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Waxy polyethylenes from solution thermolysis of high density polyethylene: inert and H-donor solvent dilution effect

Laurent Guy, Bernard Fixari*

Laboratoire des Matériaux Organiques à Propriétés Spécifiques, CNRS, BP24, 69390 Vernaison, France

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Abstract

High density polyethylene batch thermolysis has been performed in dilute solutions to obtain waxy products with number-average molar masses in the range of 2000 to 6000 g mol^{-1}. In relation to a classical bulk thermolysis (390°C, 6 h) which affords branched waxy polymers, dilution with phenylether permits controlled diffusion reactions modifying the product characteristics: low molar masses, narrow distribution, high crystallinity, rich in α-olefins and few long branching formation. A hydrogen donor solvent (tetralin), acting on the free radical degradation pathway, affords a lower fragmentation level of the main chains and short chains branching. In addition, a high level of tetralyl radicals grafting on the α-olefin is observed. Adjustment of the process conditions might give tailor-made waxy polymers to use just as they are or after chemical modifications of the olefinic functions. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: High density polyethylene; Thermal degradation; Dilution effect

1. Introduction

Thermal and thermocatalytic transformation of the most important thermoplastic in the world [1], polyethylene, is well documented and concerns the residues of its manufacturing as well as its contribution to domestic wastes. Depending on the temperature range, pure thermal processes allow the production of gas, light paraffins and waxy oils [2–5]. Production of ramified paraffins [6–8] and aromatic fractions [9] are obtained with the help of various catalysts.

All these processes are reported to be performed in the melt state and probably suffer from a high viscosity of the medium which limits the fragments diffusion during the initial step of the transformation. If the objective is to obtain transportation fuels or chemical compounds, this is apparently not a problem, even if, when a catalyst is used, its effect is at first limited to its local environment [10].

However, for some industrial applications, e.g. lubricant in plastics fabrication, colour dispersant, additive in paints, inks, in rubber industry, coating manufacture, only a low level of transformation is needed to produce waxy polyethylene with number-average molar masses in the range of 1000 to 5000 g mol^{-1} [11]. In such cases, the level of viscosity may have a direct incidence on the final chemical composition and physical properties of the desired products. They were prepared at temperatures between 350 and 400°C to avoid an intense cracking, but as a result, hours of reaction were needed [12,13].

In such conditions, the incidence of bulk thermolysis on the classical thermal Rice–Kossiakoff radical mechanism concerning polyethylene (Fig. 1) has been detailed [14]. Authors mainly involved a ''cage effect'' due to a low diffusion of the radicals; a classical consequence is the formation of ''long chains branching'' [15,16]. Effectively, after the initiation step resulting from carbon–carbon bond breaking of the most sensitive ones, i.e. the allylic bonds often present in the polymer, with a bond dissociation energy (BDE) of 257 kJ mol^{-1} and at the branching points (BDE 335 kJ mol^{-1}) [13], radicals evolution by intermolecular reactions are favoured to intramolecular ones. Therefore, propagation steps and termination reactions are controlled by diffusion in the viscous medium [16,17].

A simple way to minimise these phenomena is to dilute the medium with a solvent. This approach has recently been applied to the controlled thermal decomposition of polystyrene [18–23], but very scarcely to polyethylene. Catalytic coprocessing of coals or petroleum fractions with polyethylene has been reported, in various media and at temperature above 400°C, in order to produce fuel oil [24]. A significant

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* Corresponding author. Fax: +33-4-78027187.

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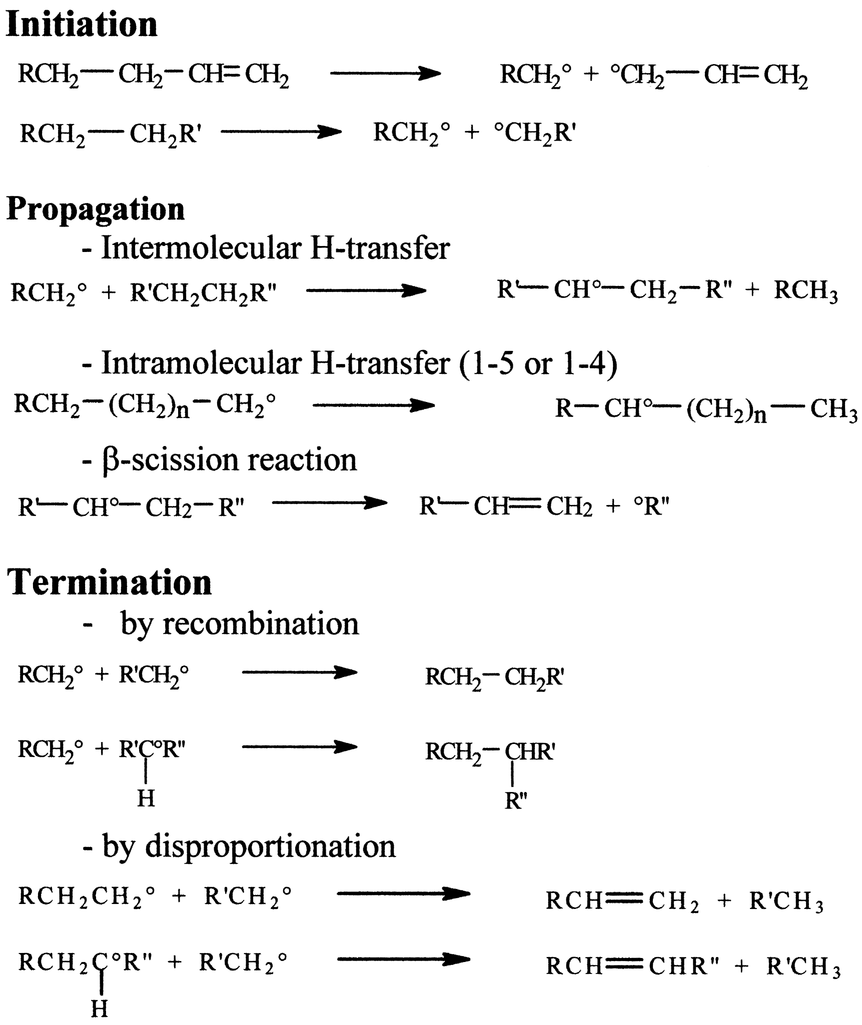


Fig. 1. Simplified free-radical mechanism of HDPE thermal degradation.

work of Lal and coworkers in the presence of decalin or α-chloronaphthalene only accounts for a thermal degradation below 220°C with only tiny modifications of the molar masses [25,26].

