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CHARACTERIZATION OF OLIGOMERIC BY-PRODUCTS PRODUCED DURING THE HIGH-PRESSURE POLYMERIZATION OF ETHYLENE

STEPHEN W. BIGGER,[1]* PETER J. WATKINS,[1] MICHAEL A. RAYMOND,[1]
SERGUEI S. VERENICH[1]† and JOHN SCHEIRS[2]

[1] Department of Environmental Management, Victoria University of Technology, St Albans Campus, P.O. Box 14428 Melbourne City Mail Centre, Melbourne, 8001, Australia; and [2] ExcelPlas Australia Ltd, P.O. Box 102, Moorabbin, 3189, Australia

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Abstract—The characterization of oligomeric compounds separated from waste material produced in the high-pressure, free-radical ethylene polymerization process is reported. A solid wax layer, constituting 11% (w/w) of the total waste material, was analysed by Fourier transform infrared (FTIR) spectroscopy and gas chromatography/mass spectrometry (GC–MS) and was found to contain mostly short-branched C_{18}–C_{26} paraffins. An oil fraction constituting 64% (w/w) of the material was identified by FTIR and NMR analyses as a polyether of complex structure. Both the wax and the oil fractions contain a degree of unsaturation. The molecular weight characteristics of the polyether were determined by gel permeation chromatography and found to be $M_n = 1716$ Da, $M_w = 1926$ Da, dispersity $M_w/M_n = 1.22$, using polystyrene standards to calibrate the chromatographic column. A liquid fraction constituting about 25% (w/w) of the waste was separated from the oil layer by distillation. It was identified by FTIR and GC–MS analyses as mainly propan-1-one. This compound is used both as a solvent for the initiator and as a chain transfer agent in the low-density polyethylene (LDPE) polymerization process.

1. INTRODUCTION

Polyethylene (PE) is the oldest commercial polyolefin and is by far the most widely produced synthetic polymer. About 8×10^9 kg of PE are produced each year in the United States alone [1–3]. Traditionally, PE is produced either by a free-radical chain polymerization process or by the use of a suitable coordination catalyst. Examples of the latter include the Ziegler-Natta catalyst [4] or chromium-based catalyst systems [5]. More recent developments in the polymerization of ethylene include hightly efficient, low-pressure processes which may be carried out in the gas or the liquid phase [6].

The free-radical polymerization of ethylene under high pressure is one of the most widely used ways of producing low-density polyethylene (LDPE) as well as a variety of other polymer and copolymer resins [7]. Since the commencement of full-scale commercial production of PE in 1942, many papers investigating aspects of ethylene polymerization, such as catalyst systems, mechanisms and synthesis conditions, have appeared in the scientific literature [8–12]. Nevertheless, there are still many aspects of ethylene polymerization processes which remain unclear or have not been investigated.

The production of LDPE is normally carried out in a tubular reactor at a high pressure (120–300 MPa) and a temperature (140–180°C) above the melting point of PE [13]. Tubular reactors are essentially jacketed, reinforced pipes that are arranged in a folded loop configuration. These have an internal diameter of 3–6 cm and a length between 0.5 and 1.6 km. The removal of the heat of reaction via an efficient heat-exchange medium promotes higher monomer conversion and reduces the formation of undesirable by-products. In commercial operations, the polymerization time in the reaction zone is quite short and can range from 20 sec to 2 min, with production rates between 6 and 18 tonne hr^{-1}.

An alkyl or acyl peroxide/hydroperoxide is typically used as the initiator in the high-pressure polymerization process [14]. Alternatively, a mixture of peroxide and/or hydroperoxide initiators may be used, in which each component of the mixture has a specific temperature range over which it decomposes. Typical initiators include *t*-butyl hydroperoxide, *t*-amyl peroxyneodecanoate, *t*-butyl peroxypivalate and *t*-butyl peroxybenzoate. The initiators are dissolved in a mineral oil diluent and are injected at different temperature zones in the reactor in accordance with the decomposition temperature of the initiator. Polymerization occurs in the highly compressed gaseous state where ethylene behaves like a liquid. The molecular weight (MW) of the polymer is controlled by adding to the reactor a small amount of a chain transfer agent (CTA) such as methyl ethyl ketone (MEK) or propan-2-ol. The addition of a CTA also increases the pressure in the reactor, thereby reducing both short-chain and long-chain branching in the polymer.

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*To whom all correspondence should be addressed.

†Current address: c/o Department of Oceanography, The University of British Columbia, 6270 University Boulevard, Vancouver, B.C., V6T 1Z4, Canada.

