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Journal of Chromatography A, 919 (2001) 255–266

JOURNAL OF CHROMATOGRAPHY A

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Study of the polymerization of anthracene oil with $AlCl_3$ by chromatography and related techniques ☆

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Received 20 November 2000; received in revised form 20 March 2001; accepted 29 March 2001

Abstract

The structure and composition of products from the reaction of anthracene oil with anhydrous $AlCl_3$ have been examined. Size-exclusion chromatography has been carried out using a column with polystyrene–polydivinylbenzene as stationary phase, 1-methyl-2-pyrrolidinone at 80°C as eluent and variable-wavelength UV-absorption detection. This system provides a chromatogram of the sample with several peaks. Molecular masses corresponding to these peaks were estimated using a calibration curve obtained with polycyclic aromatic hydrocarbon standards, ranging from 92 to 532 u. The most abundant compounds of the substrate were dimers and trimers of the main anthracene oil components. These results are corroborated on a qualitative level by synchronous UV-fluorescence spectra.

Keywords: Anthracene oil; $AlCl_3$ catalysts; Polynuclear aromatic hydrocarbons

1. Introduction

Anthracene oil (AO) is a mixture of polycyclic aromatic hydrocarbons (PAHs) with 2–5 benzene ring systems [1], obtained by the distillation of coal-tar. The polymerization of AO at a moderate temperature in the presence of different agents (sulfur, aluminium trichloride, air, etc.) results in an isotropic material with characteristics similar to those of commercial pitches [2–4]. The polymerization of AO with anhydrous $AlCl_3$ is a suitable method for obtaining pitch-like products with excellent properties for use as precursors of anisotropic carbons [4].

The polymerization of aromatic hydrocarbons catalysed by $AlCl_3$ or other Friedel–Craft catalysts [5–9] involves carbocationic reactions, which yield oligomers with a variable molecular mass and a high content of aliphatic hydrogen [7–9]. Polymerisation at moderate temperatures is a non-dehydrogenative process; therefore, the resultant oligomers are rich in naphthenic structures and contain alkyl groups formed by the breakage of hydrogenated rings [7,9]. Naphthenic structures are desirable in pitches that are intended as precursors of highly anisotropic cokes, fibres and special carbons [10–12]. In order to optimise the conversion of AO into pitch-like prod-

☆Presented at the 29th Scientific Meeting of the Spanish Group of Chromatography and Related Techniques, Alcalá de Henares (Madrid), 12–14 July 2000.

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0021-9673/01/$ – see front matter
PII: S0021-9673(01)00811-1

ucts suitable for advanced applications the extent of the polymerization of the AO components and the influence on the properties of the products, especially coke yield and coke anisotropy, should be determined. To this end, it is necessary to take advantage of analytical methods able to reveal the molecular size and structure of the resultant oligomers.

Size-exclusion chromatography (SEC) using polystyrene–divinylbenzene as stationary phase and 1-methyl-2-pyrrolidinone (NMP) as eluent has proved to be effective for molecular size separations of components of complex coal-derived mixtures [13,14]. The column used in the present work, calibrated using polystyrene standards, has been shown to give a separation based mainly on size or molecular mass [15,16] for small polar and non-polar molecules. Polycyclic aromatic standards tend to deviate from the polystyrene calibration by (at times) slightly more than 1 min. The effect is thought to be due to the more compact shapes – apparent smaller size – of polynuclear aromatic ring systems or to surface effects. The polystyrene calibration predicted elution times of most of the standard molecules to within about 1 min although there were some exceptions – fullerene, a dye and 9-anthracene carboxylic acid. This situation contrasts with that of the first use of NMP as eluent in SEC [17], where significant deviations of elution times of small standard molecules were observed compared with the polystyrene calibration, amounting to 10.7 min early elution for acetone and dihydroxybenzenes and 5.6 min late for fluorene. In this earlier work, alkyl derivatives of aromatics tended to elute later than expected with octylbenzene and dimethylnaphthalenes eluted late by between 5 and 7 min.

In the present study, the polystyrene calibration is expected to provide a reasonable indication of shifts in molecular mass from the AO to the catalysed products, although not necessarily an absolute measure of mass for any one SEC peak. Parallel characterisation of the samples has been undertaken by UV-fluorescence spectroscopy. UV absorption and UV fluorescence yield information on the size of the aromatic ring systems in the molecules rather than on the molecular size itself. Clearly, if the size of the aromatic cluster increases, then it is likely that the molecular size will also increase but the relation between the two depends on the structure and the manner of linking aromatic groups within molecules. In previous work, we have found that the higher the wavelength of the maximum UV intensity and/or the greater the wavelength of UV fluorescence, the greater the molecular mass of the substrate [18–20]. The wavelength of maximum fluorescence was directly related to the molecular mass of components of SEC fractions of coal-tar pitches [21]. Although the UV-fluorescence spectra of complex mixtures do not allow accurate determinations of size distributions, the existence of aromatic systems of varying size can be inferred [20].

This paper reports on the ability of SEC with detection by UV absorption (UV), probe mass spectrometry and UV-fluorescence (UV-F) spectroscopy to characterise $AlCl_3$ polymerized samples. To relate SEC elution times with molecular mass, calibration curves based on the polystyrene standards and on the limited range of elution times of standard PAHs with different structures [15,16] were used.

