Size exclusion chromatographic investigation of the conversion of a precursor polymer to poly(*p*-phenylene)

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A substituted poly(cyclohexadiene) precursor polymer has been pyrolysed (aromatized) in *N*-methylpyrrolidinone solution to poly(*p*-phenylene). For aromatizations up to 40% the polymer remains in solution, but size exclusion chromatography shows that the initially narrow molecular weight distribution fractions become bimodal with a high molecular weight peak appearing even at low percentage aromatizations. At the same time, the main component of the polymer rapidly decreases in molecular weight. Size exclusion chromatography using detection specific for phenylene residues indicates that their concentration is the same across the whole distribution. These results were confirmed by fractionating a partially aromatized polymer. The data indicate that aromatization occurs both randomly and in sequences and is accompanied by scission. Molecules with long sequences of phenylene groups aggregate, forming the high molecular weight fraction observed by size exclusion chromatography. The low molecular weight fraction has the same degree of aromatization but the phenylene units are randomly distributed and do not aggregate intermolecularly.

(Keywords: size exclusion chromatography; aromatization; poly(*p*-phenylene))

INTRODUCTION

Poly(*p*-phenylene) (PPP) is a polymer that has been of interest for many years. In principle, highly linear PPP should have distinctive thermal, electrical and mechanical properties. Its highly conjugated structure makes it susceptible to manipulation of the conductivity by doping and it has also been used in light emitting diodes[1]. The linearity and symmetry of the molecule should lead to high crystallinity and high mechanical strength. Unfortunately, there are problems with the synthesis of the polymer. Direct routes to PPP have not been totally successful, since the polymer produced usually comprises only 10 to 12 phenylene rings and may also have stereochemical and chemical defects[2,3]. Furthermore, PPP is an intractable polymer to process[4] since it is insoluble and degrades before the melting point is reached.

An attractive alternative route to obtaining PPP is to synthesize a more easily handled precursor polymer which can be processed, and is only finally converted to PPP when the required end product or device has been produced. Marvel and Hartzell[5] were perhaps the first to utilize poly(cyclohexadiene)s for this purpose, and of late there have been attempts via the coupling of substituted aromatics to produce a soluble substituted PPP[6–8]. One of the most novel approaches has been that of Ballard *et al.*[9], who utilized microbial oxidation of benzene to produce a *cis*-dihydroxycyclohexa-1,3-diene which could be subsequently functionalized at the hydroxy groups, polymerized and converted to PPP. This polymer has been shown to provide high pre-tilt angles for liquid crystal displays[10]. This route also has some defects since the free radical polymerization of the substituted monomer introduces a proportion (10–15%) of 1,2 additions rather than the desired 1,4 addition. The resulting kinks in the molecule are thought to be the weak links at which chain fragmentation preferentially takes place in the conversion of the molecule from a random coil to the rigid rod PPP.

We discuss here the results of using size exclusion chromatography (s.e.c.) to investigate the influence of aromatization of poly(cyclohexadiene) precursor polymer, and we suggest a general mechanism by which the aromatization proceeds and the possible organization of the partially aromatized polymer.

EXPERIMENTAL

Synthesis of monomer

The monomer, 5,6-*cis*-dimethylcarboxycyclohexa-1,3-diene (DHCDDMC), was prepared from recrystallized 5,6-*cis*-dihydroxycyclohexa-1,3-diene (DHCD) obtained from the biological oxidation of benzene[9]. DHCD (200 g) was dissolved in pyridine (367 g) to form a 40% w/w solution, which was subsequently mixed with methylene

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chloride (5 l) and cooled to ~233 K with stirring. Methyl chloroformate (370 g) was then slowly added with stirring and at such a rate that no temperature rise took place. On complete addition of the chloroformate, stirring was ceased; the temperature of the mixture (now containing precipitated pyridine hydrochloride) was allowed to rise to ambient and the salt was filtered off. The filtrate was washed, by shaking repeatedly with a 10% (w/v) solution of sodium hydrogen carbonate, and finally washed with water before being concentrated by removal of methylene chloride on a rotary evaporator. The crude liquid product obtained was purified by vacuum distillation yielding ~440 g of clear liquid, which n.m.r. showed to contain ~15% aromatic impurities (usually as phenolic compounds from degradation of the DHCDDMC). These were removed by recrystallizing twice from isopropanol at 308 K and vacuum drying at 293 K overnight.