It is the intention of the present work to prepare waxy polyethylenes with the help of an intermediate range of temperature thermolysis. A study was undertaken of the impact of dilution and thermal conditions (temperature, time) on the thermolysis in a pressurised batch reactor of a high density polyethylene (HDPE) in phenylether as a solvent, chosen for its chemical inertia, and in tetralin, a well-known hydrogen donor able to modify the free radical mechanism of the thermal decomposition [27,28]. Differences in the products structures obtained during a bulk thermolysis and a mechanistic discussion are presented.

2. Experimental part

2.1. Starting materials and reagents

HDPE was obtained from Aldrich Chemicals. It was produced by the Phillips process, and its main characteristics, as obtained from size-exclusion chromatography data, are: mass-average molar mass 146 400 g mol^{-1}; polydispersity index 13.8. Solvents and model compounds (Aldrich Chemicals): phenylether (99%), tetralin (1,2,3,4-tetrahydronaphthalene) (99%), tetracosane ($C_{24}H_{50}$) (99%), 1-eicosene ($C_{20}H_{40}$) (90%), *trans*-7-tetradecene ($C_{14}H_{28}$) (98%).

2.2. Size-exclusion chromatography

Number- and mass-average molar masses (M_n, M_w) and polydispersity index (M_w/M_n) of the starting HDPE and related products were obtained using a Waters 150CV instrument equipped with two Shodex columns AT806MS mounted in series. HPLC-grade 1,2,4-trichlorobenzene was used as solvent. The operating temperature, flow rate, and injection volume were 145°C, 1 ml min^{-1} and 200 μl respectively. Samples were prepared for injection at a concentration of 0.5% by dissolving at 145°C for 2 h. Calibration of the data collected from the refractometer detector was obtained using standard polystyrene samples from Polymer Laboratories. Viscosity measurements allowed the determination of the experimental intrinsic viscosity $[\eta]_{ex}$/mg l^{-1} of the samples; this data is useful for comparison with that calculated $[\eta]_{cal}$ using the Mark–Houwink relationship (in the case of HDPE: $\log(K) = -1.2874$ and $a = 0.69$, from the Polymer Handbook).

2.3. Differential scanning calorimetry

Melting points and enthalpy of fusion (ΔH_f/J g^{-1}) of the samples were obtained using a Dupont DSC10 calorimeter following a procedure described by Kim et al. which removes the effects of the thermal history and molecular heterogeneity of the samples [29]. The sequence includes heating of the sample under argon atmosphere to 160°C at a 10°C $\min^{-1}$ rate, 10 min at this temperature, cooling at a cooling rate of 10°C $\min^{-1}$ and heating again to 160°C (10°C $\min^{-1}$). The degree of crystallinity of the samples is obtained from a comparison of the obtained enthalpies of fusion with that of a pure crystalline polyethylene (293 J g^{-1}) [30].

2.4. Melt rheology

Viscoelastic functions, storage modulus G' and loss modulus G'', of some samples were determined under nitrogen with a Rheometrics RMS800 in the dynamic mode with the parallel plates geometry at different temperatures from 140 to 210°C. The frequency range was from 10^{-2} to 10^{2} rad s^{-1} in the linear viscoelastic region. The Newtonian viscosity $[\eta_0]$/Pa s at 150°C and the flow activation energies E_a/kJ mol^{-1} of the samples were thus obtained.

2.5. NMR spectroscopy (^1H and ^{13}C)

Spectra were obtained using a Brücker DRX400 spectrometer. ^{13}C NMR conditions to obtain a pseudo-quantitative structural characterisation of the initial HDPE and of the waxy products were chosen according to published data [31,32]. Sample preparation: 10 wt% of products in 2/1 mixture of tetrachloroethylene (TCE) and perdeuterobenzene; chemical shifts were obtained from TMS (^1H NMR) and from TCE in the case of ^{13}C NMR. Acquisition temperature was 363 K; the conditions for ^{13}C spectra recording were: pulse angle 70°; number of scans around 4000 (12 to 13 h of acquisition), acquisition sequence powergate (Waltze decoupling); total repetition time was 14.56 s, with an acquisition time of 4.56 s, and a delay between these acquisitions of 10 s. Combined analysis of ^{13}C and ^1H spectra allows quantification of the classical structural parameters as defined by Kuroki et al. [33]. The precisions of the integrations performed using the Brücker WINNMR software were estimated to be 1% for the proton and 2% for the carbon analysis.

2.6. Gas chromatography–mass spectrometry

Analysis and identification of the products issued from the pyrolysis of the model compounds was accomplished using a GC-MS HP5970B apparatus equipped with a 15 m × 0.32 mm DB-1 capillary column (0.25 μm thickness).

2.7. Batch experiments

The reactions were conducted batchwise in a stainless-steel reactor (300 cm^3) which was heated in a fluidized sand bath and pressurised with argon in order to keep the reaction mixture in the liquid phase (2 MPa at room temperature and about 3–4 MPa during pyrolysis). In a typical run, 20 g of HDPE (or model compounds) and 120 ml of phenylether or tetralin were charged in the reactor. When more-diluted solutions were prepared, the total volume was kept the same. The run temperature was reached within 20–30 min, while stirring of the medium at 100–150 rpm. At the end of the reaction, gases were vented and the solid–liquid mixture was filtered and washed several times with diethyl ether to remove any traces of phenylether or tetralin. The solid was then dried under vacuum and weighed in order to establish the amount of gas and light soluble paraffins (found in the solvent) formed during the pyrolysis. When no solvent was added, thermolysis was conducted without stirring and a solid product was obtained without further purification.

3. Results

3.1. Choice of thermal conditions

To determine the impact of solution thermal degradation of an HDPE on the final characteristics of the waxy polyethylenes chosen to be prepared, the effect of thermal conditions on molar masses evolution was first examined. Inspired from studies on bulk thermal degradation [12,13,15], runs at different temperatures and times were performed with the Phillips HDPE polymer diluted at 15 wt% in phenylether, and the formation of light fragments (gas or soluble products in the solvent) was investigated.

