absorptivity coefficient with frequency would be required for quantitative analysis. To add to the misery, the validity of the van't Hoff procedure to determine the enthalpy of hydrogen bond formation must be questioned when we have direct evidence that the average strength of the hydrogen bond is not constant with temperature. We reluctantly conclude that we cannot simply describe the average strength of the intermolecular hydrogen bond in polyurethanes and polyamides in terms of a single ΔH.

The carbonyl stretching region of the infrared spectrum of PU64, which is analogous to the amide I region of polyamides, contains contributions attributed to ordered and disordered hydrogen bonded carbonyl groups together with "free" groups. Distinction between ordered and disordered hydrogen bonded carbonyl groups is a consequence of dipole/dipole interactions. The difference between the absorptivity coefficients of the "free" and hydrogen bonded carbonyl bands is significant but not radical as in the case of the N–H stretching mode. Accordingly, quantitative analysis is feasible with a procedure that accounts for the variation of absorptivity coefficients of the different carbonyl bands. Approximately 40% of the carbonyl groups in PU64 are "free" at 200 °C in the amorphous state.

The infrared band observed in the spectrum of PU64 at approximately 1540 cm^{-1} is akin to the amide II band in polyamides and contains an appreciable contribution from the N–H in-plane bending vibration. The striking shift to lower frequency with temperature is again an indication of the weakening of the hydrogen bonds. Significant changes in the spectra recorded at different temperatures are also seen in the region below 1500 cm^{-1}. An undistorted difference spectrum, representing the preferred polymer chain conformation perturbed by intermolecular hydrogen bonding, was successfully obtained by subtracting the amorphous spectrum from that of a semicrystalline spectrum, both recorded at the same temperature. The degree of order suggested by the subtraction procedure was in agreement with that determined independently from curve fitting the carbonyl region of the spectrum.

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Registry No. (Hexamethylene diisocyanate)·(1,4-butanediol) (homopolymer), 25748-74-7; poly(1,4-butylene hexamethylenecarbamate), 25035-42-1.

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Mass Spectrometric Analysis of the Thermal Degradation Products of Poly(*o*-, *m*-, and *p*-phenylene sulfide) and of the Oligomers Produced in the Synthesis of These Polymers

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ABSTRACT: Gel permeation chromatography and mass spectrometry have been used to detect and identify the oligomers formed in the polymerization reactions leading to poly(*o*-phenylene sulfide) (*o*-PPS), poly(*m*-phenylene sulfide) (*m*-PPS), and poly(*p*-phenylene sulfide) (*p*-PPS). The thermal degradation of *o*-PPS, *m*-PPS, and *p*-PPS was investigated by direct pyrolysis in the ion source of a mass spectrometer. The results indicate that *o*-PPS, *m*-PPS, and *p*-PPS decompose, producing cyclic oligomers. The distribution of the pyrolysis products is different in the three cases and is dependent on the structure of each isomeric polymer.

Introduction

The formation of cyclic oligomers in polycondensation reactions is a phenomenon frequently observed.[1-5]

Current methods of detecting oligomers contained in polymer samples are based on gas, liquid, and size-exclusion chromatography, followed by a suitable method of structural identification. These techniques are indeed powerful, but sometimes low volatility of samples, low solubility, and low resolution problems in gel permeation chromatogtraphy (GPC) make alternative and rapid methods of detection and identification for mixtures of low molecular weight compounds highly desirable.

Mass spectrometry (MS) is particularly suitable to the detection of these materials since they are volatile under

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Table I
Viscosity, Temperature of Maximum Rate of Polymer Degradation (PDT), Residue of Polymers I–IV, and Temperature of Maximum Evolution Rate of Cyclic Oligomers Formed in the Synthesis of These Polymers

polymer	η_{inh}	PDT, °C	%R[a]	temperature of maximum evolution,[b] °C					
				dimer	trimer	tetramer	pentamer	hexamer	heptamer
I, *o*-PPS	0.05	430	6	105	140	210	280	320	
II, *m*-PPS	0.1	520	11		185	225	290	330	370
III, *p*-PPS	ins	560	37						
IV, *p*-PPS[c]	ins	560	42			270	300	335	375

[a] Residues taken at 800 °C, from TG experiments under nitrogen. [b] MS experiments at a heating rate of 10 °C/min. [c] After heating at 350 °C for 3 h.

high vacuum at relatively low temperatures, at which polymers remain undecomposed and therefore undetected.[4-6]

We have been interested in investigating by direct pyrolysis mass spectrometry (DPMS) the effect of structure on the composition of thermal degradation products of poly(phenylene sulfide) (PPS) and have synthesized the three (ortho, meta, and para) PPS isomers (Table I). Furthermore, we have used MS to detect and identify the oligomers formed in the polymerization reactions (Table I).