Polymerization

The DHCDDMC monomer obtained was polymerized in bulk using azobisisobutyronitrile as initiator. For this purpose the monomer and initiator, in a 100:1 molar ratio, were placed in a round-bottomed flask mounted in an oil bath at 323 K. When the contents of the flask had melted, they were repeatedly subjected to stirring under vacuum and nitrogen sparging to remove oxygen. The system was then held under vacuum for 70 h at 323 K, followed by 24 h at 328 K and finally 24 h at 333 K. On cooling, the contents of the flask were a clear, brittle glass. This was broken into fragments, dissolved in chloroform and precipitated in a large excess of well stirred hexane, which was filtered off and washed with 1:5 chloroform/hexane mixture before being dried at 373 K under vacuum. The yield of polymer was such that the percentage conversion based on the monomer was 67%.

Fractionation

The poly(DHCDDMC) obtained underwent fractional precipitation by addition of methanol to an acetone solution of the polymer, the polymer concentration being ~2% w/v. For this purpose a three-necked 2 l round-bottomed flask was modified by having a tap fitted to a blister blown in the flask bottom. The modified flask was mounted in a thermostat bath set at 298 K and the acetone solution of the polymer added. After insertion of a stirrer and nitrogen inlet and outlet, the flask and contents were left to come to equilibrium. Small volumes of methanol were then added into the vortex formed by the stirrer: addition was continued until the precipitate formed was permanent and judged to have the required mass. The temperature of the thermostat was then raised until the solution clarified (generally an increase of 5 K was sufficient) at which point stirring was ceased and the thermostat allowed to cool overnight to 298 K. The precipitate, which settled into the blister, was then drawn off, redissolved in acetone, precipitated in methanol, filtered and dried under vacuum at 313 K for at least 24 h.

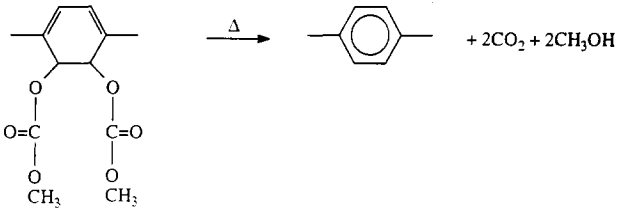
Size exclusion chromatography

S.e.c. analysis of the poly(DHCDDMC) fractions was performed using chloroform as the solvent and three PL gel columns (Polymer Laboratories, Church Stretton, Shropshire, UK) with pore sizes of 10^2, 10^3 and 10^5 Å. A refractive index detector was used with toluene as the flow marker, the system being calibrated using narrow molecular weight distribution polystyrenes which covered a relative molecular mass range from 162 to 4×10^8. The output from the refractive index detector was fed directly to a data capture unit (Polymer Laboratories) and subsequently analysed by a data station (Polymer Laboratories).

Some s.e.c. analyses were made on aromatized polymer which was subsequently fractionated in an attempt to relate degree of aromatization to molecular weight (see below). For these analyses, an additional u.v. detector was placed after the refractive index detector with the wavelength set to 320 nm for observation of the phenylene units of PPP sequences. In these cases, acetophenone was used as the flow marker.

Aromatization

Conversion of poly(DHCDDMC) to PPP, i.e. aromatization, is achieved by pyrolysis of the polymer either in solid state or in solution. The reaction scheme is:



The reaction is base catalysed, and in a suitably basic solvent the reaction takes place at lower temperatures than in the solid state. For this reason, the aromatization studies reported here were made using solutions in *N*-methylpyrrolidinone (NMP). There are a number of additional advantages to this: firstly, the polymer remains in solution up to 40% conversion to PPP; second, NMP is a high boiling solvent which permits relatively high temperatures to be used so that aromatization proceeds at a reasonable rate. However, NMP must be maintained dry and used under a nitrogen atmosphere, otherwise the solvent discolours rapidly. All aromatizations used here were performed at 448 K.

Before preparation of partially aromatized samples was begun, a number of preliminary aromatization reactions were made in order to note the progress of reaction and to attempt to quantify the kinetics of the reaction. A 5% solution of poly(DHCDDMC) in NMP was maintained at 448 K and small samples withdrawn at 15 min intervals and precipitated in methanol. After drying, each of these specimens was subjected to thermogravimetric analysis to ascertain the degree of aromatization at the point where the solution was quenched by precipitating in methanol. Knowing the mass of the partially aromatized specimen, ω_1, and the mass after 100% aromatization had been achieved by thermogravimetry, ω_f, the percentage aromatization of the quenched specimen was calculated from:

$$\% \text{ Aromatization} = [(3\omega_f - \omega_1)/2\omega_f] \times 100$$

From these data it was observed that the use of time of aromatization as a means of determining the percentage aromatization was highly unpredictable (*Figure 1*). Furthermore, it was noted that, up to 40% aromatization, the precipitated polymer could be redissolved in NMP. Above this percentage, a gel formed which would not redissolve in NMP after precipitation. However, for