Fig. 2 illustrates M_w and M_w/M_n data evolution between 370 and 410°C for reaction times of 3 and 6 h. As exemplified by Kuroki et al. [15] during bulk experiments, a net decrease in M_w values was obtained at 370°C: from 150 000 to 20 000 g mol^{-1} in 3 h of reaction. At the upper thermolysis temperature (410°C), always in 3 h of treatment, the M_w value was divided by a factor 10 and had a narrow polydispersity of 1.7. But in counterpart a high level of light compounds was observed (20 wt% in 180 min and even 40% in 360 min). Along with non-analysed gas, they were comprised of a nearly equimolar distribution of linear alkanes and alkenes with carbon numbers from C5 to C24

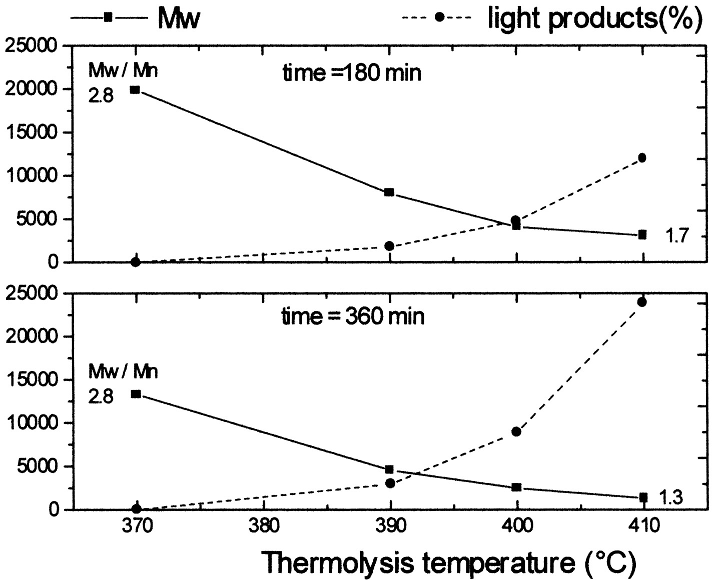


Fig. 2. HDPE thermolysis in phenylether; SEC data evolution with thermal severity, correlation with light products formation.

(from GC-MS). In order to obtain a smaller amount of gas and soluble paraffins (less than 5 wt%), the maximal thermal severity is therefore below 400°C—this is not surprising from the TGA analysis of polyethylene [34]—with longer reaction time.

3.2. Thermolysis of model compounds

In order to get a clear idea of the impact of the thermal conditions on the fragmentation level of the initial and thermally formed long-chain alkanes and alkenes present in the Phillips HDPE polymer [35], pyrolysis of some model compounds, tetracosane, 1-eicosene (terminal olefin) and *trans*-7-tetradecene (internal olefin), was performed. After a run for 6 h of phenylether at 390°C, only a slight transformation of the linear alkane was observed (less than 1 wt% of conversion). In great contrast, the level of transformation of 1-eicosene was above 85 wt% with formation of 10 wt% of gaseous products and a solution containing a continuous distribution of alkanes–alkenes (from C5 to C17). Such a difference is in conformity with the low energy of dissociation of the allylic C–C bonds (257 kJ mol^{-1}) compared with that of an aliphatic C–C bond (364 kJ mol^{-1}) [36]. At 390°C, it is calculated that the allylic bond breaking rate is 2.5×10^8 faster than for an aliphatic bond. It is interesting to observe that, in similar conditions, an internal olefinic compound is less converted (40 wt%).

Therefore, in these thermal conditions, molar masses evolution seems largely due to terminal olefin conversion. To explain the M_w/M_n evolution (from 13.5 to 1.9) during HDPE thermolysis, it is also possible to take into account some breaking of the branches in the aliphatic chain (BDE of 335 kJ mol^{-1}) [37] or an easier abstraction of tertiary hydrogen located at these points, with consecutive C–C bond scission. Another hypothesis is the activation of linear alkanes by radicals issued from alkenes fragmentation. Thus, the pyrolysis of a 1/1 mixture of these two model compounds was tested: no modification of alkene conversion level was observed, but the alkane was, this time, affected with a 25 wt% conversion into lighter products.

In conclusion, to obtain waxy polyethylene products, the level of transformation is closely controlled by the occurrence of alkenes, both for initiation of the free radical process and propagation steps.

3.3. Bulk versus solvent thermolysis

A detailed analysis of bulk and phenylether solvent thermodegradation of HDPE is now presented. Based on the preceding results, it was decided to perform runs at a medium conversion level (runs 1 and 2, 370°C/6 h) and at 390°C/6 h (runs 3 and 4), conditions which allowed us to obtain two different grades of waxy polyethylene. Bulk pyrolyses were performed without stirring to avoid any mechanical shearing [38]. Table 1 affords an overview of the structural and physical characteristics of the products. This includes a determination of molar masses, polydispersity index, intrinsic and Newtonian viscosities, enthalpies of fusion and results from an NMR analysis.

At first, bulk pyrolysis affords less light products at these two temperatures (runs 1 and 3), but this is not significant since in these cases no solvent extraction occurred. A better view of the lower conversion level obtained in bulk is given by the SEC data: important differences were obtained between the M_w values and, to a lesser extent, the M_n values. For example, at 390°C, the M_w and the M_n bulk/solvent ratios are equal to 6.7 and 2.2 respectively. The polydispersity index is thus lowered to 1.9 versus 5.5 in bulk. For thermal degradation of various polymers it has been claimed that such a final M_w/M_n value was the sign of a

Table 1
Comparative thermolysis of HDPE diluted in phenylether (PROPR) and in bulk

	HDPE	Run 1	Run 2	Run 3	Run 4
Temperature (°C)	—	370	370	390	390
Time (min)		360	360	360	360
Solvent	—	none	PhOPh	none	PhOPh
HDPE (wt%)		100	15	100	15
Light products (wt%)		< 0.5	$< 1\%$	1	5%
M_w/M_n	13.8	5.5	2.8	5.5	1.9
$M_{w\ SEC}$ (g mol^{-1})[a]	146 400	42 760	13 820	30 500	4550
$M_{n\ SEC}$ (g mol^{-1})[a]	10 640	7790	4700	5440	2450
$M_{n\ NMR}$ [b]	13 365	24 535	5910	7580	2815
$M_{n\ NMR}/M_{n\ SEC}$	1.25	3.15	1.26	1.4	1.15
$[\eta]_{ex}$ (ml g^{-1})[c]	178	49.5	35.5	42	15.5
$[\eta]_{cal}$ (ml g^{-1})[c]	147.5	68.5	34	53.5	16.5
η_0 (Pa s)[d]	98 000	290	6.3	—	—
E_a (kJ mol^{-1})[d]	29	40	31.5	—	—
Crystallinity (%)[e]	63	53	78	58	68
Melting (°C)	131	131	130	121.6	123.5
Butyl per molecule[f]	2.27	2.8	0.85	1	0.33
LCB per molecule[f]	0	2.06	0.24	0.77	0.17
C=C$_{ter/int}$ [g]	6.6	1.73	4.44	1.38	3.45
C=C per molecule[h]	1.02	0.57	1.1	0.59	0.94

[a] From SEC analysis.
[b] From ^{1}H and ^{13}C NMR analysis.
[c] From SEC and viscosimetric analysis.
[d] From melt rheology analysis.
[e] From DSC analysis.
[f] From NMR analysis, average number of butyl and long chains branching per molecule.
[g] From NMR analysis, ratio terminal versus internal unsaturation.
[h] From NMR analysis, number of unsaturations per molecule.

purely random bond breaking process [39]. As predicted, diminution of medium viscosity by the solvent favours products diffusion, thus lowering free radicals coupling reactions.