The "polyoils", which are low MW by-products particularly rich in carbon fractions C_{12}–C_{40}, as well as waxes, can accumulate in the recycled CTA. These materials can adversely affect the properties of the product, particularly the optical properties of LDPE films. Indeed, there is an increase in film haze and a decrease in film gloss as the level of polyoils in the film increases. A 2% (w/w) increase in the polyoil content of LDPE film increases its haze from 8% to 10% and decreases its gloss from a value of 60 units to 54 units. Polyoils also cause sealing and blocking problems with LDPE films and impart a "plastic smell" to LDPE products.

The process by which ethylene is polymerized under conditions of high pressure is summarized in the flow diagram shown in Fig. 1. The conversion per pass is low, usually 15–20% for a single zone reactor where no additional injections of reactants are made, and 20–30% for multi-zone reactors [7]. Owing to such low conversions, unreacted ethylene is recycled to the reactor after the waxes and oils are separated. The process thus results in the production of low MW by-products that are commonly disposed of by combustion.

In keeping with the current move towards cleaner production technologies, many environmentally responsible industries are investigating ways to reduce or eliminate wastes efficiently and/or utilize by-products in a cost-effective manner. For example, a low MW paraffinic by-product from the production of HDPE can be incorporated successfully in hot-melt adhesive formulations that are used in the manufacture of cardboard containers [15, 16]. However, at present, the mainstream scientific literature contains little information relating to the chemical nature of by-products formed during the production of PE. This makes difficult the identification of possible commercial uses for these products.

This paper deals with the spectroscopic and chromatographic characterization of typical low MW by-products that are formed during the polymerization of LDPE. The characterization was undertaken with a view to gaining information about the polymerization process as well as identifying possible uses to which these waste materials may be put in the future.

2. EXPERIMENTAL

2.1. *Material*

The crude waste material was obtained from a commercial producer of LDPE and is a heterogeneous mixture. When allowed to stand for approximately 3 hr, it forms two distinct layers or fractions which can be separated easily. The bottom layer appears as a golden-coloured, transparent oil (referred to herein as the oil layer) whilst the top layer consists of a white, solid, wax-like material (referred to as the wax layer).

A sample of the wax layer was purified by washing it with three portions of pure ethanol (volume ratio of ethanol to wax, $v_{\text{ethanol}}/v_{\text{wax}} = 3.0$). The purified wax was dried in air at room temperature and constitutes (11 ± 2)% (w/w) of the total by-product. The oil layer was purified by rotary evaporation at 75–90°C under weak vacuum. This process removes a liquid phase [about 25% (w/w) of the total by-product] that was shown by gas chromatography–mass spectrometry (GC–MS) to be comprised mostly of a mixture of propan-1-one and a small amount of butan-1-one. The presence of propan-1-one in the waste material is explained by the fact that it is used both as a solvent for the initiator and as a chain transfer agent in the polymerization process. The mass of oil collected constituted (64 ± 2)% (w/w) of the total by-product.

2.2. *Instrumental methods*

2.2.1. Infrared spectral measurements. Infrared spectra were recorded on a Perkin–Elmer 1600 Fourier transform infrared (FTIR) spectrophotometer. A single-beam spectrum was recorded for each sample and corrected by