2. Experimental

2.1. Materials used

An industrial AO with a boiling point distribution between 250 and 370°C was used as received. The AO was polymerized by treatment at 300°C for 2 h in the presence of 10% (w/w) of anhydrous $AlCl_3$ [4]. After the reaction, the sample was washed at 80°C with an aqueous solution of hydrochloric acid (5%, v/v) and then twice with water. The product, named AO1, showed an elemental composition (%, w/w) of: C, 92.3; H, 5.41; N, 0.69; S, 0.45 and O, 1.13. However, H and O values should not be considered accurate since free water presence was ascertained by ^{1}H-nuclear magnetic resonance (NMR). The carbon yield of AO1 at 1000°C was 32% (w/w).

2.2. Size-exclusion chromatography

SEC was carried out using a polystyrene–polydivinylbenzene column, 30 cm×7.5 mm O.D. (5 μm particle size; ''Mixed-D'', Polymer Labs., Shropshire, UK); the method has been described previous-

ly [15,16,22]. In this column polystyrene molecular mass (M_r) standards from 104 (monomer) up to about 300 000 u elute with a linear relationship between $\log_{10}$ molecular mass and the elution volume (or time). Larger molecular mass polystyrene standards up to $2 \cdot 10^6$ u elute at shorter times with a different relationship between molecular mass and time, and are classed as excluded from the column porosity. The void volume of the column has been identified using soot at between 6 and 7 min [22] and corresponds to a cross-sectional diameter of 20 nm. Samples were run at 80°C, with NMP flowing at a rate of 0.5 ml min^{-1}. Detection was carried out at 280, 300, 350, 370 and 450 nm, using a Perkin-Elmer LC290 variable-wavelength UV-absorption detector and an Applied Biosystems UV-diode array detector in series. The eluent was pumped using a Perkin-Elmer isocratic pump with a maximum pressure of 14 MPa. Chromatograms have been presented in area-normalised mode to allow comparison of sample solutions of different concentrations. AO1 was also fractionated using the analytical SEC column, with fractions being collected every 2 min from 9 to 25 min. These fractions were chromatographed again, using the same experimental conditions.

2.3. UV-fluorescence spectroscopy

A Perkin-Elmer LS50 luminescence spectrometer was set to scan at 240 nm min^{-1} with a slit width of 2.5 nm; synchronous spectra were acquired at a constant wavelength difference of 20 nm over the 200–800 nm range. A quartz cell with 1 cm path length was used. The spectrometer featured automatic correction for changes in source intensity as a function of wavelength. Emission, excitation and synchronous spectra of the samples were obtained in NMP. Only the synchronous spectra are shown. The spectra have been presented in peak-normalised mode to show shifts independent of changes in intensity. Solutions were diluted with NMP to avoid self-absorption effects: dilution was increased until the fluorescence signal intensity began to decrease.

2.4. Probe mass spectrometry

A Jeol JMS-AX505W double focusing mass spectrometer equipped with a standard solids injection probe and electron impact ionisation was used. Mass spectra in nominal mass were collected during the pressure pulse caused by the evaporation of volatiles, using an ionising voltage of 70 eV. For the first minute of the run the probe was not heated. After 1 min, the probe was heated to a temperature of 300°C over a period of 8 min while the spectra were collected. This temperature was maintained for 1 min before terminating the run. The spectra were summed to produce one overall spectrum for each sample.

2.5. ^{1}H-NMR spectroscopy

A 400 MHz AMX Bruker NMR instrument has been used. Samples were dissolved in deuterochloroform with trimethylsilane (TMS) as reference.

2.6. Gas chromatography

Gas chromatography (GC) of AO was carried out using a Hewlett-Packard HP-6890 chromatograph with a flame ionisation detector. A 1-μl volume of a toluene solution of AO was injected in split mode (24:1 ratio) into a HP-5 capillary column (cross-linked PH ME siloxane, 30 m×0.32 mm I.D.), using hydrogen as the carrier gas at a flow-rate of 1.4 ml min^{-1} and a programmed temperature of 4°C min^{-1} from 50 to 300°C, this temperature being maintained for 30 min.

The average molecular mass of AO was calculated from the molecular mass and the peak area of the 20 most abundant compounds of AO (from naphthalene to triphenylene). The area of the peaks was quoted as the mean values from 10 experiments.

3. Results and discussion

3.1. Characterisation of the polymerized anthracene oil

AO is a mixture composed of a large number of aromatic compounds, mainly hydrocarbons, with 2–5 aromatic rings. The major components [4] are anthracene/phenanthrene (25% w/w), fluoranthene/pyrene (22%, w/w), acenaphthene (5.5%, w/w),

fluorene (4.5%, w/w) and others with concentrations between 1 and 2% (w/w). The most reactive are those bearing anthracene type structures and methylene groups.

The extent of polymerization was studied by probe mass spectrometry of AO1. Fig. 1 shows that the main molecular ions are those of the unreacted anthracene oil, at *m/z* 202 (fluoranthene/pyrene) *m/z* 216 (methylfluoranthene/pyrene), *m/z* 228 (chrysene isomers), *m/z* 252 (benzofluoranthene/pyrene) and *m/z* 266 (methylbenzofluoranthene/pyrene). These are compounds normally expected in anthracene oils. A group of ions have been observed at higher masses, which could be attributed to the dimers and codimers of the most abundant and/or most reactive components, however there is no direct evidence of this. Ions have been observed at *m/z* 302–306, which could be dimers of acenaphthene/acenaphthylene, at *m/z* 326–330, dimers of fluorene, at *m/z* 352–354 dimers of anthracene/phenanthrene, at *m/z* 402 dimers of fluoranthene/pyrene while ions at *m/z* 340–344 could be codimers of anthracene/phenanthrene with fluorene.

