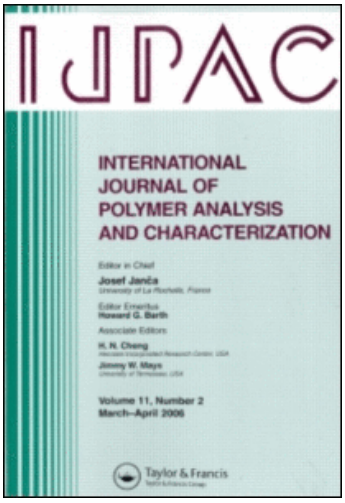

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Determination of End Groups in Thermoplastic Addition Polymers by Oligomer Separation and Characterization*

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Low-molecular-weight fractions have been isolated from polystyrene, poly(vinyl chloride) and high-density polyethylene (HDPE) by fractionation methods. These fractions were subjected to high-performance gel permeation chromatography (HPGPC) to separate individual oligomer species. Repeated injection of fractions and collection of the individual oligomers allowed characterization by nuclear magnetic resonance spectroscopy and mass spectroscopy. Structures for end groups in these oligomers have been deduced, and shown to be consistent with polymerization mechanisms for the formation of each addition polymer. An example of an HPGPC procedure is provided for quantifying the concentration of an oligomer in HDPE by a standard addition method.

Keywords: Gel permeation chromatography; Fractionation; Oligomers; End groups

INTRODUCTION

Several addition polymers have extensive applications as thermoplastics. Typically, these thermoplastics are high polymers whose linear chains have quite low concentrations of end groups (about 10^{-3} g/g chain for a molecular weight near 10^5).[1] The end groups are very dependent on the chemistry of the polymerization mechanism with

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type of initiator, initiation/side reactions, and chain formation reactions arising from termination and chain transfer, all contributing to the structures of chain ends. Whilst the concentration of these groups in a polymer is low compared with monomer units, oligomers will contain quantifiable terminal units. End groups can be significant because their stability may be questionable during processing of thermoplastics.[2] A polymer having a most probable molecular weight distribution with number-average degree of polymerization of 10^2 contains an oligomer weight fraction up to and including decamer of about 0.005.[3]

The aim of this work was to develop a sequential methodology in which a low-molecular-weight fraction was isolated from a high polymer followed by chromatographic separation of oligomers from this fraction. The repeated injection and collection of oligomers allowed the characterization of end groups in oligomers. It was hoped that this would provide important structural information with relevance to the polymerization mechanism and the stability of a high polymer. Separations of as-prepared low polymers, prepolymers and oligomers by high-performance gel permeation chromatography (HPGPC) are documented,[4] and for example, important details may be obtained from the study of the structure of oligomers.[5] Information can also be obtained on the identity and quantity of end groups and structural defects at branch points.[6,7] The combination of fractionation with HPGPC requires selective consideration of the fractionation method dependent on the type of thermoplastic addition polymer. Removal of low-molecular-weight species by fractional extraction based on differential solubility is known,[8] for example, by Soxhlet extraction for poly(vinyl chloride) (PVC),[9] and low polymers may be isolated by fractional crystallization from semicrystalline high-density polyethylene (HDPE).[10]

Previously, GPC has been used to separate *n*-alkanes from low-molecular-weight waxes[11] or hydrocarbon oil fractions,[12] but not from extracts of high-molecular-weight HDPE. Our initial HPGPC studies[13] of oligomers incorporated the alternate pumping recycle technique devised by Henry *et al.*[14] As performed by Mori,[15] isolation and characterization of individual oligomers from polystyrene (PS) prepared by anionic polymerization provide a performance indicator for a set of columns, and we have adopted this approach to

establish our HPGPC procedure. The methodology of fractionation followed by HPGPC has been studied for samples of PS, HDPE and PVC obtained from industrial sources. Individual oligomers have been separated and the end groups determined. A mechanism could then be proposed for the formation of the observed end groups and this could lead to an insight into chain formation for high polymers.