The influence of phenylether dilution on these reactions can be observed from various types of analysis.

- A significant reduction of the ratio between the M_n obtained from SEC analysis and that obtained by NMR; in the case of runs performed at 370°C, it decreases from 3.15 in bulk to 1.26 in solution. Since M_n determination is sensitive to polymer branching level, this gives an indication for a linear waxy polyethylene formation in solution with a structure close to that of initial HDPE.
- Similar intrinsic viscosity, experimental and calculated from the Mark–Houwink relationship, is also a good visualisation of a low ramification level: data are very close in the case of solvent experiments in contrast with bulk ones.
- When measurable (products obtained at 390°C were too fluid), Newtonian viscosities in the melt state are also interesting for comparison; from an initial value of 98 000 Pa s, a very low value of 6.3 was obtained in solution and, in contrast, 290 Pa s in bulk. This evidently comes from a more intense cracking as observed from molar masses evolution. Furthermore, from $[\eta_0]$ values collected at different temperatures, products flow energies of activation are estimated. Values close to 30 kJ mol^{-1} are obtained for initial HDPE and products prepared in solution; higher data are obtained in bulk condition (40 kJ mol^{-1}), a sign of a more branched polymer [40].
- DSC analysis also gives evidence that, compared with results obtained in bulk, solution thermolysis affords less ramified waxy polyethylenes, with higher percentages of crystallinity.

Physical characterisation by a lot of techniques gives convergent evidence that solution thermolysis affords products largely in contrast with bulk pyrolysis, i.e. a higher level of conversion, lower intrinsic and Newtonian viscosities; branching is also significantly lowered and affects the products physical properties.

Table 1 also presents some data obtained by the treatment of ^{1}H and ^{13}C NMR spectra as recommended by Kuroki et al. [33]. At first, since the question of branching level is of interest, the number of short-chain branching (SCB,

Table 2
Thermolysis of HDPE in phenylether: effect of the dilution level

	HDPE	Run 5	Run 4	Run 6	Run 7
Temperature (°C)	—	390	390	390	390
Time (min)	—	360	360	360	360
HDPE (wt%)	—	50	15	5	1
Light products (wt%)		5	5%	—	—
M_w/M_n	13.8	2.1	1.9	1.9	1.8
$M_{w\ SEC}$ (g mol^{-1})[a]	146 400	5250	4550	3820	3615
$M_{n\ SEC}$ (g mol^{-1})[a]	10 640	2515	2450	1960	2070
$M_{n\ NMR}$ [b]	13 365	3674	2815	2040	2010
$M_{n\ NMR}/M_{n\ SEC}$	1.25	1.46	1.15	1.05	1.03
$[\eta]_{ex}$ (ml g^{-1})[c]	178	17	15.5	14.4	13.9
$[\eta]_{cal}$ (ml g^{-1})[c]	147.5	17.5	16.5	14.3	13.9
Crystallinity (%)[d]	63	59	68	72	77.6
Melting (°C)	131	118	123.5	126	124
Butyl per molecule[e]	2.27	0.40	0.35	0.45	0.4
LCB per molecule[e]	0	0.78	0.17	0.05	< 0.01
C=C$_{ter/int}$ [f]	6.6	1.1	3.4	3.1	3.5
C=C per molecule[g]	1.0	0.73	0.95	1.05	0.9

[a] From SEC analysis.

[b] From ^{1}H and ^{13}C NMR analysis.

[c] From SEC and viscosimetric analysis.

[d] From melt rheology analysis.

[e] From NMR analysis, average number of butyl and long chains branching per molecule.

[f] From NMR analysis, ratio terminal versus internal unsaturation.

[g] From NMR analysis, number of unsaturations per molecule.

below six carbon atoms) and long-chain branching (LCB, above six carbon atoms) per molecule was determined. NMR spectra show that, in all products, SCB is only butyl chains, inherent to the Phillips process of HDPE production. Solvent thermolysis affords a lower SCB level per molecule compared with bulk runs (1 and 3) with data divided by a factor of three.

Concerning the LCB occurrence, initially absent in the HDPE, they are formed in large quantities in bulk thermolysis (two chains per molecule at 370°C), therefore modifying product physical properties as observed above. In contrast, smaller amounts are observed when a solvent is added. This is consistent with a higher degree of crystallinity and flow energy of activation values (runs 2 and 4).

Finally, it was also observed that the SCB and LCB amounts (in bulk or solvent thermolysis) are greatly affected by treatment severity, probably in relation to some C–C bond breaking at the branching points. Effectively, studies have reported a higher thermal sensitivity for branched polymers [10]. Blouri et al. made a similar observation when comparing 6-methyleicosane and linear eicosane thermal sensitivities [41].

Other useful information obtained from NMR analysis is the nature and quantity of double bonds contained in the products. Around one olefin per molecule is found for the initial HDPE, standard data for a Phillips polyolefin; they are mainly terminal with a 6.6 ter/intern ratio. A similar analysis is obtained for samples coming from solvent thermolysis. This is in contrast with samples obtained from a bulk pyrolysis with only 0.5 to 0.6 C=C per molecule and a net decrease in terminal olefin. Kuroki et al. put forward a cage effect induced by medium viscosity to explain these last results [15].

In summary, the use of an inert solvent contributes to form α-olefinic linear polymers with weak molar masses.

3.4. Effect of higher dilution

The impact of solvent thermolysis of a polyethylene is clearly demonstrated from this comparison. These runs were performed with a level of dilution of 15 wt% of HDPE in phenylether, which well minimises the ‘‘cage effect’’ inherent to the high medium viscosity observed during bulk thermolysis.

As described by Jellinek, in solution a segmental diffusion of the free radicals occurs, which is controlled by the solvent solvating power and its concentration [17]. As a result, a better diffusion of the radicals favours the conversion to lower molar masses since recombination reactions are diminished as well as LCB. Furthermore, migration of radical chains out of this cage slows down intramolecular reactions such as 1–5 hydrogen transfer (or back-biting) [42,43].