As mentioned above, the polymerization of aromatic hydrocarbons in the presence of $AlCl_3$ and other Friedel–Craft catalysts is non-dehydrogenative [7–9]. Usually, the resultant oligomers are thermally unstable, changing later into a more stable structure. This transformation occurs via reactions of hydrogen transfer, cyclation, isomerisation and molecular rearrangements. As an example, 9,9′-bi-9H-fluorene ($C_{26}H_{18}$) gives dibenzo[*a*,*c*]triphenylene ($C_{26}H_{14}$) by rearrangement and successive loss of hydrogen [23]. Hydrogen exchange involves the formation of hydroaromatic and naphthenic structures. The molecular ions of these compounds are probably responsible for the signals near those of their dimers or codimers.

It is known that the polymerization of pure aromatic hydrocarbons assisted with $AlCl_3$ produces the formation of dimers, trimers, tetramers, etc. [7,9]. However, in our case probe mass spectrometry only shows ions up to *m/z* 450, the effective upper limit of the method. For a better understanding of the extent of the polymerization of AO, the polymerized sample (AO1) was examined by SEC, using the same experimental conditions as Lázaro and coworkers [15,16,22].

Fig. 2 compares the SEC chromatograms of AO (Fig. 2a) with that of the product AO1 (Fig. 2b) obtained by UV detection at several wavelengths. These chromatograms show that the parent AO contained mainly components that eluted at longer times, characteristic of small molecules, with only a barely observable peak of large material before 10 min. The profiles of AO1 were more complex, with

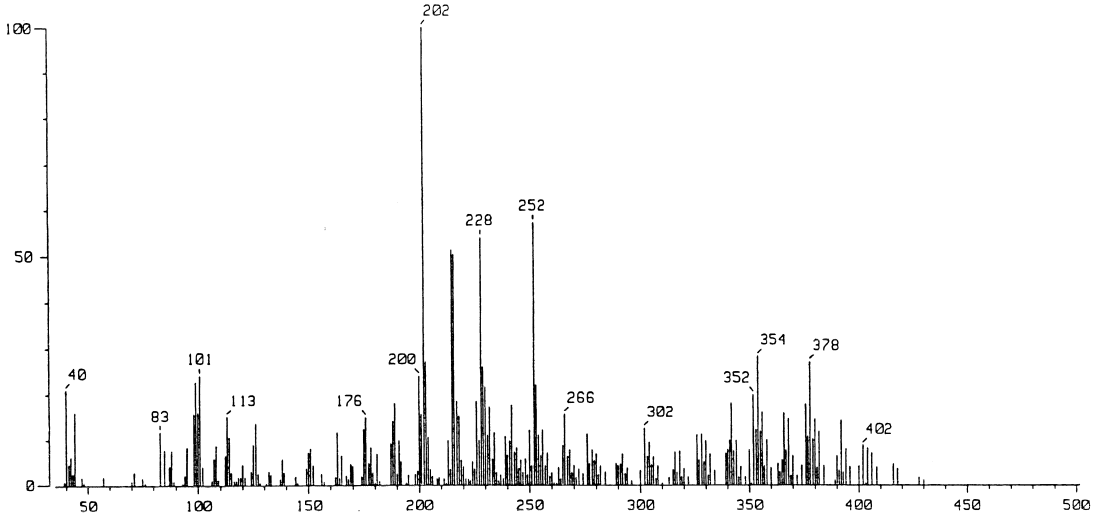

Fig. 1. Probe mass spectrometry of polymerized anthracene oil.

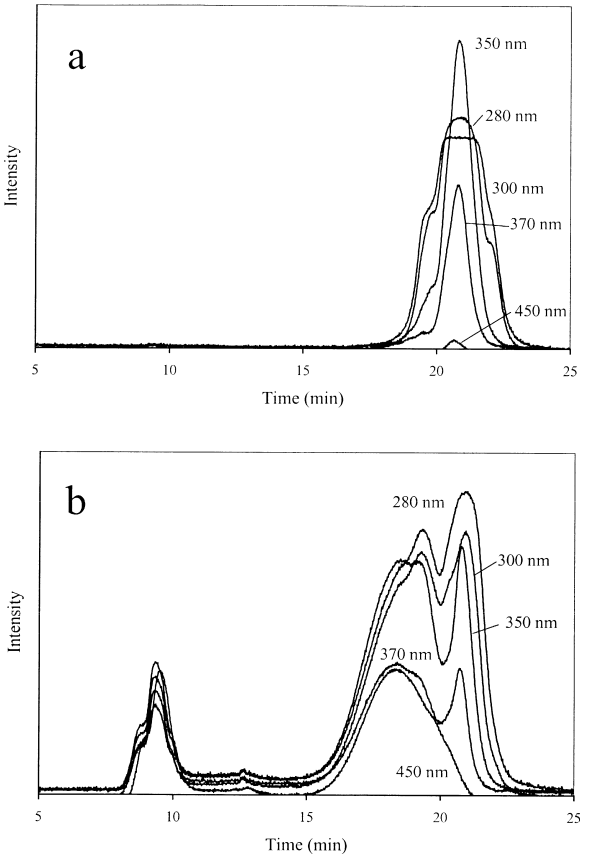

Fig. 2. SEC chromatograms of (a) parent and (b) polymerized anthracene oil.

evidence of a greater proportion of larger, early eluting molecules (before 10 min). The exclusion limit for this column, determined using polystyrene standards is at about 11 min, corresponding to the same time limit observed in Fig. 2 for the excluded material of both the anthracene oil and the product. We have recently shown that elution times in the present SEC system are relatively independent of structural features of the sample molecules [15]; it appears probable that the size-exclusion limit and the polystyrene size calibration apply equally to the standard and the samples although the precise level of agreement remains to be demonstrated. It must also be noted that the intensity of UV absorption by large and small molecules is different; the relative sizes of the peaks cannot therefore be taken as a quantitative indication.