EXPERIMENTAL

Polystyrene

The PS standard (PS580) prepared by anionic polymerization was obtained from Polymer Laboratories Ltd., and had a quoted number-average molecular weight M_n of 580. A PS sample originating from an industrial source was supplied by the Institute of Polymer Technology and Materials Engineering at Loughborough University. The molecular weight was determined by HPGPC, using two Mixed-B columns (Polymer Laboratories Ltd., Shropshire, UK), and tetrahydrofuran (THF) (HPLC grade, Fisons, Loughborough, Leicestershire, UK), as eluent at a flow rate of 1 mL/min. The system was calibrated using a set of narrow PS standards (Polymer Laboratories) in the molecular weight range 1,270–1,290,000 and a linear calibration fitted to the data points. The value of M_n was found to be 8,000 with a polydispersity of 2.1.

Polyethylene

Two samples of HDPE were obtained from industrial sources. The samples were characterized by GPC with a Waters 150CV instrument at RAPRA (Shawbury). The first sample (HDPE1) had a value of M_n of 8,280 with a polydispersity of 8.56. The second sample (HDPE2) had a value of M_n of 20,000 with a polydispersity of 8.81. The samples were confirmed to be linear by matching their IR spectra with a reference spectrum for a nonbranched polyethylene. Samples of *n*-alkane standards were supplied by Aldrich (Gillingham, Dorset, UK).

Poly(vinyl chloride)

The PVC sample produced by mass polymerization was supplied by Atochem (Thatcham, Berkshire, UK), and had a M_n value of 34,400 with a polydispersity of 2, determined according to the GPC method described by Skillicorn *et al.*[16] This sample had a K value of 56 as determined from the relative viscosity of a 1% PVC solution in cyclohexane.[16]

Isolation of Oligomers from Polystyrene Standard

The PS580 standard was separated into its constituent oligomers using a recycle HPGPC system based on the alternate pumping recycle technique described by Henry *et al.*[14] The system comprised four PLgel columns, 300 × 7 mm, 5 μm, 50 Å (Polymer Laboratories Ltd.) operating at room temperature with a flow rate of 1 mL/min. Injections were performed with a Rheodyne 7125 injection valve, fitted with a 200 μL loop. Recycling was achieved using a Rheodyne 7000 switching valve as described by Dawkins *et al.*[13] The PS standard was dissolved in unstabilized THF at a concentration of 40 mg/mL. The chromatogram profile was established with a Pye Unicam UV detector at a wavelength of 254 nm. Repeated injections of the PS580 standard and collection of the individual oligomers generated sufficient quantities for characterization.

Isolation of Oligomers from a Polystyrene Sample

A low-molecular-weight fraction was removed from the PS sample using a Soxhlet extractor. To minimize the possible contaminants present, no extraction thimble was used and the bottom of the extractor was packed with glass wool. A breather tube then placed through the glass wool, close to the outlet hole to enable the solvent to recycle. The PS sample (in bead form) was then added to the extractor and glass wool placed on top. This extractor was then placed onto a 1000-mL round-bottom flask containing hexane, HPLC grade (Fisons) as the extraction solvent (400 mL). The system was brought to reflux on a heating mantle and left to extract overnight. After cooling, the solvent was removed under reduced pressure to obtain the extract, typically

around 3 wt% of the PS extracted. The extract was then separated into oligomers using the same system as outlined in the previous section.

Isolation of Oligomers from Polyethylene Samples

A low-molecular-weight fraction was obtained from the HDPE samples by dissolving the polymer in xylene, reagent grade (Aldrich) and slowly cooling the solution to room temperature. Samples of HDPE (HDPE1 and HDPE2) (40 g) were added to xylene at 110°C (1000 mL) in a 2000-mL beaker. The polymer was stirred with a magnetic flea and kept at this temperature overnight to ensure all of the polymer was dissolved. The polymer solution was then slowly brought to room temperature at approximately 20°C/h with stirring. When the polymer solution was at room temperature, the phase-separated mixture was filtered with suction and the crystallized polymer was washed with xylene (3×50 mL). Removal of the xylene from the filtrate was performed under reduced pressure to yield the low-molecular-weight fraction.

A high-temperature GPC system was established to separate the oligomers, which comprised a PL-GPC110 instrument (capable of operating at 110°C) and a set of six columns with specification 300×7 mm PLgel 5 μm, 50 Å. The eluent was *o*-dichlorobenzene (ODCB) HPLC grade (Aldrich) at a flow rate of 0.6 mL/min and a temperature of 110°C. The low-molecular-weight fraction was dissolved in ODCB at a concentration of 10 mg/mL with gentle heating (~ 50°C) to dissolve the polymer and injected into a 100 μL loop. Chromatograms were obtained with a differential refractive index detector integral to the instrument. Repeated injections of the low-molecular-weight fraction and collection of the individual oligomers generated sufficient quantities for characterization.