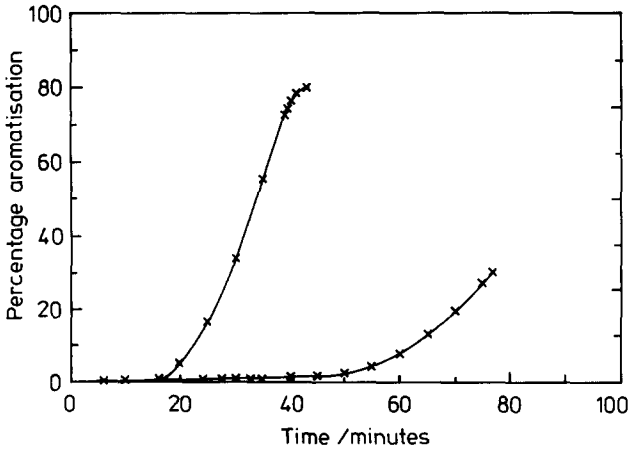


Figure 1 Percentage aromatization of poly(DHCDDMC) as a function of time for two specimens

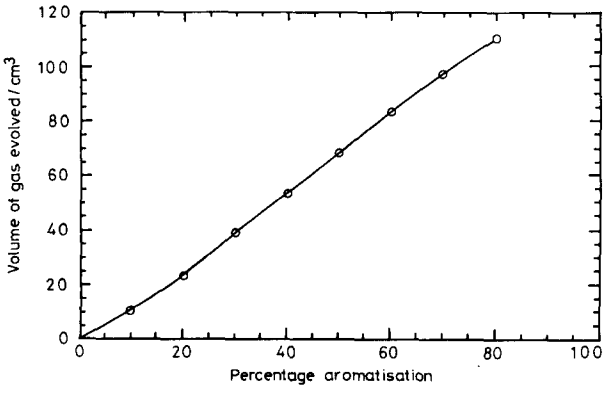


Figure 2 Correlation of evolved gas volume with percentage aromatization

aromatizations up to 60%, the precipitated polymer could be redissolved in chloroform. Above this higher percentage aromatization, the polymer could not be redissolved in either solvent or in dimethylsulfoxide or hexafluoropropanol. Because the time of aromatization could not be relied on to determine the percentage aromatization, the volume of CO_2 evolved was investigated. *Figure 2* shows the volume of CO_2 evolved as a function of the percentage aromatization of the polymer subsequently obtained from thermogravimetric analysis. Evidently there is a linear correlation between the two parameters. Nine fractions of poly(DHCDDMC) were aromatized to varying extents, from 0 to 40%, by quenching the reaction by pouring the solution into methanol immediately the required volume of carbon dioxide had been evolved. The polymer was filtered off, washed with methanol and dried under vacuum before being stored in a freezer.

RESULTS

Table 1 reports the relative molar masses and polydispersities obtained from s.e.c. on the poly(DHCDDMC) fractions before aromatization. It should be noted that these, and all molar masses reported here, are obtained using a polystyrene calibration of the s.e.c. columns. However, we are not concerned with *absolute* values of molecular weight; our aim is to gain some insight into the structural changes wrought by aromatization.

Typical computed molecular weight distributions from s.e.c. data, of fractions whose initial molecular weights were high, intermediate and low, as a function of aromatization are shown in *Figure 3*. The most noticeable

Table 1 Relative molar masses and polydispersity of fractions of poly(DHCDDMC)

Fraction	$\bar{M}_n(\times 10^3)$	$\bar{M}_w(\times 10^3)$	$\bar{M}_w/\bar{M}_n$
As polymerized	87	200	2.29
H_i	1225.0	2312.0	1.89
A	256.8	405.5	1.58
B	229.0	308.0	1.35
C	193.2	260.0	1.35
D	134.0	178.0	1.33
E	102.0	125.0	1.23
F	91.6	119.5	1.31
G	66.4	84.0	1.27
L_o	17.1	26.5	1.55