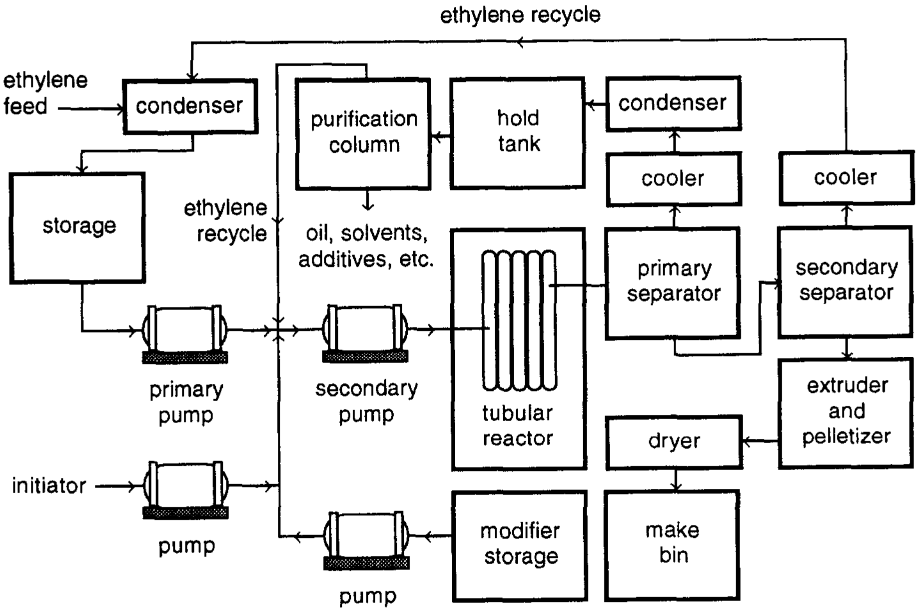

Fig. 1. Flow diagram showing the high-pressure polymerization of ethylene process.

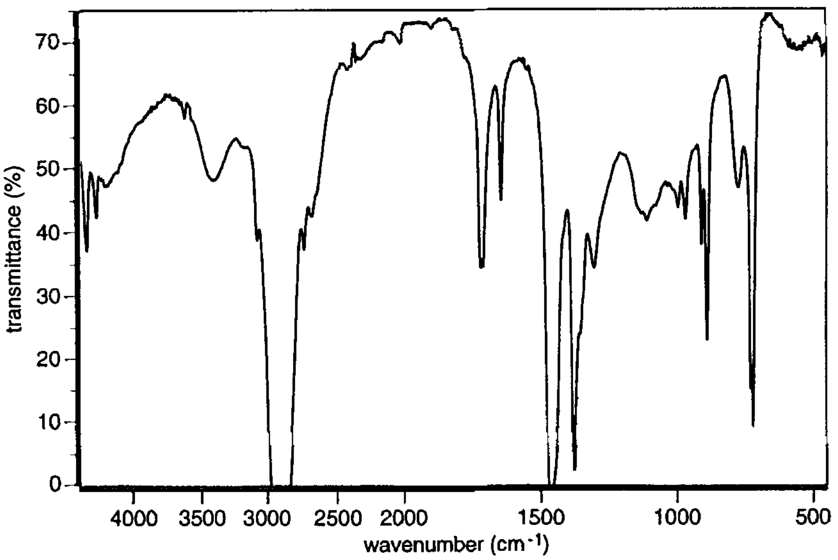

Fig. 2. FTIR spectrum of the wax layer in the region 4400–500 cm^{-1}.

subtracting the signal due to the instrumental background. A thin film of the purified oil layer was prepared for FTIR analysis by spreading a drop of the oil between two KBr plates. The FTIR spectrum of the wax was recorded by dissolving a small amount of wax in CCl_4, spreading a few drops of the solution on to a KBr plate, and evaporating the solvent to produce a thin film for subsequent FTIR analysis.

2.2.2. Gel permeation chromatographic analyses. A Waters Model 510 liquid chromatograph equipped with a Waters Model 410 refractive index detector was used for the gel permeation chromatographic analysis of the purified oil phase. The oil was injected into the chromatograph as a solution of 0.5 g of oil in 100 ml of toluene. Separation was achieved at room temperature using three Ultrastyragel columns packed with cross-linked polystyrene particles having pore sizes of 1×10^2, 1×10^3 and 1×10^4 nm. Toluene (flow rate 1.0 ml min^{-1}) was used as the eluent.

The MW characteristics of the oil were calculated on the basis of a standard polystyrene calibration curve. The latter was obtained by determining the elution volumes of seven polystyrene standards of $M_n = 4.50 \times 10^2$, 4.00×10^3, 1.81×10^4, 3.79×10^4, 1.90×10^5, 3.55×10^5 and 7.00×10^5 Da. Using this method, values of $M_n = 1716$ Da and $M_w = 1926$ Da were obtained for the oil, giving a dispersity value of $M_w/M_n = 1.22$.

2.2.3. GC–MS analyses. Analysis of the wax by GC–MS was carried out using a Hewlett-Packard (HP) Model 5890 Series II gas–liquid chromatograph interfaced to a HP Model 5971 mass selective detector. The chromatograph was equipped with a 25 m silica-modifed, bonded-phase column (type DB5MS, J. & W. Scientific Ltd) with a film thickness of 0.33 μm and an inner diameter of 0.2 mm. A 1.0 μl splitless injection of a 20 mg ml^{-1} solution of the wax in chloroform was used for the analysis. Helium (flow rate 0.1 ml min^{-1}) was used as the carrier gas. Separation of the components was achieved with the following temperature conditions: injector 260°C, detector 300°C and oven 180–320°C linearly ramped at 5° min^{-1}.