Isolation of Oligomers from a Poly(vinyl chloride) Sample

A similar procedure was used to extract a low-molecular-weight fraction from the PVC sample as for the PS sample. The bottom of a large-volume Soxhlet extractor was lined with glass wool and a breather tube placed through to allow the solvent to recycle. The PVC (in powder form) was placed in the extractor and covered with glass wool to prevent splashing. The Soxhlet extractor was then placed on a

1000-mL round-bottom flask containing diethyl ether, HPLC grade (Fisons), and a condenser placed on top of the system. The round-bottom flask was then placed on a heating mantle and the PVC was extracted overnight. Most of the diethyl ether was then removed from this extract under reduced pressure. This solution was precipitated in pentane, HPLC grade (Fisons) to remove the higher molecular weight PVC. Polar impurities were then removed by passing the pentane solution through a Merck Lobar size B adsorption column, packed with Si60 (40–63 μm). The resulting purified low-molecular-weight fraction was separated into its constituent oligomers using the system outlined above for the PS580 standard with the tetrameric vinyl chloride (VC) fraction being collected. The tetramer fraction was then separated into two isomers using normal-phase HPLC system comprising a Hichrom 25 cm × 4.6 mm column containing S5W silica and a mobile phase of hexane/methyl *t*-butyl ether, (99.5/0.5%) at a flow rate of 1 mL/min (both solvents were HPLC grade obtained from Fisons).

Spectroscopic Techniques

All NMR spectroscopy was performed on a Bruker DPX 400 instrument. Samples were dissolved in $CDCl_3$ 99.8 at.% (GOSS Scientific Instruments Ltd., Great Baddon, Essex, UK) at a concentration of approximately 3 mg/mL. Mass spectra were carried out on a Kratos MS-80 instrument. IR spectroscopy was performed on a Nicolet 20 DXC FTIR spectrometer.

RESULTS AND DISCUSSION

Polystyrene Standard

It was found that one pass of the column set (i.e., 120 cm of gel bed) was insufficient to resolve the individual oligomer species, but with four passes of the column set (i.e., 480 cm of gel bed by recycling) the oligomers were fully separated, as shown in Figure 1, where the numbering of the oligomers is based on their oligomer number, that is number 3 is trimer.

An individual oligomer was collected manually with peak collection starting at a time just after the start of elution of peak 3 and finishing

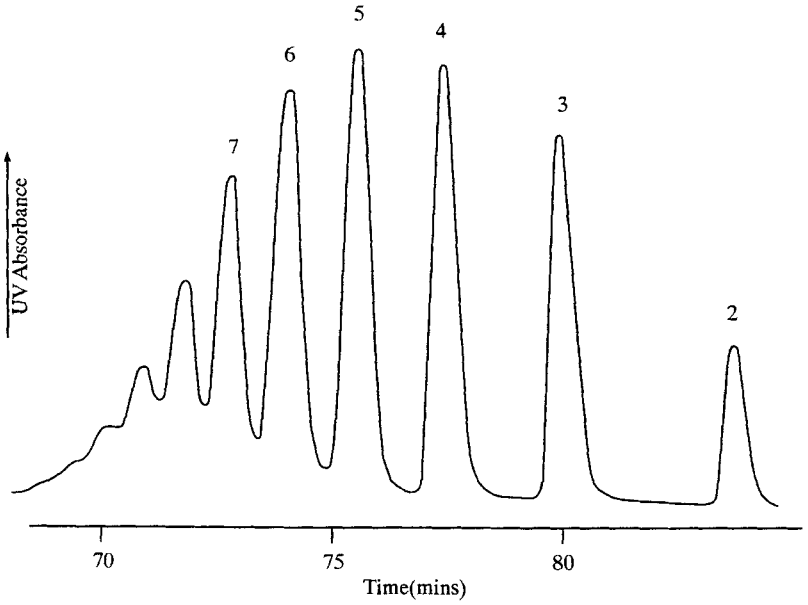
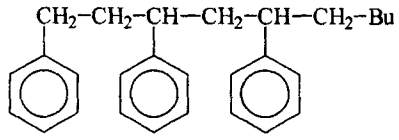