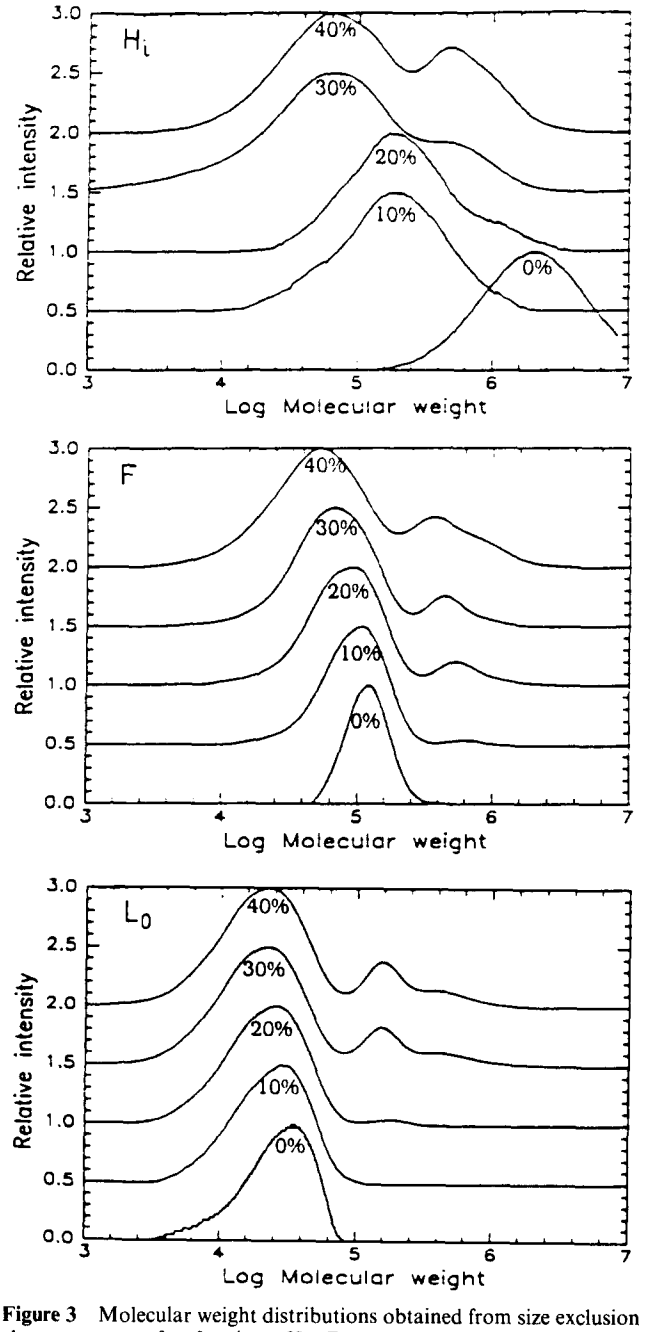


Figure 3 Molecular weight distributions obtained from size exclusion chromatograms for fractions H_i, F and L_o at varying percentage aromatizations

Table 2 Average molar masses ($\times 10^3$) as a function of percentage aromatization

	Aromatization (%)									
	0		10		20		30		40	
Fraction	M_w	M_n	M_w	M_n	M_w	M_n	M_w	M_n	M_w	M_n
H_i	2312.00	1225.00	252.00	135.00	243.00	105.50	147.00	153.00	242.00	44.00
A	405.50	256.80	304.00	191.00	273.00	129.50	357.50	91.50	569.50	69.00
B	308.00	229.00	206.00	124.00	207.50	98.00	241.50	80.50	–	–
C	260.00	193.20	208.50	116.00	205.00	81.50	192.00	76.50	215.00	37.50
D	178.00	134.00	149.50	92.00	198.50	96.00	197.00	68.50	266.00	39.50
E	125.00	102.00	158.50	99.00	110.00	664.00	87.00	538.00	–	–
F	119.50	91.60	110.00	74.50	139.50	61.50	117.50	49.00	154.00	36.00
G	84.00	66.40	80.50	54.50	84.50	49.00	–	–	152.00	32.00
L_o	26.50	17.10	26.00	17.50	26.00	15.50	107.30	18.80	62.00	15.50

Table 3 Peak molar masses ($\times 10^3$) for main (M_m) and secondary (M_s) peak, and percentage secondary peak (%S)