The SEC chromatograms of AO1 are similar to those of complex samples derived from coals, which show a wide range of molecular sizes [14]. Two main regions can be distinguished. The first region, before the exclusion limit of the column at 11 min, consists of a single peak (peak 1) at about 9 min elution time. The excluded material is made up of molecules with structures bearing large aromatic ring systems, as indicated by the greater relative intensity of the signal for 450 nm. While the small compounds contained in the retained fraction show the maximum relative intensity for 280 nm. The second region (between 15 and 25 min) shows signal from material able to penetrate the porosity of the column packing; three partially resolved peaks can be observed (peaks 2, 3 and 4) at 350 nm, at 18.5, 19.1 and 20.7 min, respectively, and include most of the material.

Comparing with Fig. 2a, these data suggest that peak 4 (20.7 min) consists mainly of unreacted AO compounds. Peaks 2 and 3 are likely to be made up of oligomers formed from different amounts of monomers. The increase of relative absorbances at 450 and 370 nm indicated that aromatic ring cluster sizes increased in peaks 2 and 3 compared with the original AO sample.

The problem associated with the use of SEC for the determination of molecular mass distributions in complex coal-derived samples has been addressed in the current system [15,16]. There are no adequate PAH calibration standards commercially available for the higher molecular mass ranges. Once the ranges of GC–MS and probe MS are exceeded, the structures and functionalities of the components of the complex samples derived from coal are normally unknown; recent work using pyrolysis–GC–MS and ^{13}C-NMR has allowed some structural insights into fractions of a sample of coal tar pitch and a coal liquefaction extract [24,25]. In the absence of more realistic standard compounds, polystyrene appears to offer a reasonable compromise and covers a very wide range of mass and size. However, the present column has been tested using a range of PAHs [15,16] which cover the range of the components of AO; these molecular masses up to 550 u can be used to establish a separate curve in the range of 100–550 u. According to the retention time values obtained by Lázaro and co-workers [15,16] for a series of 19 PAHs (Fig. 3) with different structures (planar

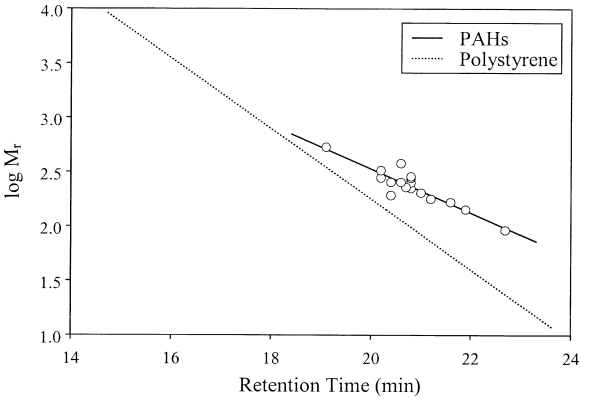

Fig. 3. Calibration curves with PAHs and polystyrene standards.

catacondensed, planar pericondensed, no planar and alkyl and/or phenyl substituted) the following equation is obtained:

$$\text{Log } M_r = 0.2034 t_R + 6.6003 \; (R^2 = 0.8324) \qquad (1)$$

The calibration curve is somewhat different from that obtained with the polystyrene standards (Fig. 3, dashed line), which is not best suited for PAHs with $M_r < 550$ u. As mentioned above, these differences (less than 1.5 min in every case) may be due to the more compact configurations of PAHs or to surface adsorption.

As discussed above and elsewhere [15,16], the delay in elution time causes an underestimation of molecular masses of aromatics when using the polystyrene calibration, although the trend in changes of mass remains similar. We have noted elsewhere [26] that when using tetrahydrofuran (THF) (a weaker solvent) as eluent where the surface adsorption is a problem, the difference in elution times of aromatics compared with polystyrenes is much greater than in the present system; perylene, mass 252 eluted more than 1 min after toluene, mass 92, more than 2 min after carbazole m/z 167 and considerably later than the permeation limit defined by polystyrenes.

It is possible to approach the molecular masses of the compounds responsible for peaks 2–4 of Fig. 2b by using Eq. (1). The excluded material of peak 1 however, can only be considered to have an effective molecular size greater than polystyrene standards of mass 300 000 u, since the peak elutes before the exclusion limit; the exclusion limit clearly applies to the material of the peak, as discussed above and extrapolation of the calibration line for aromatics cannot be considered to be entirely reasonable beyond mass 550. By evaluating the masses corresponding to the peak elution times using Eq. (1) (with equivalent values for the polystyrene calibration in parentheses), we have: peak 2: 704 (543), peak 3: 522 (336) and peak 4: 244 (99) u. The range of material in each peak would lead to a considerable overlap and indicate masses (compared with polystyrenes) up to about 7000 at 15 min (Fig. 2b). The corresponding chromatogram for original sample of anthracene oil (Fig. 2a) shows signal from about 18 min. The average M_r of AO determined from the percentage in area of the peaks of the gas chromatogram is about 190 u. Taking into account this value, the material eluted at 20.7 min (peak 4, average $M_r = 244$ u) would be a mixture of about 30% (w/w) of heavier compounds (''dimers'') and about 70% (w/w) of monomers. Peaks 2 and 3 would correspond to material with more complex structures. Similar results were reported by Mochida et al. [9] for the polymerization of pure aromatic hydrocarbons with HF/BF_3, on the basis of the M_r values obtained by field desorption (FD)–MS. However, the different wavelength absorbances of Fig. 2b suggest the aromatic structures of peaks 2 and 3 are considerably more complex than simple dimers, trimers, etc., and the real structures involved have not yet been investigated. According to this approach the largest components of the separated material (i.e., resolved by the column) would have an approximate M_r of 7000 u, whereas the M_r for the excluded material would be higher than 300 000 u. However, it is hard to understand the absence of components with M_r between 7000 and 300 000 u. A possible explanation for this apparent lack could be that molecules with a mass over 7000 u could not penetrate the porosity of the column packing because of their peculiar molecular shape.