FIGURE 1 Separation of oligomers from a PS580 standard, peak numbers denote oligomers. Conditions: four columns, 300 × 7 mm PLgel, 5 μm, 50 Å, four passes of the column set with THF as eluent.

at a time just as the detector response returns to the baseline. The oligomer corresponding to peak 3 was then characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectroscopy. The ^{1}H NMR spectrum showed resonances at 0.77 ppm (quartet, methyl), 1.10 ppm (multiplet, butyl group), and the methylene groups were found as multiplets between 1.5 and 2.3 ppm. The aromatic protons are found at 7.1 ppm as a multiplet. Assignment of the peaks is in agreement with Fujishge and Ohguri[17] who characterized resolved oligomers from a PS600 standard using 60 MHz ^{1}H NMR spectroscopy. The ^{13}C NMR spectrum showed resonances at 14.03, 27.09, 31.85, 33.70, 37.66, 37.87, 39.81, 43.26, 43.36, 43.58, 125.5–128.4, 142.61, 145.28 ppm.

The mass spectrum showed a M^+ peak at 370 and a base peak of 91 corresponding to the tropyllium ion ($C_7H_7^+$) which is characteristic of an aromatic system. Combining all the spectroscopic information, it is confirmed that the structure of the oligomer corresponding to peak 3 is as shown in Structure 1.



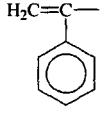
STRUCTURE 1 Structure of trimer isolated from PS standard PS580.

The structure is as expected from an anionic polymerization of styrene with the butyl end group arising from butyl lithium as initiator. Thus, the collection and characterization of this oligomer are good evidence for the effectiveness of the HPGPC procedure.

Polystyrene Sample

Separation of the oligomers from the low-molecular-weight fraction was achieved using four passes of the column set (i.e., recycling to provide 480 cm of gel bed), and baseline resolution is shown by the chromatogram in Figure 2. Individual oligomers were collected manually (peaks 8, 9 and 10 in Figure 2) and were characterized using ^{1}H, ^{13}C NMR spectroscopy and mass spectroscopy.

In the ^{1}H NMR spectra, all three oligomers collected showed a resonance at 7.2 ppm corresponding to the protons on a phenyl ring. The resonance at 5.4 ppm corresponds to protons attached to a carbon which is connected via a double bond to a carbon which in turn is attached to a phenyl ring (Structure 2). This structure represents one end group of an oligomer. Further evidence for this structure was observed in the ^{13}C NMR spectrum which showed a resonance at 146 ppm corresponding to the terminal carbon in Structure 2.



STRUCTURE 2 End-group structure of trimer obtained from PS sample.

This end group has been found in PS produced from thermal initiation, the thermal initiation producing 2,4-diphenyl-1-butene.[18] However, this end group has also been observed by Still and Peters[19] who found a similar resonance in the ^{13}C NMR spectrum of a PS

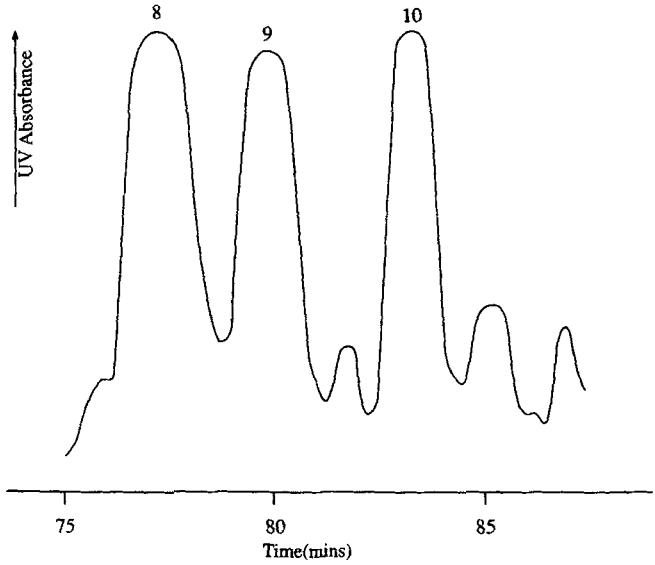


FIGURE 2 Separation of oligomers from a low-molecular-weight extract of an industrial PS sample, numbers denote fractions. Conditions: four columns, 300 × 7 mm PLgel, 5 μm, 50 Å, four passes of the column set with THF as eluent.