	Aromatization (%)													
	0			10			20			30			40		
Fraction	M_m	M_s	%S	M_m	M_s	%S	M_m	M_s	%S	M_m	M_s	%S	M_m	M_s	%S
H_i	192.30			–	–	–	–	–	–	65.50	417.00	15.00	66.00	496.00	32.00
A	415.00			–	–	–	–	–	–	157.00	774.50	31.00	92.50	771.00	32.00
B	324.00			186.50	940.00	2.00	152.00	798.00	5.00	132.00	748.00	20.00	–	–	–
C	239.00			157.50	723.00	6.00	150.00	807.00	11.00	132.50	694.00	14.00	51.50	423.00	30.00
D	167.00			–	–	–	152.50	872.00	9.00	109.50	606.00	20.00	55.50	458.00	33.00
E	120.50			128.50	799.00	5.00	116.00	664.00	9.00	87.00	538.00	20.00	–	–	–
F	118.50			108.50	630.00	2.00	91.00	546.00	11.00	68.00	449.00	12.00	52.50	367.00	24.00
G	80.00			64.50	484.00	3.00	60.50	398.00	7.00	–	–	–	47.50	289.00	29.00
L_o	29.50			–	–	–	26.00	175.00	2.00	51.50	152.00	19.00	22.00	153.00	21.00

feature of the chromatograms is the occurrence of a second peak at higher molecular weight on even the smallest amount of aromatization. This second peak grows in amplitude as the percentage aromatization increases and the peak maximum moves to slightly lower values of molecular weight as the aromatization proceeds. This shift to lower molecular weight with increased percentage aromatization is also seen in the main chromatographic peak, which we initially identify with unaromatized poly(DHCDDMC). This shift to lower molecular weight of the main peak is most marked for the fraction with the highest initial molecular weight (fraction H_i) and less noticeable for the lowest molecular weight fraction (fraction L_o).

Table 2 reports the molecular mass averages for all the partially aromatized fractions for which results were obtained. These data were obtained by analysing the whole of the chromatogram, i.e. including both the main and the secondary peak which develops as aromatization proceeds. All of the fractions except fraction L_o show the same behaviour as aromatization proceeds. The weight average molecular weight initially falls at low percentage aromatization but then rises as aromatization reaches 40%. By contrast, the number average molecular weight falls continuously as aromatization proceeds. We also note from *Table 2* that, on average, the polydispersity index increases as the aromatization proceeds. In most cases, we have been unable to resolve the secondary peak in the chromatogram sufficiently to analyse it separately in order to obtain molar mass values for this peak. However, we have been able to identify the molecular weight at each peak maximum and we have attempted to estimate the contribution of the polymer in the secondary peak by taking the ratio of the secondary peak area to the total area under the chromatogram. However, these latter parameters must be viewed with caution owing to the difficulty of resolving these secondary peaks from the main peak, and the change in sensitivity due to changes in refractive index on aromatization. These values are reported in *Table 3* together with the peak molar mass for the main peak in the chromatogram. From these data we note that both main peak and secondary peak molar mass decrease with percentage aromatization; for all fractions except fraction L_o, the main peak molar mass values appear to be converging when the percentage aromatization is high. A value for M_m of $\sim 50 \times 10^3$ to 60×10^3 seems to be approached. Furthermore, the average percentage of the total sample in the secondary peak increases as the percentage aromatization increases. Thus for 10% aromatization, $4 \pm 2\%$ of the total mass is in the secondary peak, and this increases to $8 \pm 3\%$, $18 \pm 6\%$ and $28 \pm 4\%$ for aromatization percentages of 20, 30 and 40, respectively.

Since the secondary peak becomes an increasing proportion of the chromatogram as the aromatization proceeds, a possible explanation of these observations is as follows. Aromatization, when initiated on a poly(DHCDDMC) segment, catalyses aromatization of contiguous segments and a blocky structure results with long sequences of PPP being formed. The PPP blocks,

being insoluble in NMP, aggregate, and the aggregate is solubilized by the unconverted poly(DHCDDMC). Inspection of the number average molar masses and peak molar masses in *Tables 2* and *3* also shows that aromatization is accompanied by a decrease in molar mass for both peaks, and hence aromatization is accompanied by considerable fracture of the molecules.