The evidence from solution state ^{1}H-NMR in Fig. 4, indicates that substantial changes occurred between AO and the product. The signal at a shift of 7.2 became more intense in the product with many smaller shifts of intensity of other aromatic hydrogen peaks, in what is a very complex aromatic hydrogen

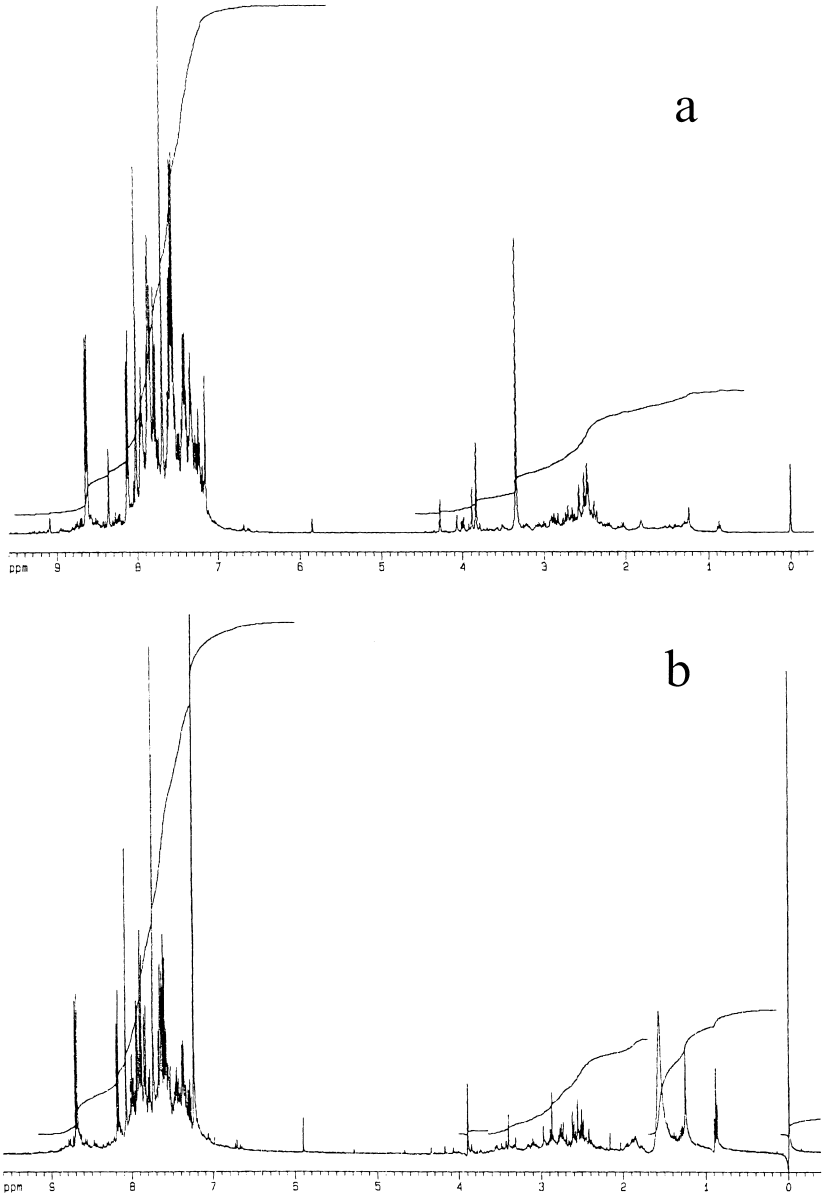

Fig. 4. ^{1}H-NMR spectra of (a) parent and (b) polymerized anthracene oil.

signal. In some cases, peaks were lost in the product compared with the oil but in other cases, peaks appeared in the product but not in the oil. In the aliphatic hydrogen region, shifts of relative intensity were also observed, with an increase in methyl (0.9 ppm), methylene (1.3 ppm) and water (1.6 ppm) in the product. The water may originate from reactions of phenolic groups but more probably, from the work-up of product after the reaction. The methyl and methylene peaks are presumed to come from the opening of cyclic aliphatic structures. The broad unresolved hump underlying the aromatic region peaks and to a lesser extent, the aliphatic region, may be considered to indicate the presence of large rigid

molecules in both oil and product. For rigid molecules, where the hydrogen atoms are not free to rotate, the spin–spin relaxation time varies with the third power of the molar volume and linewidths for such molecules tend to be very broad [27].

3.2. Fractionation of AO1 and analysis of the fractions

In order to study in more detail the molecular size and structure of the components of the excluded and separated materials of AO1, fractions from the SEC eluent were collected every 2 min from 9 to 25 min and chromatographed on the same column. The injection was made immediately after their collection to detect possible effects of the solute concentration on the mechanism of separation. This was done to test for changes in signal due to dilution, which would have suggested the presence of aggregates. If aggregates were formed as the excluded material, then the dilution in the collected eluent may lead to dissagregation, with elution at longer times, since the formation of aggregates is improbable in diluted solutions obtained by preparative SEC. Evidence presented elsewhere [15,22,28] tends to support the view that aggregates are not likely but cannot be ruled out completely.