oligomer obtained from the vacuum pyrolysis of a PS sample and assigned it accordingly. Lai and Locke[20] also found this end group when they pyrolyzed a PS sample used in the manufacture of clear PS cups and separated the pyrolysate into its constituent oligomers. Under thermal degradation conditions, this chain end has been observed and a mechanism proposed (as shown in Figure 3), producing decreasing concentrations of dimer, trimer, tetramer and pentamer.[2]

It is possible therefore that some species in the oligomers collected might not originate from the parent polymer itself but in fact are degradation products derived from thermal degradation of PS during the polymerization or processing of the polymer thereafter. Thus, the mechanism in Figure 3 is an additional contribution for producing the chain end represented by Structure 2 during thermal-initiated styrene polymerization. Owing to the complexity of the ^{1}H NMR spectrum for oligomers collected corresponding to peaks 8, 9 and 10 compared to the PS580 oligomer fractions, it was difficult to assign other peaks in the spectrum. It is possible that the second end group may not always have the same structure as the other end group, that is, variable

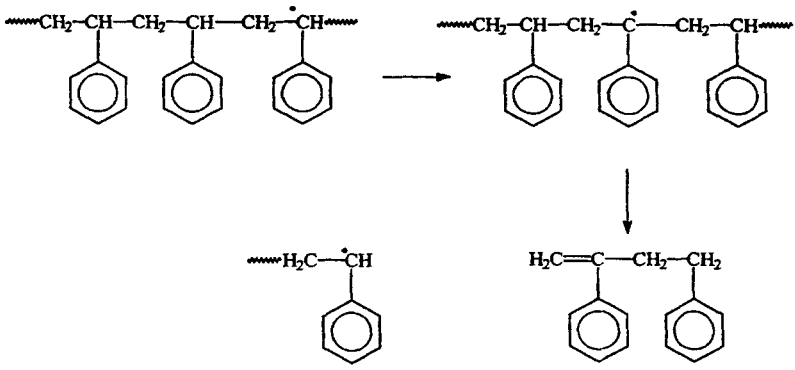
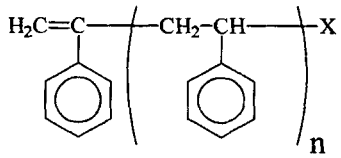


FIGURE 3 Thermal degradation sequence for PS (according to Ref. [2]).

structures may arise because of the conditions of the solution polymerization. For example, it has been suggested that the reaction order may change as a function of monomer concentration, changes in temperature and with changes in oxygen concentration.[21]

Unfortunately, mass spectroscopy did not yield a molecular ion for any of the isolated oligomers. However, as the same HPGPC conditions were used to resolve the oligomers of the PS standard and the PS from an industrial source, it is possible to compare elution times and thus estimate the size of the oligomers. A comparison of Figures 1 and 2 show that there is a reasonable match of peaks 8, 9 and 10 of Figure 2 with peaks 4, 3 and 2 of Figure 1, indicating that peaks 8, 9 and 10 are tetramer, trimer and dimer, respectively, allowing for differences in end groups and inadequate information about end-group X in Structure 3. A possible structure for the oligomers would then be as shown in Structure 3 where $n = 2$, 3 or 4.



STRUCTURE 3 Proposed structure for oligomers isolated from industrial PS.

Interestingly, there is no indication of initiator fragments being part of the oligomer structure, which suggests that oligomers with initiator

fragments have not been isolated by the methodology described here or that added initiators are not involved in the polymerization. Therefore, this work has demonstrated that evidence from end-group structure obtained in isolated oligomers from a high polymer can be related to mechanisms for thermal initiation and/or thermal degradation during the polymerization, and/or degradation during the processing of the PS.

Polyethylene

It was demonstrated that the HPGPC system was capable of resolving a series of *n*-alkanes, by preparing a mixture of C_{11}, C_{12}, C_{14}, C_{18}, C_{26}, C_{30}, C_{40} *n*-alkanes by dissolving each alkane in ODCB at a concentration of 1 mg/mL. This solution was injected onto the column set in the PL-GPC110 instrument and the separation is shown in Figure 4 (where C_{11} corresponds to the linear alkane $C_{11}H_{24}$), demonstrating that a series of oligomers could be resolved using this system, for example, almost resolution to baseline for the C_{11} and C_{12} *n*-alkanes.