In order to ascertain whether the majority of aromatization was confined to the secondary peak, some further experiments were made on unfractionated poly(DHCDDMC). Samples of this polymer were aromatized to different extents in NMP using the same procedure described earlier, and the relative molar masses were obtained via s.e.c. but with an additional u.v. detector placed after the usual refractive index detector. This u.v. detector was set to a wavelength of 320 nm where there is strong absorption by the partially aromatized polymer but a negligible contribution from unaromatized polymer. For calibration purposes using standard polystyrenes, the absorption wavelength was set at 260 nm. Typical dual chromatograms are shown in *Figure 4*; the bimodality is clearly evident in the refractive index detector trace as aromatization proceeds, and although it is also evident in the u.v. traces, there is considerable broadening and spreading of the chromatograms for the aromatized specimens. This broadening was evident at both high and low molecular weight ends of the chromatogram, and for aromatizations above 20% the tails of the chromatograms spread beyond the limits of total exclusion and total permeability for the s.e.c. columns used. Results from the molar mass analyses (not tabulated here) of both refractive index curves and u.v. curves were in fair agreement, and the values of peak molar mass from the main peaks were in exact agreement. For the secondary peak, the maximum obtained from the u.v. curve was generally at a lower molar mass than that from the refractive index detector. However, the main conclusion to be drawn from these experiments is that aromatization is essentially uniform over the whole molecular weight range and does not appear to be dominant in the high molecular weight secondary peak observed on aromatization. An assumption that is made here is that the u.v. absorption does not alter for a sequence of phenylene groups and a single phenylene group in the partially aromatized polymer.

To explore this aspect further, a large amount (~2 g) of unfractionated polymer was aromatized in NMP solution to 30% conversion. Around 1.3 g of partially aromatized polymer was obtained, which was dissolved in chloroform to make a 1% (w/v) solution. This was then fractionated by addition of hexane and three fractions were recovered, each of ~0.2–0.3 g. S.e.c. chromatograms for the unfractionated, partially aromatized polymer and each of the fractions are shown in *Figure 5*. Although there is overlap between the peaks, it is evident that fractions 1 and 3 are very different from each other. Analysis of the complete chromatograms for relative molar masses produced the values tabulated in *Table 4*. Each fraction was then further analysed by thermogravimetry, elemental analysis, mass spectrometry, ^{13}C n.m.r. (deuterochloroform solution) and Fourier transform i.r. spectroscopy on a film cast from chloroform. The n.m.r. and mass spectra revealed little difference between the fractions, and percentage aromatizations were calculated from the other techniques. The results of these calculations are shown in *Table 5*. The absolute agreement between each method is around ±1%; however, all three methods have the same common features,

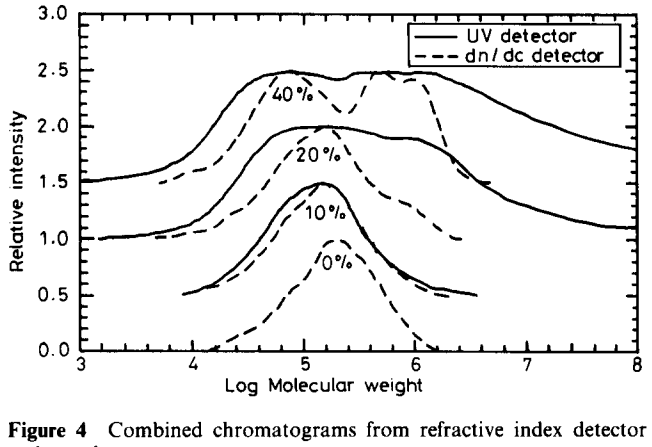


Figure 4 Combined chromatograms from refractive index detector and u.v. detector

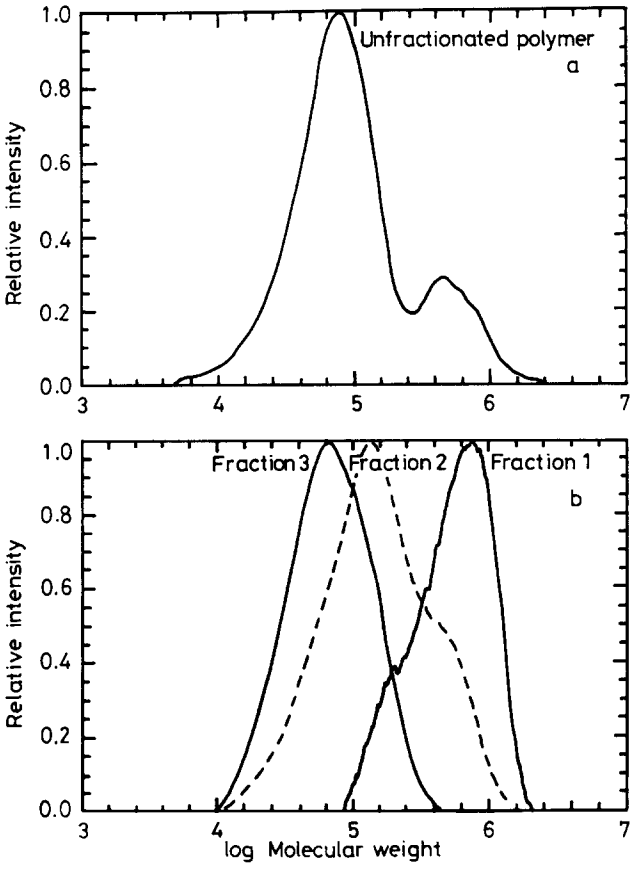


Figure 5 Size exclusion chromatograms for (a) an unfractionated poly(DHCDDMC) sample with an average aromatization of 30%, and (b) three fractions obtained from the original specimen