SEC profiles of fractions 1, 5, 6, 7 and 8 are shown in Fig. 5 at 350 nm; the chromatograms have been area normalised for comparison. These fractions contain almost the total amount of the material. Fraction 1, obtained at the shortest elution time, was mainly composed of excluded material with a minor part of lower molecular mass material resolved by the column porosity. This shows it was the size and/or shape of the molecules that was mainly responsible for the exclusion. To the extent that dilution would be expected to disaggregate aggregated molecules, the data suggest that the formation of aggregates was not significant.

The amount of material isolated in fraction 2 was negligible; that in fractions 3 and 4 (13–17 min) was very small. However, when fractions 2 and 3 were chromatographed again, most of their material appeared in the region showing signal from excluded material. This unexpected finding has been observed previously [15] where a narrow fraction of the excluded peak of a coal tar pitch, eluted earlier on reinjection, than the previous elution time. The effect has been attributed to the different sample capacities of the excluded region and the retained region for sample, with overloading in the excluded region long before the sample capacity of the retained region overloaded. The material from the exclusion region appears to spread into later eluting (apparently lower M_r) fractions. To a lesser extent, the same effect was also observed in fractions 5, 6 and 7 (Fig. 5). In these fractions, a small amount of excluded material appears. SEC profiles in Fig. 5 show that separation mainly occurs following a size-exclusion mechanism, since the predominant molecular size decreased as the fraction number increased. A comparison of the profiles in Fig. 5 with that of the whole AO1 sample (Fig. 2b) suggests that most of the material of peak 2 is isolated in fraction 5, while the light material of peak 4 was found in fractions 7 and 8. Fraction 6 contained material of peaks 3 and 4. Fraction 7 appears to contain material, which overlaps with the material of fractions 6 and 8; the reason for this may be that the resolution of the column is not adequate to resolve broadly similar molecular sizes. The width of peaks for pure standards was about 2 min so considerable overlap between fractions collected at 2 min intervals would be expected. Finally, fraction 8 was very dilute and seems to contain a small amount of the lightest unreacted hydrocarbons of AO1.

Worthy of special attention is the wavelength at which fractions show the maximum intensity of UV absorbance, because this maximum is related with the size of polynuclear aromatic ring systems in the material. It was found that the higher the wavelength of the maximum intensity of UV absorbance, the greater the conjugated aromatic cluster size and as a consequence, the greater the molecular size of the material. In this respect the excluded material (largest apparent molecular mass) showed the highest intensity at 450 nm (not shown), suggesting that it contains larger polynuclear aromatic ring systems, while the material isolated in fractions 6, 7 and 8 showed the highest intensity at the lowest wavelength used (280 nm). In fraction 5 the separated material showed the highest intensity at 300 and 350 nm with small changes in intensity depending on wavelength. This suggests that the material of fraction 5 consists of components with a molecular size