2.2.4. Nuclear magnetic resonance spectrum. A low-resolution ^{1}H-nuclear magnetic resonance (NMR) spectrum of the oil was recorded on a 60 MHz Hitachi Perkin-Elmer model R-24B spectrometer using tetramethylsilane (TMS) as the reference and deuterated chloroform ($CDCl_2$) as the solvent. The sweep time was 150 sec.

3. RESULTS AND DISCUSSION

3.1. Analysis of wax layer

3.1.1. FTIR analysis. The FTIR spectrum of the wax in the region 4400–500 cm^{-1} is shown in Fig. 2. The strong absorptions at 2934, 1460, 774 and 720 cm^{-1} are characteristic of paraffinic compounds and are due to C—H stretching, bending and rocking modes, respectively [17]. The peak at 1378 cm^{-1} which overlaps a weak methylene band at 1365 cm^{-1} indicates the presence of a significant number of branched species [18–20] which have been formed as a result of chain transfer processes that occur during polymerization.

The absorption centred at 3393 cm^{-1} may be attributed to the presence of olefinic groups, but the broad nature of this band more probably suggests the presence of some hydroxyl groups in the sample. The quite strong absorption at 1643 cm^{-1} is due to an olefinic carbon–carbon stretching vibration and the peak at 888 cm^{-1} is consistent with a carbon–hydrogen (alkene) out-of-plane bending mode. The moderate absorption at 1303 cm^{-1} may also be assigned to olefinic groups in the sample. The presence of unsaturation in the wax is consistent with the occurrence of disproportionation reactions during the polymerization of LDPE. Such reactions are responsible for blocks of unsaturation that can occur in LDPE [21]. The peak at 1719 cm^{-1} is assigned to a carbonyl absorption originating from end-groups on the polymer chains which were formed by CTA molecules during the polymerization process. Indeed, the characteristic carbonyl absorption at about 1720 cm^{-1} can be used as a means to identify tentatively some LDPE resins produced by different LDPE manufacturers.

3.1.2. GC–MS analysis. A gas chromatogram of the wax is shown in Fig. 3. Mass spectrometric analysis of this chromatogram reveals the presence of isomers which are eluted in regular succession and

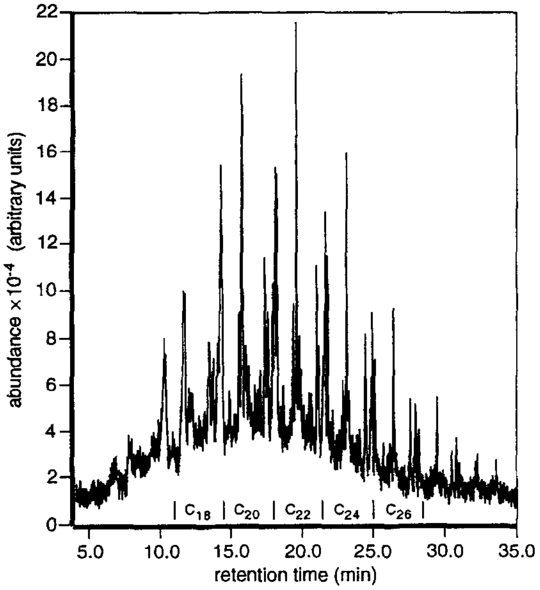

Fig. 3. Gas chromatogram of the wax layer showing the presence of C_{18}, C_{20}, C_{22}, C_{24} and C_{26} paraffins.

which originate from an homologous series of C_{18}, C_{20}, C_{22}, C_{24} and C_{26} paraffins. The parent compounds were identified by comparing their retention times with those obtained for the corresponding paraffinic analytical standards run under identical chromatographic conditions.

Figure 4 shows an expanded section of the chromatogram in Fig. 3 between the retention times of 18.0 and 24.6 min. Close inspection of the expanded chromatogram reveals that the elution pattern between 18.0 and 21.3 min is repeated between 21.3 and 24.6 min, although the resolution and intensity of the peaks decrease at longer retention times. The identities of the major peaks in Fig. 4 were assigned by mass spectral analysis and were found to correspond to isomers of docosane (C_{22}, *ca.* 18.0 to 21.3 min retention) and tetracosane (C_{24}, *ca.* 21.3 to 24.6 min retention).