Table 4 Relative molar masses and peak molar mass (M_p) for partially aromatized (30%) poly(DHCDDMC) and fractions obtained

Sample	$\bar{M}_w(\times 10^3)$	$\bar{M}_n(\times 10^3)$	$M_p(\times 10^3)$	$\bar{M}_w/\bar{M}_n$
Unfractionated	145	53	74(449)[a]	2.7
Fraction 1	589	384	714	1.5
Fraction 2	202	88	134	2.3
Fraction 3	79	49	65	1.6

[a] Secondary peak in chromatogram

Table 5 Percentage aromatizations, calculated from different techniques, for fractions from an unfractionated partially aromatized (30%) sample

Fraction	Thermogravimetry	Elemental analysis	*FT*i.r.
1	31.4	33.6	33.1
2	30.1	32.3	30.0
3	28.5	30.7	27.2

namely no large difference in percentage aromatization between the fractions, but a small decrease between fraction 1 and fraction 3. These results confirm the observation based on the u.v. detected chromatograms, i.e. that the concentration of phenylene groups is approximately constant over the whole molecular weight range.

DISCUSSION

The complete pyrolysis of poly(DHCDDMC) to PPP is expected to be accompanied by a decrease in weight of 66.37%, hence the anticipation is that the number average molecular weight should also decrease by this percentage. For many of the fractions of poly(DHCDDMC) investigated, the decrease in $\bar{M}_n$ was much larger than theoretical predictions (*Figure 6*), consequently we conclude that aromatization is accompanied by an increase in the number of molecules present, i.e. a scission process takes place in parallel with aromatization. Since $\bar{M}_n$ values are proportional to the number of molecule ends present, the occurrence of scission accounts for the decrease in $\bar{M}_n$ observed. Aromatization is also accompanied by an increase in $\bar{M}_w$; this observation may be explained by aggregation taking place between partially aromatized molecules where there are sufficient contiguous phenylene units that these sequences become insoluble, but are able to remain solvated by aggregation of the phenylene block sequences which are stabilized in solution by unconverted poly(DHCDDMC) units in the same molecule. This aggregation becomes significant when aromatization is greater than 20%, which is where the secondary peak in the s.e.c. chromatograms becomes a notable contribution. This is also the percentage aromatization above which Ballard *et al.*[9] noted a marked increase in the viscosity of NMP solutions of these polymers. They attribute this increase primarily to the increased molecular size due to rod-like sequences in the molecule, leading to solution behaviour more akin to a rigid rod structure than a random coil. They also make a passing comment that such an increase could also be due to aggregation via π–π interaction between phenylene segments. The results obtained here suggest that it is this aggregation which dominates the solution properties and the aggregates are clearly visible as the secondary peak in the chromatogram, which although constituting only a small proportion of the total sample is of much higher molecular weight. An approximate idea of the number of molecules in the aggregates can be obtained by dividing M_s values in *Table 3* by M_m values for the same percentage aromatization; this process assumes that the molecules in the secondary peak all started with the same peak molar mass as the main peak molar mass. This is by no means true, since the aggregate may contain molecules of lower total percentage aromatization with long phenylene sequences, which were formed at an earlier stage in the process and thus have a higher molecular weight. On the basis of this simplistic approach, the number of molecules per aggregate is on average from five to seven.

There is clear evidence that aromatization is not confined to those molecules wherein long sequences of phenylene units occur. The analysis of the fractionated partially aromatized polymer shows that the phenylene content varies little between the fractions, even though the molecular weights differ markedly. What appears to be happening during aromatization is that the conversion takes place both randomly and in a concerted fashion throughout the reaction. Concerted aromatization leads to long sequences of phenylene units which aggregate, owing to their insolubility, and form higher molecular weight entities which remain in solution. These concerted aromatizations lead to fracture of the molecule where they encounter a 1,2 unit, because of increased steric strain arising from the rod-like configuration of the aromatized sequences. However, to maintain solubility, the PPP sequences must retain some long poly(DHCDDMC) to solvate the whole assembly. The fracture process is clearly more complex than can be explained merely by the presence of 1,2 addition units. Grubbs and co-workers[11,12] succeeded in synthesizing a linear precursor where there was no 1,2 addition. Contrary to expectations, the linear precursor polymer underwent more fracture on pyrolysis than the 'kinked' polymer used here, an observation that Grubbs *et al.* attribute to the fracture temperature of the stereoregular molecule being lower than the pyrolysis temperature. Hence, long sequences of regular 1,4 addition may also be undergoing fracture as well as aromatization; the kinetic competition for these two events is not known and thus we cannot speculate as to the relative rates.