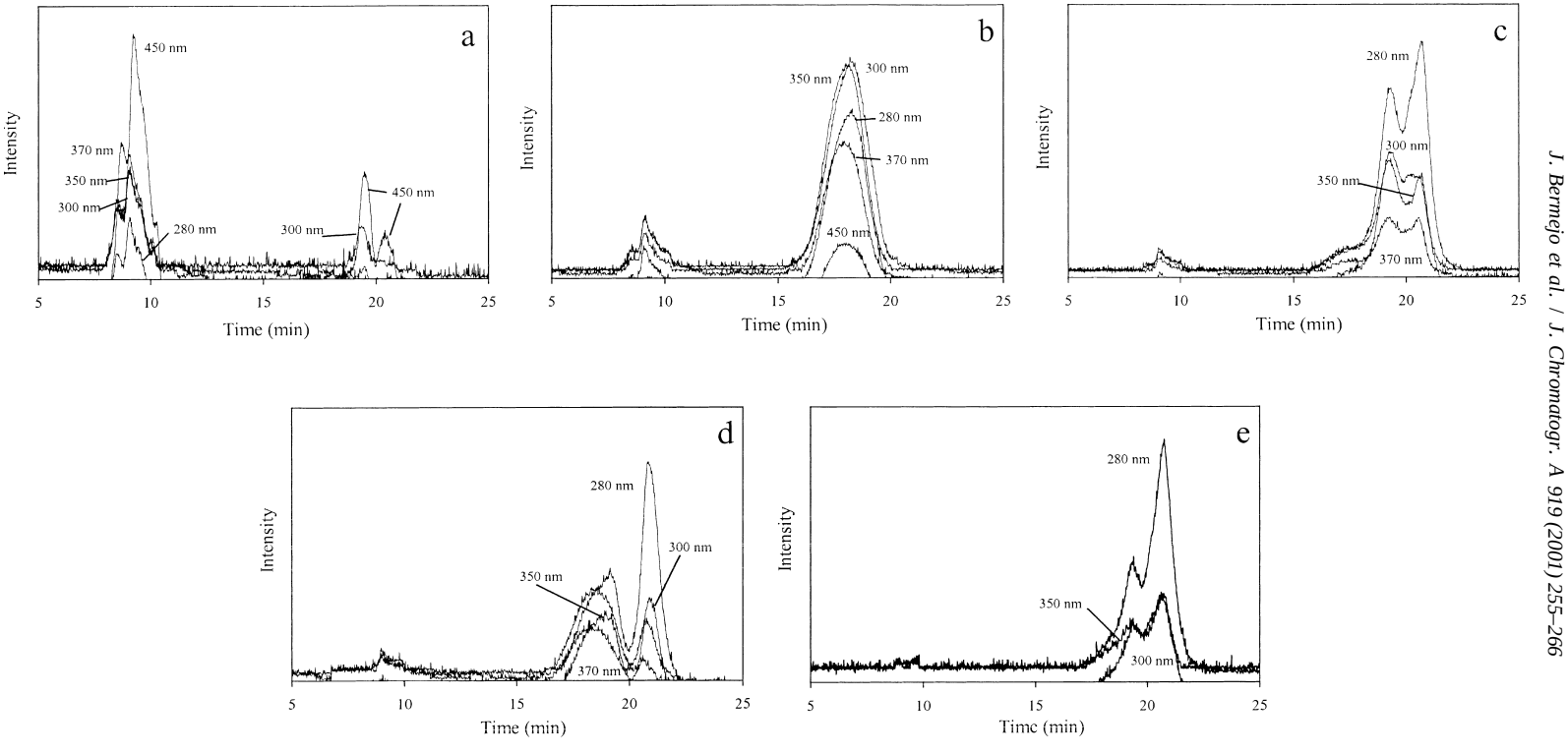

Fig. 5. Area normalised SEC profiles of: (a) fraction 1, (b) fraction 5, (c) fraction 6, (d) fraction 7 and (e) fraction 8, at 350 nm.

higher than that of fractions 6, 7 and 8; in parallel with these observations, fraction 5 eluted before fraction 6 and would be expected to be of larger molecular size.

3.3. UV-F spectroscopy of SEC fractions

We have previously reported observing that the size and frequency of occurrence of polynuclear aromatic ring systems embedded in large molecules increased with overall molecular mass [20]. In this work UV-F spectroscopy has been used to confirm trends of M_r values found in AO1 and its fractions. On this basis, the polymerization of AO is clearly reflected by the synchronous UV-F spectra of AO and AO1 (Fig. 6). Polymerisation not only produces a significant shift of fluorescence to longer wavelengths but also important changes in intensity. However, the quantitative information provided by the UV-F spectra of aromatic mixtures with a wide range of molecular sizes is limited because of the weak fluorescence of large aromatic systems, which can be swamped by the much greater intensity of smaller structures. On the other hand, in this particular case, it is necessary to bear in mind that besides polymerization, other structural features might occur, producing a shift of the spectrum to longer wavelengths. The formation of naphthenic rings and alkyl-substituents [7], and five-membered rings bearing quaternary carbon atoms, could contribute to this shift [29]. The fractionation of AO1 in order to shorten the range of M_r distributions could eliminate most of the problems mentioned above.

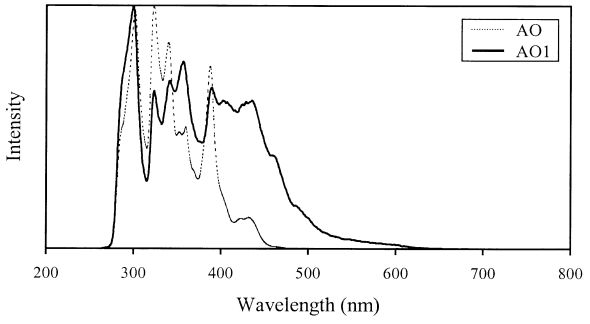

Fig. 6. Synchronous UV-F spectra of parent and polymerized anthracene oil.

The synchronous UV-F spectra of the fractions of the polymerized AO (i.e., AO1) are shown in Fig. 7. The spectra have been peak normalised in order to compare the positions of peaks between high and low molecular mass samples; the intensity of the former are very low. As was to be expected, the UV-F spectra of fractions 1 and 2 show very weak fluorescence, which confirms again that the excluded material consists of large polynuclear aromatic compounds. The signal shown in Fig. 7a is mainly the residual fluorescence of the solvent before 300 nm. A similar observation could be made about the spectra of the low intensity fractions 3 and 4, where the solvent peak before 300 nm can be observed. The spectrum of fraction 6 agrees with that of AO1 in the number and wavelength of the maxima and differs in the intensity of those at the shortest wavelength, which correspond to the lightest components. Therefore, from the point of view of UV-F spectroscopy, fraction 6 can be considered as containing most of the characteristic fluorescence features of AO1. In the same way, the UV-F spectrum of fraction 8 is similar to that of the unreacted AO, mainly differing in the intensity of the maxima, especially at high wavelengths (346 and 386 nm). This indicates that the components of AO1, which take the longest time to elute are the lightest components of AO.

The spectra of fractions 5 and 7 were similar. Both show the highest fluorescence intensity at about 360 nm, where the fluorescence of AO is very small (Fig. 6). Consequently, the fluorescence at 360 nm of fractions 5 and 7 must correspond to compounds formed during polymerization. The higher intensity of the fluorescence at longer wavelengths of both fractions with respect to that of the parent AO corroborates this assertion. The main difference between the two spectra consists of a small shift to a larger wavelength in the spectrum of fraction 5, in agreement with the larger molecular size of the components of this fraction.