The low-molecular-weight fraction from HDPE1 was dissolved in ODCB at a concentration of 10 mg/mL and injected onto the column set producing the separation of the oligomers shown in Figure 5. The peak elution times in Figure 5 show a good correlation with the peak elution times in Figure 4 indicating that these peaks probably

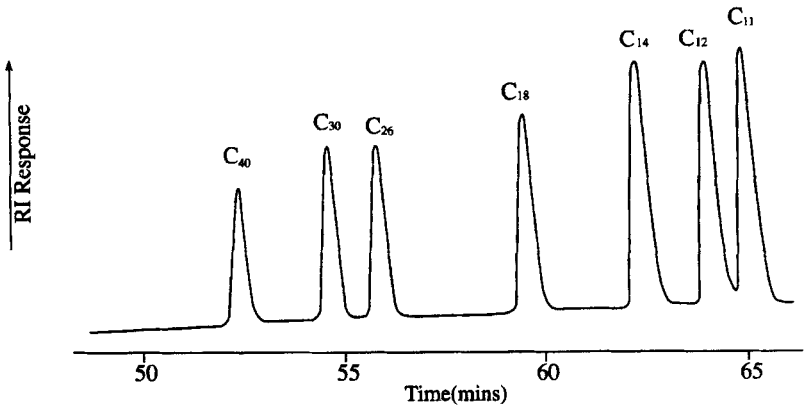


FIGURE 4 Separation of alkane standards. Conditions: six columns 300 × 7 mm PLgel 5 μm, 50 Å, with *o*-dichlorobenzene as eluent.

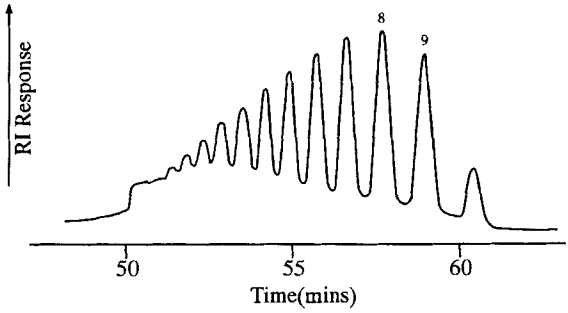


FIGURE 5 Separation of low-molecular-weight fraction of HDPE1, labeled peaks denote samples isolated. Conditions: six columns, 300 × 7 mm PLgel 5 μm, 50 Å, with *o*-dichlorobenzene as eluent.

represent linear alkanes. To confirm this identification, two oligomer samples were collected, labeled peaks 8 and 9 in Figure 5. ^{1}H NMR spectroscopy and mass spectroscopy showed that the oligomer from peak 9 corresponded to $C_{18}H_{38}$ and the oligomer from peak 8 to $C_{20}H_{40}$.

The low-molecular-weight fraction from HDPE2 was analyzed in the same way and the separation is shown in Figure 6. Although the sample shows a large excluded peak and a more complex peak profile after the elution of peak 9, the peaks labeled 9 and 8 in Figure 6 were characterized in the same way as outlined earlier and were shown to represent linear alkanes corresponding to $C_{18}H_{38}$ and $C_{20}H_{40}$, respectively.

The isolated oligomers are linear and have no branches, and so are consistent in structure with the original HDPE sample. Mechanisms for the formation of these linear chains have been proposed.[22–24] The absence of any chemical shifts relating to vinyl protons suggests that the methyl end groups are provided by using hydrogen as a chain-transfer agent, which functions by cleaving the metal alkyl bond to give a dead chain and hydrogenating the catalyst.

Using the fractionation procedure outlined previously, 0.95 g of a low-molecular-weight fraction was removed from the HDPE1 sample. This fraction was then dissolved in ODCB (20 mL). Aliquots of this solution were taken (2.5 mL) and to each aliquot was added a quantity of $C_{18}H_{38}$ (0, 1, 2, 3, 4 mg). Each solution was then injected onto the column set previously described and the peak height for the