In order to ascertain solvent effects on degradation

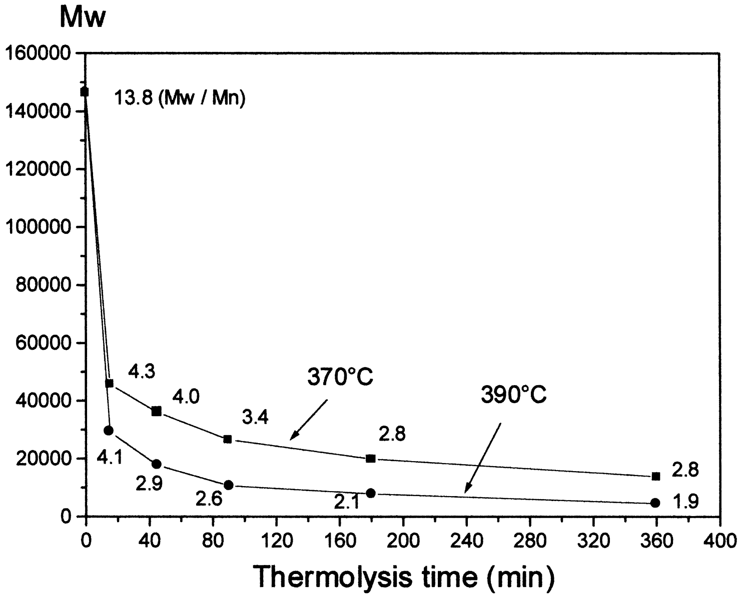


Fig. 3. HDPE thermolysis in phenylether; time evolution at 370 and 390°C of molar masses and polydispersity index.

mechanisms, runs were performed at different dilution levels: from 50 to 1 wt% of HDPE in phenylether (Table 2).

Effectively, a regular molar masses decrease is observed from low to high dilution levels. In the last case, this is associated with very close $M_{n\ SEC}$ and $M_{n\ NMR}$ values, a sign of lesser faults in the products. Higher crystallinity data confirm such observations (from 58 to 78%) as well as the diminution of LCB values from 0.77 in bulk to less than 0.01 in the very diluted condition (run 7).

Run 5 (1/1 mixture) is apart, even if more converted than in bulk (run 3), with an M_w value of 5000 g mol^{-1}. But, a high initial medium viscosity probably explains that much of the data are very close to those obtained in bulk: M_n ratio, crystallinity, LCB and olefinic levels.

In summary, a quite high dilution level in phenylether is necessary to get all of its advantages. Controlling the unfolding of the polymer chains elongation and their free motion from a lowering of the local viscosity allows one to observe products similar to those predicted from the classical Rice–Kossiakoff radical mechanism of thermal fragmentation: no branching formation during the thermolysis, only C–C bond fragmentation [14].

3.5. Effects of thermal parameters on HDPE kinetics of transformation

The following experiments give detailed information on the kinetic evolution of physical and structural parameters of the products. For various thermolysis times, recorded at 370 and 390°C (Fig. 3), a very rapid M_w decrease was initially observed in the pyrolysis: divided by a factor of five after only 15 min at 390°C. After that, the process regularly tends to produce low molar mass polyethylenes, with a continuous narrowing of the polydispersity data. Such observation proves the importance of pyrolysis time to obtain the desired products, since the possibility of increasing the temperature above 390°C is limited, as established above (excessive cracking).

In the case of runs performed at 370°C, it is interesting to correlate Newtonian viscosity evolution with the M_w data obtained from SEC (Fig. 4). Furthermore, E_a values are found to be stable during all the process times around the initial value (29 ± 2 kJ mol^{-1}), clearly supporting a low level of LCB in the products. From the relationship $\eta_0 = KM_w^n$, a value of 4.2 is found for n. Usually a value of 3.4 is applied to monodisperse polyethylene, and above a critical mass of 3800 g mol^{-1} [44]. But, it was recently observed that this value might shift towards higher values, both for polydispersed samples [45] and in the presence of branching [40]. In the present study, a value of 4.2 seems to be more representative of the polydispersity of the products (from 13.5 to 2.8).

Fig. 5 presents some structural parameters evolution with thermolysis time obtained from NMR analysis. As expected, a regular decrease in the SCB values (i.e. butyl chains) is depicted. Thus, taking into account the thermal sensitivity of the branching points, it is obvious that a steady-state in LCB concentration is observed due to the superposition of two effects: control of LCB formation by dilution and slower thermal cracking.

An estimation of process kinetics as well as activation energy value is possible from these runs performed in solution at different thermolysis times and temperatures. The molar mass distribution evolution was chosen as a representative factor, as previously described for the kinetic simulation of polymer degradation [46–48].

Based on the hypotheses concerning the nature of the thermal fragmentation (random scission or depropagation),

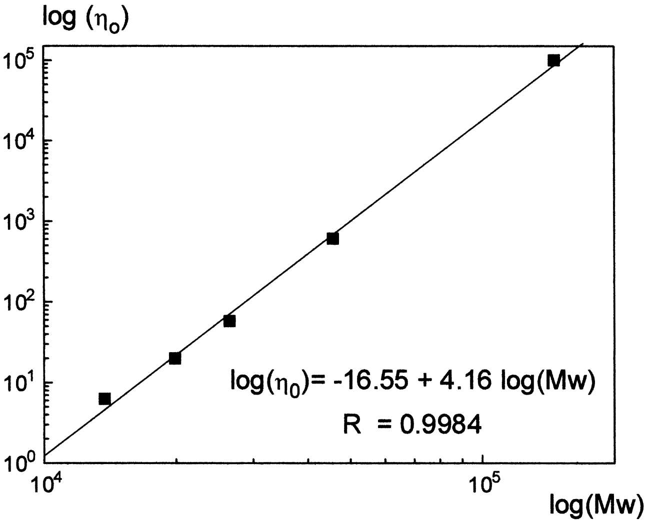


Fig. 4. HDPE thermolysis at 370°C in phenylether; correlation between Newtonian viscosity and M_w evolution with reaction time.

reaction order and the possibility of some recombinations, theoretical data help to establish population balance equations that govern the kinetic behaviour of the transformation. This ''continuous mixture model'' has been applied both to coal liquefaction and to oxidative thermodegradation of polystyrene [49,50].

The mathematical treatment described by Wang et al. [46] was adapted to the HDPE thermolysis in order to take into account the polyethylene specificities and the solvent impact on the process:

- following previous work on bulk thermolysis of polyethylene, the transformation is assumed to be a first-order reaction with random scission;
- in view of the very low branching level, equations related to chain branching reactions were omitted;
- considering the high polydispersity of the HDPE, as proposed by Wang et al. [46] in the case of coal degradation, the parameter b found in the expression of the rate coefficients ($k(x) = k_b x^b$) was set to a value of 1; this suggests that larger molecules are more easily thermally degraded.