Our results show that *o*-, *m*-, and *p*-PPS decompose mainly through thermal processes, producing cyclic oligomers. A marked structural effect is observed in the distribution of the cyclic oligomers of the three polyphenylene sulfide isomers.

Furthermore, the distribution of the oligomers produced in the pyrolysis of *o*- and *m*-PPS is identical with that of oligomers formed during the polymerization reactions.

Experimental Section

Polymerization Reactions. All the polymers were prepared starting from *o*-, *m*-, or *p*-dibromobenzene and disodium sulfide in *N*-methyl-2-pyrrolidone (NMP) as solvent, according to the procedure of Edmonds and Hill.[9] In a typical procedure 6.0 g of $Na_2S{\cdot}9H_2O$ (0.025 mol) were mixed with 8 mL of NMP in a Pyrex ampule under nitrogen stream and heated for 1 h at 160 °C in a silicone oil bath. $C_6H_4Br_2$ (0.02 mol, 5.9 g) was added to the cooled mixture. The ampule was sealed with a torch under vacuum, placed in a reactor, and heated at 230 °C for 150 h. After cooling, the ampule was opened and the contents were poured in diluted HCl and boiled under stirring. The solids were filtered, water-washed, and dried under vacuum.

Cyclic Oligomer Extraction. *o*-PPS. The crude polymer was refluxed under stirting in acetone and an insoluble residue was filtered off. The acetone portion was dried in a rotary evaporator and the residue was analyzed by MS and gel permeation chromatography (GPC). It resulted essentially constituted of thianthrene and traces of higher oligomers.

***m*-PPS.** The crude polymer was dissolved in hot NMP. The white powder precipitated on cooling, was poured in water, was filtered, and was dried under vacuum. GPC and MS analyses show that it is constituted of cyclic oligomers from trimer to heptamer and others of higher molecular weight. The most abundant component, cyclic trimer, was separated by sublimation at 170 °C under vacuum and crystallized from toluene/ethanol (mp 127–128 °C); ^1H NMR analysis ($CDCl_3$) gave a complex multiplet centered at 7.3 ppm.

***p*-PPS.** The crude polymer was refluxed under stirring in acetone. The insoluble residue was identified as poly(*p*-phenylene sulfide) (*p*-PPS). The acetone-soluble fraction was dried in a rotary evaporator and the residue was analyzed by MS. Only traces of cyclic oligomers were found.

Thermal Treatment of *p*-PPS. *p*-PPS (0.1 g) was placed in a Pyrex ampule and sealed under vacuum. This ampule was maintained at 350 °C for 3 h. MS analysis of the treated sample shows the presence of cyclic oligomers (from tetramer to heptamer), distilling in a wide range of temperature (Table I), before polymer thermal degradation occurs.

Viscometry. Inherent viscosities of the polymers investigated ($\eta_{inh} = \ln \eta_r/c$, $c = 0.5$ g/dL) were measured in a Desreux–Bishoff suspended level viscometer that contains a coarse sintered-glass filter attached just below the reservoir through which the solution passes as it rises into the capillary. Pertinent values are reported in Table I.

Thermogravimetry. A Perkin-Elmer thermal analyzer TGS-2 was used to determine the thermal stability of the samples. Experiments were carried out on a sample of about 2 mg under a nitrogen flow rate of 60 mL/min and a furnace heating rate of 10 °C/min up to 800 °C. Temperatures of maximum rate of polymer degradation (PDT) and residues at 800 °C (%R) are collected in Table I.

Mass Spectrometry. Pyrolysis was carried out by the direct insertion inlet of a Kratos MS 50 S double-focusing mass spectrometer, according to a technique described elsewhere;[6] the heating rate was 10 °C/min. Electron impact (EI) mass spectra were obtained at 18 eV. Chemical ionization (CI) NH_3 spectra confirm the EI results and are not reported here for brevity.

GPC Analysis. A Waters 6000 A apparatus equipped with four μ-Styragel columns (in the order 500, 1000, 10000, 100 Å pore size) was used. A differential refractometer Model R 401 from Waters was used as the detector. The analyses were performed at 25 °C in tetrahydrofuran (THF) as eluent at a flow rate of 1 mL/min.