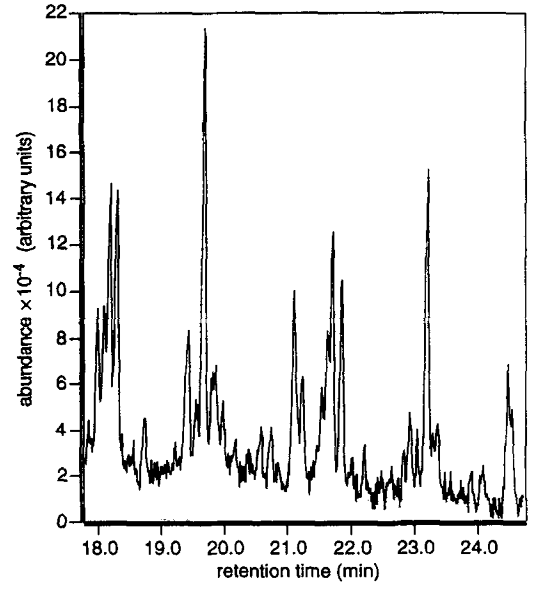

Fig. 4. Expanded section of the gas chromatogram shown in Fig. 3 between the retention times of 18.0 and 24.6 min.

Table 1. Characteristics of C_{22} and C_{24} oligomers present in the oil layer isolated from waste reactor material produced during LDPE polymerization

Chain length	Retention time (min)	Saturation		Branching	
		Saturated	Unsaturated	Short	Long
C_{22}	17.98		x	x	
	18.08	x			x
	18.18	x			x
	18.28	x			x
	18.74	x		x	
	19.43	x		x	
	19.67		x	x	
	20.58	x			x
	20.74	x		x	
	21.10	x		x	
	21.24	x		x	
C_{24}	21.56		x	x	
	21.65	x			x
	21.72	x			x
	21.86	x			x
	22.24	x		x	
	22.96	x		x	
	23.22		x	x	
	23.93	x			x
	24.12	x		x	
	24.50	x		x	
	24.57	x		x	

Table 1 lists the clearly resolved, intense peaks of the chromatogram in Fig. 4 along with the structural characteristics of the compounds that produced these peaks. Based on the available mass spectral data, the various structural isomers appear to be complex combinations of branched ethylene oligomers which are either saturated or unsaturated [22, 23]. The branching in these structures is either long or short (see Table 1).

The analysis of the wax by GC–MS confirms the FTIR data analysis in so far as it suggests that the wax is comprised of several structurally different fractions of PE homologues. The variety of structural heterogeneities in the wax is consistent with the structural features that are expected to arise as a result of the free-radical polymerization process used in the production of the LDPE [21].

3.2. Analysis of the oil layer

3.2.1. FTIR analysis. The FTIR spectrum of the purified oil layer is shown in Fig. 5 and exhibits similar spectral characteristics to those reported elsewhere for poly(ethylene oxide) [24]. The intense peak at 1095 cm^{-1} corresponds to the polyethylene glycol (PEG) analytical band and is most characteristic of aliphatic ethers [25]. It arises as a result of the asymmetric stretching of the ether linkages in the polymer backbone. The intense peak at 2875 cm^{-1} is due to a symmetric methylene stretching mode and is also consistent with a PEG type of structure. The peak at 1456 cm^{-1} is assigned to methylene carbon–hydrogen bending and the peak at 1350 cm^{-1} is due to the symmetric bending of methyl carbon–hydrogen bonds. The assortment of peaks oc-

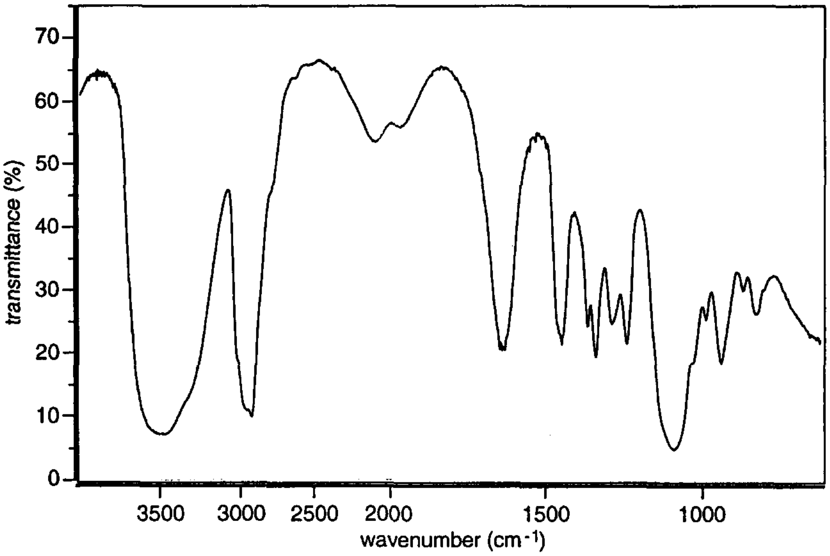

Fig. 5. FTIR spectrum of the purified oil layer in the region 4000–700 cm^{-1}.

curring in the region of about 1360–800 cm^{-1} are most likely associated with modes such as carbon–carbon stretching and methylene twisting and wagging.