The results of the analysis of the s.e.c. data may be open to question on the basis of the change in hydrodynamic properties of the partially aromatized molecules. We dismiss the notion of rigid rod-like molecules being formed on aromatization since the evidence obtained here and in other experiments[13] does not support this view. Turning now to the influence of aggregation on the s.e.c. data, aggregation leads to a

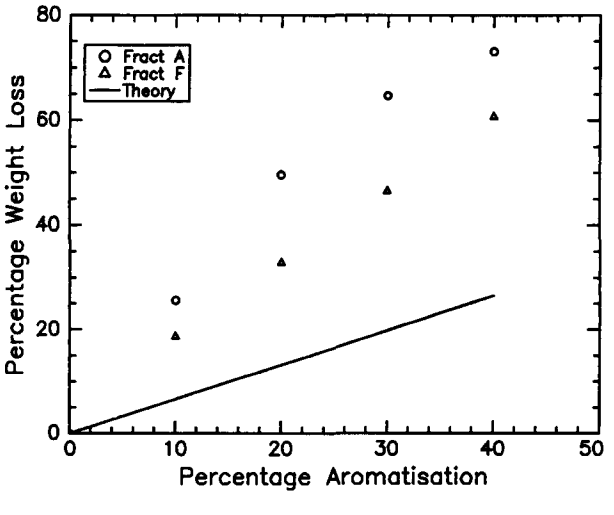


Figure 6 Percentage weight loss based on number average molecular weights as a function of aromatization: —, theoretical weight loss based on stoichiometry

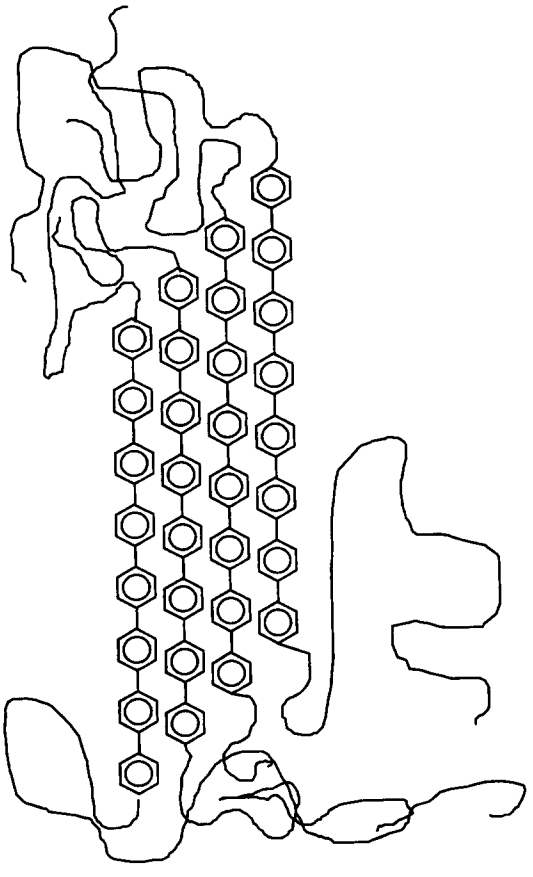


Figure 7 Schematic sketch of possible organization of partially aromatized polymer in aggregates

structure of larger hydrodynamic volume and consequently the aggregates would appear at higher molecular weights in the distribution. Consequently this behaviour is entirely consistent with our analysis.

We believe that the polymer in solution on aromatization in NMP solution consists of phenylene groups randomly distributed along the molecule and where there has been significant chain fracture leading to an overall reduction in molecular weight. The second and minor component contains molecules where the phenylene groups are in continuous sequences which have aggregated together, but where there are still significantly long poly(DHCDDMC) units which will solubilize the assembly. If the aggregate is held together by π–π interaction in the phenylene rings, then this suggests the lath-like structure shown in *Figure 7*. This structure is rather akin to a multi-arm star, wherein the arms may be polydisperse; the notion of this structure being present, especially at high percentage aromatizations, will be discussed in a subsequent paper on small angle neutron scattering from these solutions.

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