3.4. Probe mass spectrometry of SEC fractions

The probe mass analysis of SEC fractions was carried out with the aim of testing the distribution of the PAHs and simple polymers of PAHs in AO1 (Fig. 1) among fractions 5, 6, 7 and 8. All the fractions

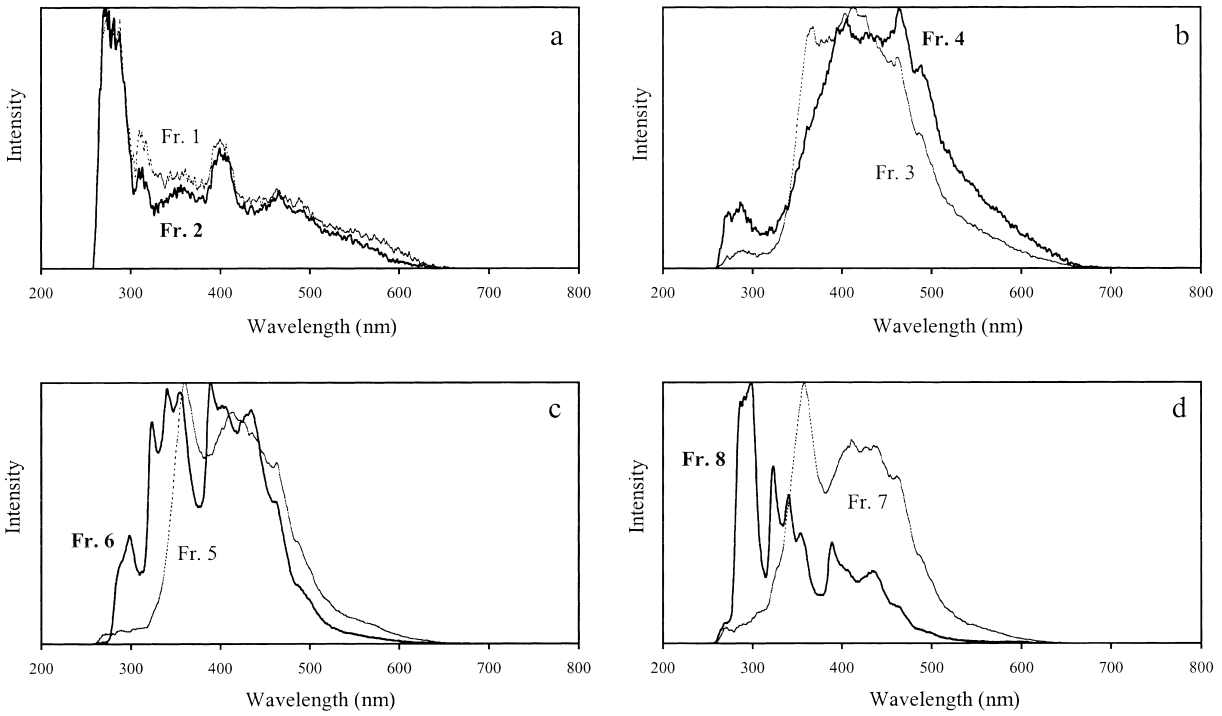

Fig. 7. Synchronous UV-F spectra of: (a) fractions 1–2, (b) fractions 3–4, (c) fractions 5–6 and (d) fractions 7–8.

were examined, but the spectra are not shown here. As might be expected from the large molecular size of the excluded material, the spectrum of fraction 1 only shows peaks of the solvent (m/z 99) and its derivative *N*-methylsuccinimide (m/z 113). This is also the case for fractions 2, 3, 4 and 5.

The mass spectra of fractions 6, 7 and 8 showed only PAH molecular ions for those components of anthracene oil corresponding to the heavier 3, 4 and 5 ring aromatics which would not evaporate with the solvent, NMP of boiling point 202°C. The spectrum of fraction 6 showed peaks of m/z corresponding to the largest PAHs of the AO (m/z 228, 252 and 276) and some others ascribable to the small dimers and simple polymers observed in the spectrum of Fig. 1 (m/z 304–306, 318 and 342). The main peaks in the spectrum of Fraction 7 showed m/z values of 202, 216 and 232, while those of fraction 8 gave m/z values of 178 and 202. Considerable overlap of mass ranges between fractions cannot be avoided.

The probe-mass spectra reveal the presence of only those aromatics which are volatile enough to evaporate in the high vacuum of the mass spectrometer but are not lost with the high-boiling solvent; the observed masses follow the expected trend of the size-exclusion mechanism of the separation process.

4. Conclusions

SEC, with polystyrene–polydivinylbenzene as stationary phase and NMP at 80°C as eluent indicated the formation of larger molecules resulting from the polymerization of anthracene oil with anhydrous $AlCl_3$. The SEC profile of polymerized anthracene oil shows excluded material (indicated by the polystyrene standards calibration to be equivalent in size to polystyrenes of mass greater than 300 000 u) and three others only partially resolved in the retained region at retention times of 20.7, 19.1 and 18.5 min, respectively. Using a calibration curve based on elution times of standard aromatic hydrocarbons with molecular mass ranging from 92 to 532

u, the molecular mass of the retained peaks were estimated and assigned to mixtures of simple polynuclear aromatic molecules identified by probe mass spectrometry and increasingly more complex materials.

SEC of time-based fractions collected from the SEC elution of AO1, the polymerized anthracene oil, which were much more dilute than the solution injected to the column, showed the absence of molecular aggregates. The excluded material therefore consists of large or/and voluminous macromolecules.

Synchronous UV-F spectra of the SEC fractions corroborated the SEC results on a qualitative level.

Acknowledgements

The authors would like to thank the FICYT (project PA-MAT95-02) for financial support and the University of London Intercollegiate Research Service (ULIRS) for provision of mass spectrometric and NMR facilities (Kings College). R.M. also thanks the CSIC/Royal Society for financial assistance for her stay at the Imperial College of London.

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