl groups in the end groups (131.52 ppm for phenyl end group and 124.35 ppm for phenolic end group) to that in the main chain (132.57 ppm). These results are shown in *Table 6*.

Table 6 Concentration of end groups of PPE fractions determined by ^{13}C-n.m.r.

Sample	End group concentrations of PPE		
Item	HMW	MMW	LMW
$\bar{M}_n$ ($\times 10^{-4}$)	3.09	0.632	0.088
Phenyl			
 (mol%)	0.4	0.4	6.1
Phenolic			
 (mol%)	0.3	1.3	9.8

The intensity of the Pyg.c. fragment peaks were normalized by peaks G_2 and H_3 for dimeric and trimeric fragment peaks, respectively, to correlate the chain end concentrations because G_2 and H_3 peaks do not arise from both chain ends based on the above assumption. *Table 7* shows the relative intensity changes of the Pyg.c. fragment peaks that correlate well with the end groups, along with relative end group ratios determined by ^{13}C-n.m.r. in which those for the HMW fraction were defined as unity. The relative peak intensities on the pyrograms for varying molecular weight samples are in fairly good correlation with the relative end group ratios observed by ^{13}C-n.m.r. This result suggests that the HR–Pyg.c. method could be used as an effective tool for end group analysis of PPE by calibrating the data obtained using ^{13}C-n.m.r.

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Table 7 Relative concentrations of PPE fraction end groups by ^{13}C-n.m.r. and HR–Pyg.c.

Sample	Relative end group concentration of PPE[a]					
Method	HMW		MMW		LMW	
Type of end groups	Phenolic	Phenyl	Phenolic	Phenyl	Phenolic	Phenyl
^{13}C-n.m.r.	1.0	1.0	4.3	1.0	33	15
HR-Pyg.c. [peak]						
A_2	–	1.0	–	1.4	–	17
A_3	–	–	–	1.0	–	13
M_2	1.0		5.9		38	
B_2	1.0		1.3		14	
B_3	1.0		1.3		39	

[a] These values are normalized by the highest MW fraction for each type of end group in each row

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