Results and Discussion

Detection and Identification of the Oligomers Formed in the Polymerization Reactions. As an example, the analysis of the crude *m*-PPS is illustrated in some detail.

The GPC tract in Figure 1 shows that the sample contains a series of oligomers and raises the problem of their structural identification. Mass spectrometric detection and identification of oligomers contained in the crude *m*-PPS sample was achieved by introducing the sample into the ion source of the MS by the direct insertion probe for solid samples (DIP). The probe temperature was then gradually increased on a linear program (10 °C/min).

The total ion current (TIC) curve corresponding to the crude *m*-PPS sample shows an increment at low temperatures before the evolution of pyrolytic products originating from polymer decomposition (>450 °C), and five EI mass spectra detected in this temperature range are reported in Figure 2.

In the mass spectra in Figure 2, parts a–c, the peaks at m/z 324, 432, and 540 correspond to cyclic trimer, cyclic tetramer, and cyclic pentamer, respectively. The mass spectrum in Figure 2d is a mixture of cyclic pentamer (m/z 540) and cyclic hexamer (m/z 648). Finally, the mass spectrum in Figure 2e is a mixture of the latter oligomers and of the cyclic heptamer (m/z 756).

The single ion current (SIC) curves corresponding to each molecular ion allow one to resolve the mixture of the five cyclic oligomers (Figure 3).

A sensible correspondence can be observed between the oligomer distributions obtained by GPC (Figure 1) and MS (Figure 3).

The formation of cyclic oligomers has been also observed in the polymerization reaction leading to *o*-PPS (Table I). The cyclic dimer (thianthrene) is formed almost exclu-

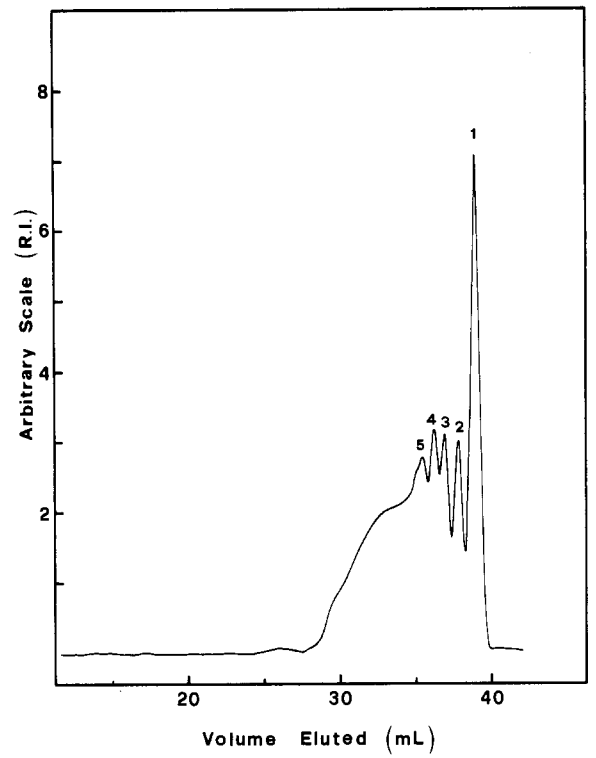

Figure 1. GPC trace of the cyclic oligomers extracted from a crude *m*-PPS sample: (1) trimer; (2) tetramer; (3) pentamer; (4) hexamer; (5) heptamer.