Effectively, it is demonstrated that these assumptions are needed to get a good fitting between the experimental molar mass distributions obtained during the thermolysis of the HDPE at 390°C and the simulated ones (Fig. 6).

As a result, kinetics constants at 370°C, 390°C and 400°C are determined (with correlation factors above 0.99) to be respectively $1.57 \times 10^{-7}\ s^{-1}$, $7.18 \times 10^{-7}\ s^{-1}$ and $15.9 \times 10^{-7}\ s^{-1}$. Therefore, from the Arrhenius relationship it is found that the activation energy is 277 kJ mol^{-1}. This result,

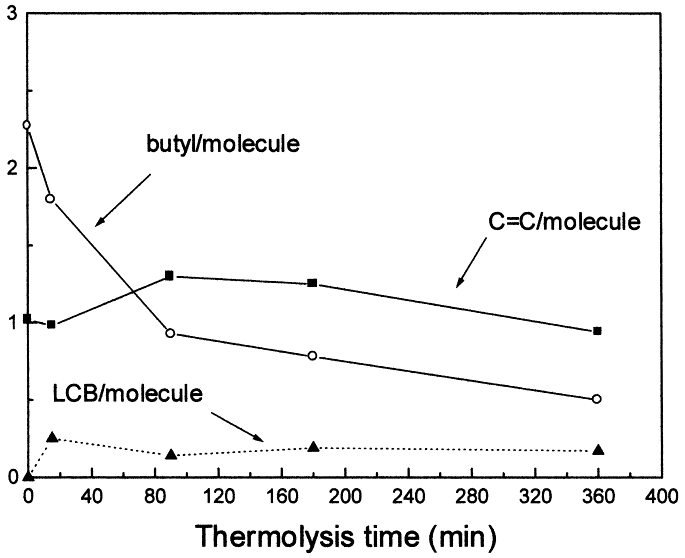
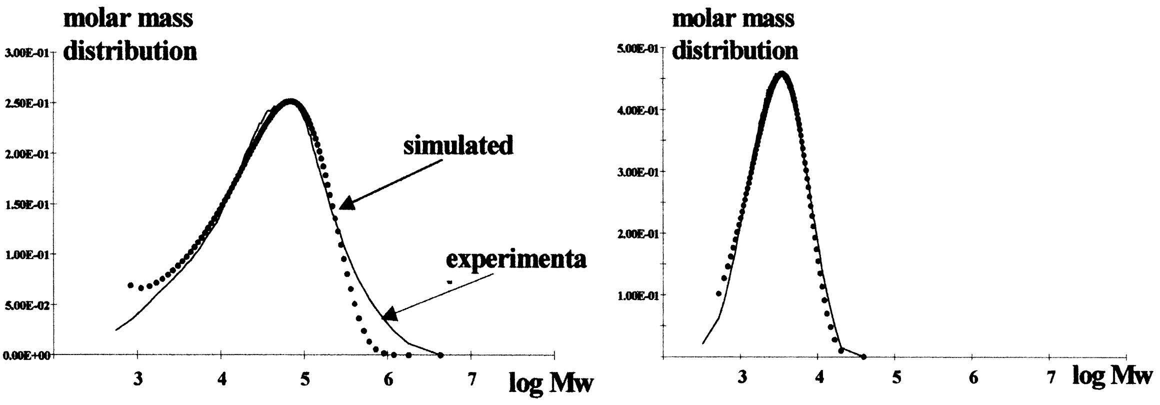


Fig. 5. HDPE thermolysis at 390°C in phenylether; NMR parameters evolution with reaction time.



initial HDPE

after 6 hours at 390°C

Fig. 6. HDPE thermolysis at 390°C in phenylether; experimental results of molar mass distributions versus model simulations

is in conformity with those proposed previously for thermal degradation of polyethylene (between 255 and 310 kJ mol^{-1}) [51]. Only a dilution effect is apparently the origin of the structural and physical changes detailed above.

In contrast, it now seems interesting to test the action of tetralin, a compound not only active as solvent but also active in the free radical mechanism.

3.6. H-donor effect on the HDPE thermolysis

The capacity of tetralin to modify the free radical evolution of the HDPE degradation (i.e. propagation steps and termination reactions) is correlated to the weak bond dissociation energy of its benzylic C–H bond (BDE: 355 kJ mol^{-1}) (Fig. 7). This data has to be compared with the BDE value of the most labile hydrogen present in the polymer: 372 kJ mol^{-1} for the allylic C–H bonds [27,28]. Therefore, when a radical is formed, the possibility of picking up a hydrogen could prevail over its classical evolution (β-scission, intermolecular H-transfer and abstraction on the polymer chains). A tetralyl radical is obtained, which, after successive loss of labile hydrogen atom, affords the stable naphthalene. As a global effect, besides a diluting function, tetralin lowers the level of conversion by preventing secondary radical initiation.

From the amount of light fractions and number- and mass-average molar masses evolution, it clearly appears that tetralin is a very efficient hydrogen donor compound. At 370°C, the M_w value is above 50 000 (Table 3, run 8) versus around 14 000 in phenylether (Table 1, run 2) and higher polydispersity values were obtained in tetralin (4.6 instead of 2.8). Bulk pyrolysis affords even more converted products (Table 1, run 1).

As presented in Fig. 8, contrasting M_w/M_n data are obtained after 360 min of thermolysis at 390°C in the different media. Conversion evolution as a time function of thermolysis at 390°C shows that transformation is largely affected by tetralin, even at the beginning of the transformation (Fig. 9).

Surprisingly, M_n values obtained from NMR determination are largely above those obtained from SEC analysis, as when runs were performed without solvent. In this last case this was interpreted as the result of LCB formation. In the presence of tetralin the diluting effect seems absent. An explanation might come from NMR spectra observation, since aromatic as well as benzylic proton and carbon atoms, typical of the tetralin structure, are present in significant quantities. Such tetralin fixation on HDPE fragments can occur in two ways. A coupling reaction between an alkyl radical and a tetralyl radical formed after a first proton donation. This type of reaction has been reported in the case of benzyl radicals produced from 1,2-diphenylethane thermolysis [52]. Another possibility is a tetralyl radical addition reaction to the alkenes present in the medium, as observed during the thermal cracking of *n*-hexadecane between 420 and 460°C [53].

The exact structure of the adduct is difficult to obtain from the NMR spectra, but its quantification is possible (from the CH_2 groups contained in tetralin). It is found that as much as 0.45 and 0.6 units per molecule are obtained at 390°C in the beginning of the run (45 min) and after 360 min respectively.