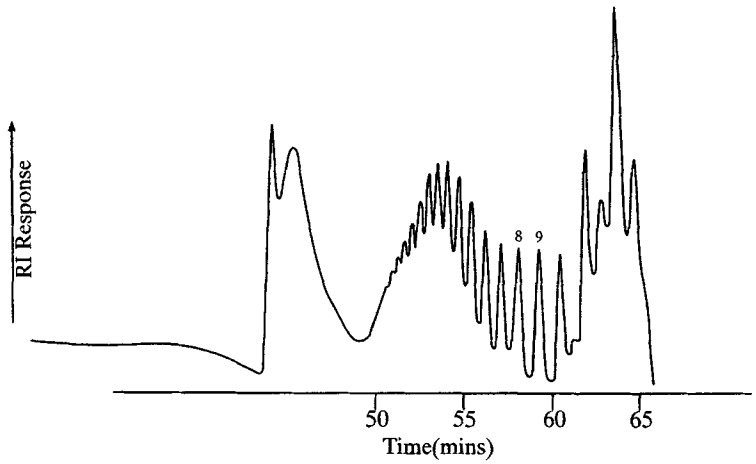


FIGURE 6 Separation of low-molecular-weight fraction of HDPE2, labeled peaks denote samples isolated. Conditions: six columns, 300 × 7 mm PLgel 5 μm, 50 Å, with *o*-dichlorobenzene as eluent.

octadecane peak measured (Figure 7, peak labeled C_{18}). To ensure that the detector response was constant, the peak height of the neighboring peak was also measured for each solution. As the height of this neighboring peak remained constant, the detector response was assumed to be constant. A graph was then plotted of observed peak height vs. octadecane added and is shown in Figure 8.

The plot was linear ($r = 0.9825$) and extrapolation showed that 3.07 mg of octadecane was present in the 2.5 mL solution as prepared. Since 0.951 g of fraction was dissolved in 20 mL of ODCB, there would be 0.12 g of the fraction in each 2.5-mL aliquot. Therefore, the quantity of octadecane in the original sample was (0.954/0.12)3.07, that is, 24 mg. Assuming that all of the octadecane present in the high-molecular-weight HDPE1 remained in the low-molecular-weight fraction, this result would equate to a value of 600 mg/kg of octadecane in the original HDPE1 sample.

This methodology can be extended to samples of branched polyethylenes. By utilizing lower crystallization temperatures, it should be possible to remove selectively high-molecular-weight polymer and then separate the isolated oligomers remaining in solution. With IR or NMR spectroscopy techniques, it will then be possible to estimate the branching frequency per oligomer.

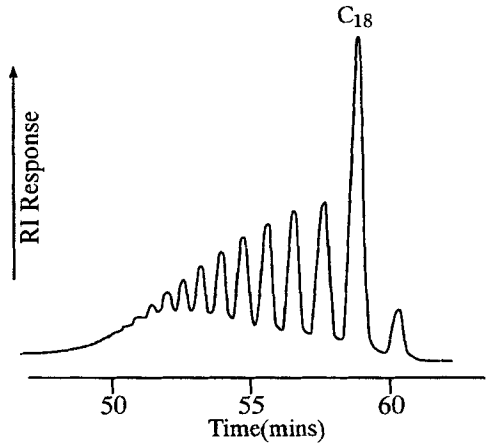


FIGURE 7 Separation of low-molecular-weight extract of HDPE1 spiked with $C_{18}H_{38}$ alkane standard. Conditions: six columns, 300 × 7 mm PLgel 5 μm, 50 Å, with *o*-dichlorobenzene as eluent.

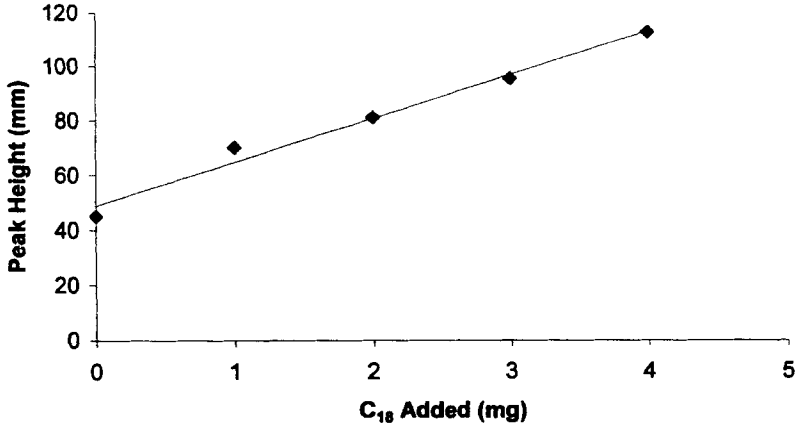


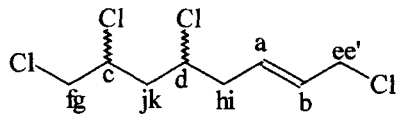
FIGURE 8 Standard addition plot of peak height (mm) vs. C_{18} (mg) added to HDPE1.