Detailed analysis of the spectrum in Fig. 5 also infers that a certain degree of unsaturation exists in the oil. This is indicated by the peak at 1643 cm^{-1} which is attributable to an olefinic carbon–carbon stretching mode. The unresolved weak absorptions at 2093 cm^{-1} and 1978 cm^{-1} may originate from cumulated unsaturation in the oil. Furthermore, the presence of intermolecularly bonded hydroxyl groups is also indicated by the broad band centred at 3422 cm^{-1}.

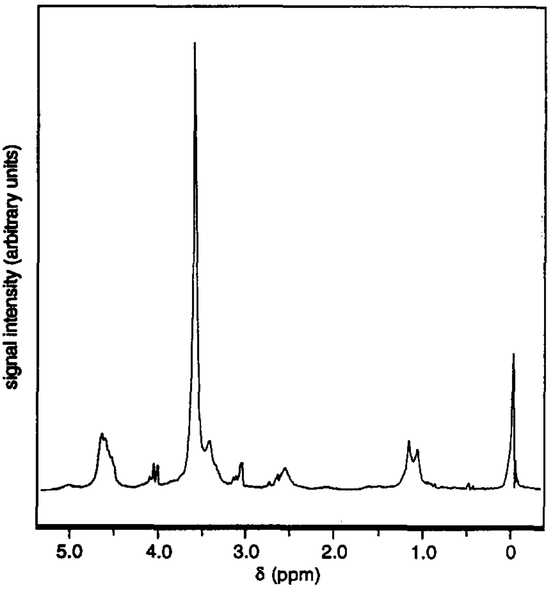

Fig. 6. Low-resolution ^{1}H-NMR spectrum of the oil layer.

3.2.2. NMR analysis. A low-resolution ^{1}H NMR spectrum of the oil in the range zero to 6 ppm is shown in Fig. 6. Despite its low resolution, the spectrum provides adequate structural information about the oil to confirm the above interpretation of the FTIR spectrum. In particular, the intense peak centred at 3.6 ppm originates from protons associated with the methylene oxide groups in the polyether backbone. The shoulder at 3.4 ppm is most likely due to the resonance of terminal methoxyl protons.

The doublet at around 1.1 ppm is assigned to terminal methyl protons situated adjacent to olefinic carbon atoms in the main chain backbone. The unresolved multiplets at around 2.6 ppm and 3.2 ppm are attributable to the resonance of methylene protons adjacent to olefinic carbon atoms and terminal ethoxyl protons, respectively. The small doublet at around 4.0 ppm is probably due to methylene oxide protons that are situated adjacent to an olefinic proton and the complex multiplet at 4.5 ppm is due to olefinic protons in the main chain or side-chains.

On the basis of the spectroscopic evidence presented above, the oil layer may be described as a low MW polyether material of complex structure. It could be formed in the reactor by the polymerization of propan-1-one via the carbon–oxygen double bond in this ketone. The oil is quite polar, which causes it to separate from the LDPE. It also tends to entrain polar compounds such as unreacted propan-1-one. Such compounds can be readily separated by distillation under slight vacuum.

4. CONCLUSIONS

The waste material produced during the high-pressure polymerization of ethylene has been characterized. It consists of a solid, paraffinic wax layer mixed with an oil layer. The oil contains dissolved propan-1-one which is present as a result of its use both as a solvent for the initiator and as a CTA in the polymerization process. The wax consists mostly of short-branched C_{18}–C_{26} paraffins, whereas the oil is a complex, irregular polyether. There is evidence to suggest that both the wax and the oil contain unsaturation. The molecular structures interpreted from the spectroscopic and chromatographic analyses reflect the nature of the LDPE polymerization process.

Possible future uses for the low MW PE wax and oil may be in the formation of anticorrosive coatings used for the packaging of metal parts, or in glue formulations used in the cardboard packaging industry. These possibilities are currently under investigation in our laboratory, along with a study of the cost of recovery of these materials.

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