At this stage, it seems useful to perform the thermolysis of an alkene as model compound in order to establish the mechanism of formation and the structure of tetralin grafted products, and to determine the impact of tetralin on the conversion level. GC analysis of the liquid mixture obtained after thermolysis of a 15 wt% solution of 1-eicosene in tetralin (390°C/360 min) allows one to quantify a 90 mol% level of olefin conversion, into lighter compounds, but also into a heavier fraction. GC-MS analysis gives effective evidence of a main product with a molar mass of 412 g mol^{-1}, corresponding to tetralin grafting on a saturated C20 skeleton. Other minor compounds with the same molar mass are probably positional isomers and other detectable ones correspond to grafting of tetralin on

Table 3
Thermolysis of HDPE (15 wt%) in tetralin

	HDPE	Run 8	Run 9	Run 10
Solvent	—	tetralin	tetralin	tetralin (20%) PhOPh (80%)
Temperature (°C)	—	370	390	390
Time (min)		360	360	360
Light products (wt%)		< 0.5	1	—
M_w/M_n	13.8	4.6	3.4	2.8
$M_{w\ SEC}$ (g mol^{-1})[a]	146 400	56 180	27 460	16 500
$M_{n\ SEC}$ (g mol^{-1})[a]	10 640	11 700	8000	5800
$M_{n\ NMR}$ [b]	13 365	34 745	15 235	10 420
$M_{n\ NMR}/M_{n\ SEC}$	1.25	2.97	1.9	1.8
$[\eta]_{ex}$ (ml g^{-1})[c]	178	90	53.5	40.5
$[\eta]_{cal}$ (ml g^{-1})[c]	147.5	87	54	37.7
η_0 (Pa s)[d]	98 000	1130	—	—
E_a (kJ mol^{-1})[d]	29	33	—	—
Crystallinity (%)[e]	63	60	67	70
Melting (°C)	131	133	129	129
Butyl per molecule[f]	2.27	3.87	2.44	1.6
LCB per molecule[f]	0	1.18	0.39	0.28
$C{=}C_{ter/int}$ [g]	6.6	1.63	1	1.83
C=C per molecule[h]	1.02	1.11	0.84	0.9

[a] From SEC analysis.
[b] From ^{1}H and ^{13}C NMR analysis.
[c] From SEC and viscosimetric analysis.
[d] From melt rheology analysis.
[e] From DSC analysis.
[f] From NMR analysis, average number of butyl and long chains branching per molecule.
[g] From NMR analysis, ratio terminal versus internal unsaturation.
[h] From NMR analysis, number of unsaturations per molecule.

C16–C19 alkanes. The yield in the main compound, from converted eicosene, is then estimated to be 50 mol% in contrast with the low yields (2–3 mol%) obtained by Khorasheh and Gray [53].

After vacuum distillation, 1-*n*-eicosantetralin was identified by analogy with ^{1}H and ^{13}C analysis of similar compounds [54]. Following the Markovnikov rule, radical addition mainly occurs on the terminal olefinic carbon (Fig. 10).

Compared with eicosene thermolysis in phenylether, it is important to put forward the consequence of this grafting reaction. Effectively, tetralin slows down any radical process, and hence the product conversion (only 40 wt% of light products). But, such an addition reaction on thermally sensitive alkenes prevents their decomposition since the grafted compounds appear more stable.

The impact of tetralin on HDPE conversion and products physical characteristics is now understandable from this aromatic branching incorporation. For example, examination of intrinsic and Newtonian viscosity values provides some interesting information. In agreement with a lower level of conversion, $[\eta]_{ex}$ data are three times higher than those obtained in phenylether (see Tables 1 and 3). But, the good agreement obtained between experimental and calculated ones ($[\eta]_{cal}$), is a sign of a low branching level induced by the dilution. This is in contradiction with the preceding observations, except if aromatic branching only slightly modifies viscosity measurements, as butyl branching does.

The discrepancy between the $M_{n\ SEC}$ and $M_{n\ NMR}$ data might now be understood from an over-estimation of $M_{n\ NMR}$ values. Effectively, the CH_2 signal intensity, which is used to quantify the number of branches or chain ends (and hence the M_n value), is largely affected by the tetralin grafting reaction on the terminal carbon of the polymer chain.

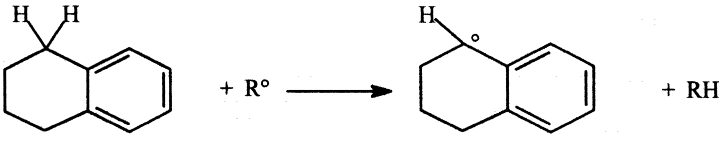


Fig. 7. Basic reaction of tetralin with a radical.

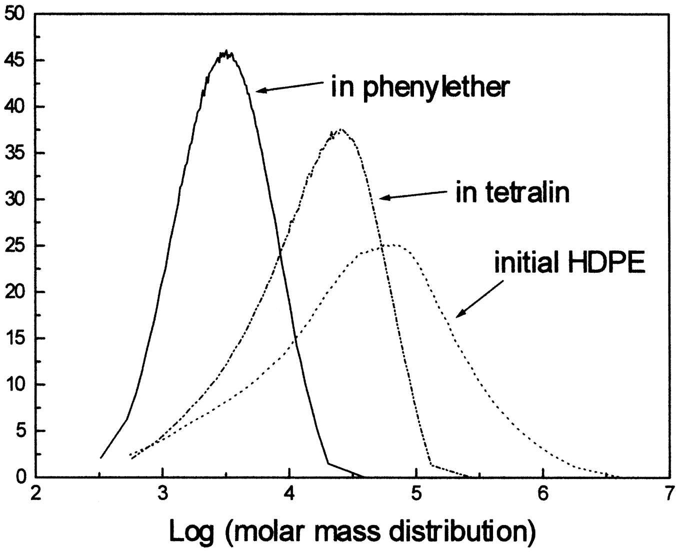


Fig. 8. HDPE thermolysis at 390°C in different media; effect on molar mass distributions after 6 h of reaction time.