Poly(vinyl chloride)

The isolation of pure oligomers from a PVC sample required several techniques within a separation scheme including HPGPC, following the procedures detailed in the experimental section. The tetrameric fraction was then selectively isolated by HPGPC using the column set

previously described, incorporating recycling and repetitive injections. This HPGPC fraction of tetramer was found by HPLC to be a mixture of isomers, yielding two isomeric tetramer oligomers (a third HPLC peak was observed but of such low concentration that collection was not attempted) which were then characterized by ^{1}H NMR and ^{13}C NMR spectroscopy.

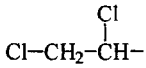
The ^{1}H NMR spectrum of isomer 1 showed resonances at 5.78 (2H, m, H_{ab}), 4.40 (1H, M, H_c), 4.23 (1H, m, H_d), 4.05 (2H, d, *J 6.4*, $H_{ee'}$), 3.82 (1H, dd, *J* 12, 4, H_f), 3.67 (1H, dd, *J* 12, 4, H_g), 2.57 (2H, m, H_{hi}), 2.26 (1H, *m*, H_j), 2.00 (1H, m, H_k) and the ^{1}H NMR spectrum of isomer 2 showed resonances at 5.80 (2H, m, H_{ab}), 4.26 (1H, M, H_c), 4.10 (1H, m, H_d), 4.05 (2H, d, *J 6.4*, $H_{ee'}$), 3.83 (1H, dd, *J* 12, 4, H_f), 3.77 (1H, dd, *J* 12, 4, H_g), 2.61 (2H, m, H_{hi}), 2.43 (1H, m, H_j), 2.22 (1H, m, H_k). To confirm the structure of the isomers, the ^{13}C spectra were also recorded and showed the following resonances: Isomer 1 showed resonances at 129.91, 129.75, 58.32, 57.96, 48.12, 44.42, 43.32, 40.89, and isomer 2 showed resonances at 130.16, 129.37, 57.41, 56.85, 47.70, 44.39, 42.61, 39.66. From these results from NMR spectroscopy, a pair of diastereomers can be represented by the structure, shown below as Structure 4. The main differences in the spectra of the two diastereomers occur at the asymmetric carbons. In one isomer, protons *c* and *d* occur as two well-defined multiplets separated from the doublet of protons *ee'*. However in the second isomer, proton *d* overlaps the doublet of protons *ee'*. It is of interest to compare the end groups in this tetrameric structure with previous studies on the characterization of PVC.



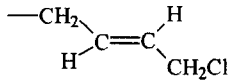
STRUCTURE 4 Structure of VC Tetramer.

Previously, much work has been carried out to determine why the stability of PVC is less than anticipated on the basis of its ideal structure. Hjertberg and Sorvik[25] found the end groups shown in Structures 5 and 6, which correspond to the end groups of our tetrameric species (Structure 4). These end groups were established by

studying a range of PVC samples of differing molecular weights, together with NMR studies on modified PVC samples (modified by phenolysis and bromination). Van den Heuvel and Webel[26] obtained a low-molecular-weight fraction by fractional precipitation from a PVC sample obtained by suspension polymerization, and using NMR spectroscopy also found these end groups. However, these previous studies have not isolated oligomeric species, and have not utilized the complete spectrum, but have assigned structures to parts of the NMR spectrum in order to identify end groups.



STRUCTURE 5



STRUCTURE 6

The structure of this tetramer species is particularly interesting as the polymer is derived from a mass polymerization of VC. No initiator fragments are found at the ends of the tetramer, and the end groups are formed from rearrangements and chlorine migrations which are well documented in the literature,[27–29] without including any initiator fragments. The nature of the end groups in Structures 5 and 6 is not what would be expected on basis of the idealized structure $-(CH_2CHCl)_n-$ for PVC, and provides a partial explanation for the observed structural changes for PVC on heating.

CONCLUSIONS

The combination of fractionation to provide a low-molecular-weight fraction together with HPGPC to separate oligomers provides sufficient quantities of an oligomer for spectroscopic characterization. Interpretation of spectra enables end-group structures to be proposed from which deductions can be made on the mechanism of polymerization for producing the parent polymer.

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