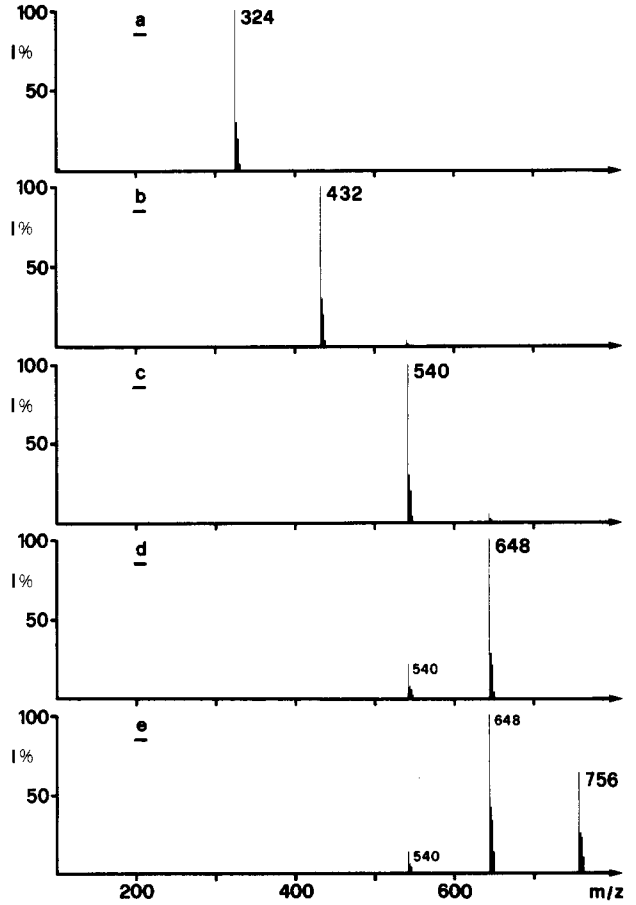

Figure 2. Mass spectra (18 eV) of a crude sample of *m*-PPS at (a) 185 °C, trimer; (b) 225 °C, tetramer; (c) 290 °C, pentamer; (d) 330 °C, hexamer; (e) 370 °C, heptamer.

sively, but traces of cyclic trimer and higher oligomers are also detected by MS analysis.

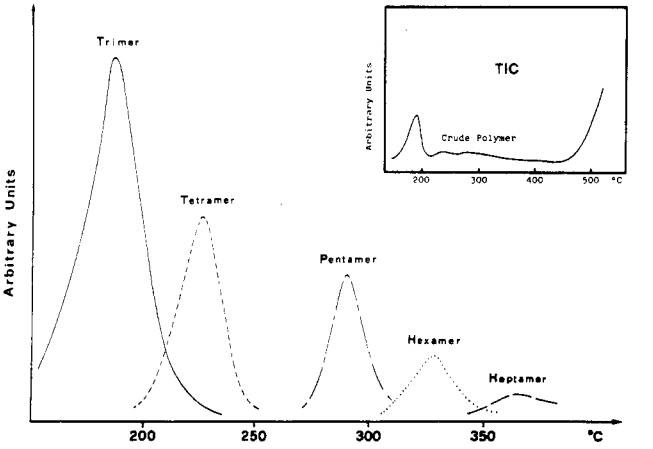

Figure 3. Single ion current (SIC) curves of the cyclic oligomers evolved from the MS of crude *m*-PPS. Inset: Total ion current (TIC) of crude sample of *m*-PPS.

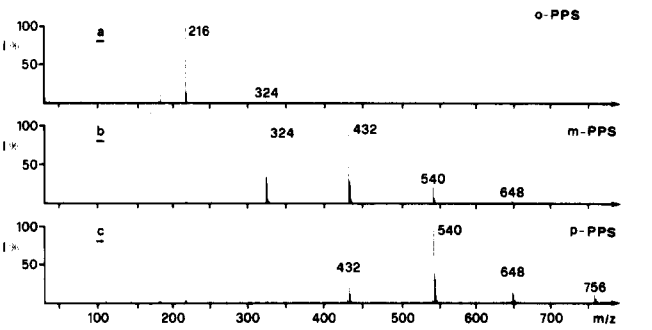

Figure 4. Mass spectra (18 eV) of the thermal degradation products of (a) *o*-PPS, (b) *m*-PPS, (c) *p*-PPS recorded at the corresponding PDT value.

Contrary to *o*- and *m*-PPS, only traces of cyclic oligomers were found to be produced in the polymerization reaction leading to *p*-PPS. However, in agreement with previous reports,[10] a *p*-PPS sample subjected to thermal treatment for 3 h at 350 °C was found to contain a mixture of cyclic oligomers Table I).

As in all cases of polymer samples containing oligomers, the oligomers started distilling under the high vacuum of the MS when a probe temperature of 150–200 °C was reached, whereas the products originating from the thermal decomposition of the polymer appeared all at once in the mass spectra at about 450 °C.

Analysis of the Thermal Degradation Products of *o*-, *m*-, and *p*-PPS. DPMS analysis was performed on polymer samples rigorously purified from oligomers.

Figure 4a shows the mass spectrum of *o*-PPS recorded at 18 eV at a probe temperature of 430 °C. The mass spectrum is constituted essentially by a peak of m/z 216 corresponding to molecular ion of cyclic dimer (thianthrene). Also present in the spectrum, with low intensity, is the peak at m/z 324 corresponding to cyclic trimer.