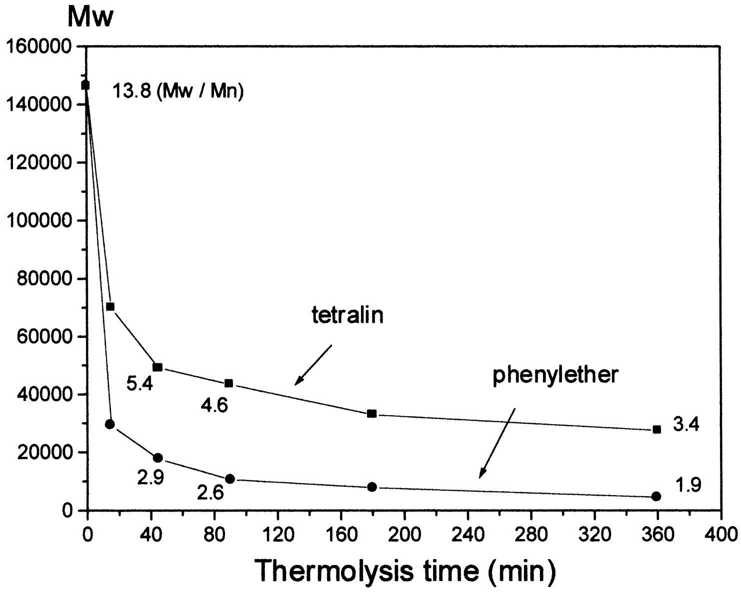


Fig. 9. HDPE thermolysis at 390°C in different media; effect of reaction time on M_w and polydispersity index.

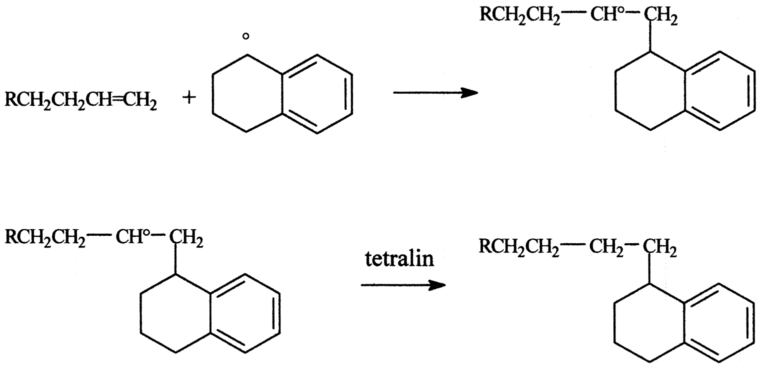


Fig. 10. Mechanism of tetralyl radical addition on alkene.

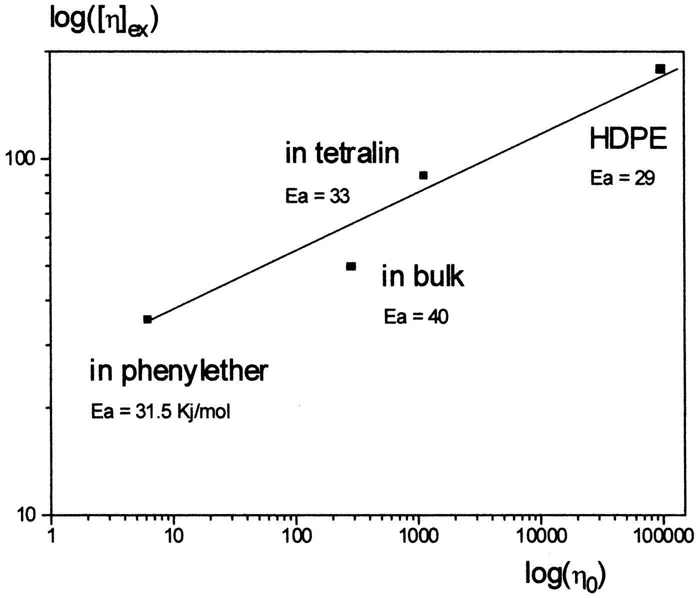


Fig. 11. HDPE thermolysis at 370°C 6 h in different media; correlation between Newtonian, intrinsic viscosities and flow energies of activation.

Fig. 11 presents results from melt rheology analysis of samples obtained at 370°C in the different media. In contrast to bulk thermolysis, the correlation between intrinsic and Newtonian viscosities obtained in solution shows a good alignment of the points. In addition, the values of flow activation energy confirm the efficiency of the solvents to control the LCB formation (31–33 kJ mol^{-1} in solution versus 40 kJ mol^{-1} in bulk). DSC and NMR analysis of products from runs 8 and 9 demonstrate that, in fact, more LCB is formed in the presence of tetralin. For example, the LCB per molecule values of 0.24 and 1.2 are obtained at 370°C in the presence of phenylether and tetralin respectively.

As detailed above, the branching points (LCB and butyl chains) are thermally sensitive. Hence, once formed, they could slowly be decomposed by direct C–C bond breaking or after H-abstraction. Tetralin is able to interact on the last reaction, as clearly observed from the behaviour of the butyl chains initially present in the HDPE. As for LCB, this remains in larger quantities in tetralin, even at 390°C: 2.44 versus 0.33 butyl per molecule in phenylether.

NMR analysis also provides interesting information about the level and the nature of the unsaturation. Despite the tetralin grafting reaction, the unsaturation level remains close to one per molecule and they are enriched in internal ones compared with runs performed in phenylether. From model compounds thermolysis it appears that this last observation takes its origin from a selective tetralin addition on the terminal double bonds. Effectively, thermolysis of *trans*-7-tetradecene in tetralin (390°C/360 min) does not afford any alkyl tetralin compounds. Furthermore, only a few weight percent of the alkene is converted into light products as reflected in the high H-donor capacity of tetralin. A last run illustrates this unique property well.

Thermolysis of the polyolefin in an 80/20 mixture of phenylether–tetralin (run 10) effectively gives data closer to those obtained in pure tetralin. Therefore, inert–active solvents balance is a possible tool to adjust some of the characteristics of these waxy polyethylenes, such as level of conversion, amount of unsaturation and SCB (including grafted tetralin).

4. Conclusion

The present work was concerned with the production of waxy low molar mass polyethylenes during the batch thermolysis of HDPE. It particularly studied the impact of the dilution level of an inert solvent (phenylether) and an H-donor compound (tetralin) on the intimate structure of the products. Particularly worthy of note was the preparation of polyethylenes with low molar mass distribution, crystalline and olefin-rich products in the case of an inert solvent. This is in great contrast with that observed from a bulk pyrolysis and shows the great importance of the medium viscosity on the free radicals mechanism of decomposition of high molar mass alkanes and alkenes. In the presence of tetralin, besides a global lowering of the conversion, an efficient grafting reaction of tetralyl radical on the terminal olefin was also pointed out as an easy way to introduce aromatic groups.

Depending on the solvent nature, composition, and dilution level, it is possible to obtain a great variety of products not easily prepared in other ways, e.g. directly from ethylene polymerisation [11]. Their utility, as described in Section 1 might be great. But other applications also seem promising, such as polymers compatibilisers, and adhesion of polymers on surfaces through their chemical modifications [55].

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