In Figure 4b is shown the mass spectrum of *m*-PPS recorded at 18 eV at a probe temperature of 540 °C. The presence of a series of peaks at m/z 324, 432, 540, 648, and 756, corresponding to molecular ions of the cyclic oligomers from trimer to heptamer, is observed. This indicates that the pyrolytic process is not as selective as in the case of *o*-PPS.

Figure 4c shows the mass spectrum of *p*-PPS recorded at 18 eV at a probe temperature of 560 °C. In agreement with previous data,[6] a family of peaks at m/z values of 432 + n108, corresponding to molecular ions of cyclic oligomers from tetramer to heptamer, is found.

Thermal Degradation Mechanisms and Structural

Effects. Evidence now exists that intramolecular-exchange processes are quite frequent in the thermal decomposition of condensation polymers.[11] The thermal fragmentation of the polymer chains may occur through a ring–chain equilibration process which originates a series of cyclic oligomers, since the formation of cyclic compounds is favored at higher temperatures.

Of course, a kinetic control of the ring–chain exchange process takes place when the low molecular weight reaction products are quickly removed from the hot zone. Therefore, the ring concentrations observed in DPMS might differ from those at the equilibrium.[12]

DPMS data concerning *o*-, *m*-, and *p*-PPS indicate that intramolecular-exchange reactions predominate in the primary thermal decomposition processes of these polymers, causing the formation of cyclic oligomers.

Furthermore, a marked structural effect is observed in the distribution of the cyclic oligomers generated in the pyrolysis of *o*-, *m*-, and *p*-PPS.

In the case of *o*-PPS, in agreement with literature data,[13] only cyclic dimer is produced, while trimer and tetramer predominate in the case of the meta isomer over pentamer, hexamer, and heptamer. The cyclic distribution is different from those mentioned above in the case of *p*-PPS, where the cyclic pentamer is the most abundant product.

It appears therefore that the influence of polymer structure and conformation on the distribution of cyclic oligomers produced by the isomeric PPS I–III (Table I) is sensible.

In each case, the most abundant cyclic oligomer seems to correspond to the energetically most stable and conformationally preferred compound, indicating that the thermal decompostion process is controlled by structural and conformational factors.

The distribution of the cyclic oligomers formed in the polymerization reactions is also governed by structural and conformational factors. In fact, it is comparable with the distribution of the oligomers formed in the pyrolysis of *o*-, *m*-, and *p*-PPS.

Finally, it can be noted that spectra reported in Figure 4 allow us to differentiate by MS analysis the three isomeric PPS, which might prove a difficult task with other techniques.

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Registry No. (*o*-$C_6H_4Br_2$)·(Na_2S) (copolymer), 102699-89-8; (*m*-$C_6H_4Br_2$)·(Na_2S) (copolymer), 102699-90-1; (*p*-$C_6H_4Br_2$)·(Na_2S) (copolymer), 57829-77-3; *o*-PPS, 82860-14-8; *m*-PPS, 32027-35-3; *p*-PPS, 25212-74-2.

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Effects of Weak Linkages on the Thermal and Oxidative Degradation of Poly(methyl methacrylates)

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ABSTRACT: The thermal and oxidative degradation mechanisms of poly(methyl methacrylate) (PMMA) were studied in atmospheres of nitrogen and air by thermogravimetry using various specially polymerized samples. Thermal degradation of PMMA polymerized with a free radical method proceeds in three steps of weight loss: the least stable step is initiated by scissions of head-to-head linkages, the second step by scissions at the chain-end initiation from vinylidene ends, and the most stable step by random scission within the polymer chain. There are no significant differences seen in the thermal or oxidative degradation of PMMA polymerized with the free radical method between azobis(isobutyronitrile) and benzoyl peroxide as the initiators. Gas-phase oxygen traps radicals resulting from chain scissions at head-to-head linkages. No weight loss is observed from this step in air. Similarly, oxygen traps radicals generated by end initiation, but it is not as effective as for the case of head-to-head linkages. Possible mechanisms for end initiation and oxidative termination of radicals initiated from scission at the head-to-head linkages are discussed.

1. Introduction

If a vinyl polymer is polymerized by a free radical initiator, a termination reaction could occur through either disproportionation or combination reactions of two radical chains or by both in the absence of transfer agents. The disproportionation reactions yield an equal number of polymer chains with unsaturated end groups and saturated end groups. A polymer chain terminated by combination produces a head-to-head (H–H) linkage within the chain.

These abnormal linkages (unsaturated end group or a H–H linkage along the chain) might have significant effects on the thermal stability of the free radically polymerized

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