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STEPWISE PYROLYSIS–LIQUID CHROMATOGRAPHY AND PYROLYSIS–GAS CHROMATOGRAPHY OF POLYSTYRENE

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SUMMARY

Stepwise pyrolysis of polystyrene followed by high-performance liquid chromatographic (HPLC) analysis of the collected pyrolyzate provides information on the sample that is lost to pyrolysis–gas chromatography. In the case of polystyrene, the monomer, dimer, trimer, and related compounds are sufficiently volatile to be eluted from the gas chromatograph; the higher homologues in the pyrolyzate are seen only by HPLC. HPLC thus becomes an additional fingerprinting technique and should aid in polymer structure elucidation, especially with cross-linked polymers, through identification of the LC peaks. Using chemical ionization mass spectrometry, over 100 compounds in the polystyrene pyrolyzate were tentatively identified. Mechanisms are proposed to account for the formation of these compounds.

INTRODUCTION

Pyrolysis followed by gas chromatographic analysis of the volatile products (Py–GC) has been used successfully for some time as a rapid fingerprinting technique for the characterization of a diversity of synthetic organic polymers and natural polymeric materials^{1–3}. In conjunction with high-resolution open tubular GC columns, GC–mass spectrometry (MS), and pattern recognition-type statistical evaluations of the chromatographic data, even subtle structural differences in polymer microstructure can be seen^{4,5}. For example, Py–GC has been used to characterize homopolymer blends of styrene and 2,6-dimethyl-1,4-phenylene oxide⁶, the isomeric structure of styrene–acrylonitrile and styrene–methacrylate copolymers⁷, the stereoregularity of styrene distribution in butadiene–styrene copolymers⁸, the degree of cross-linking of copolymers of styrene and divinylbenzene⁹, the polydispersity of methacrylate–styrene block polymers¹⁰, the dyad sequence in vinyl-type copolymers¹¹, and the tacticity of polypropylene¹².

As useful as these GC methods are, in general only a fraction of the sample is pyrolyzed to compounds sufficiently volatile to be eluted from a GC column; the balance could be viewed as lost information. The more complex the sample, the more likely this should be. For example, Van de Meent *et al.*¹³ found that pyrolysis of certain kerogen samples at 610°C in helium produced only about 10% gas chromatographable volatiles, but 40–50% each of a dark brown condensate and a black

residue. Berezkhin² too has urged that particular attention be paid to the identification of the heavy pyrolysis products, in order to give a more complete picture of the sample structure.

We report here the first application of high-performance liquid chromatography (HPLC) to the analysis of pyrolyzates (Py-LC). For polystyrene pyrolysis, the LC chromatograms show peaks for the monomer, dimer, trimer, and related compounds of styrene, as do the gas chromatograms, but in addition the LC shows peaks for higher oligomers that do not appear on the gas chromatograms. Although the resolution of the HPLC column used does not rival that of the open tubular GC column used, there are distinct changes in the LC chromatogram with stepwise pyrolysis temperature changes. Also, the LC peaks are recoverable in solution form, directly amenable to further spectrophotometric analysis, an aid in peak identification. For example, over 100 compounds in the pyrolyzate were identified by chemical ionization (CI) mass spectrometry.

The combination of Py-GC-MS suffers the same limitations as Py-GC itself, but direct interfacing of the pyrolyzer to a mass spectrometer allows, as does HPLC, one to look at higher molecular weight fractions of the pyrolyzate (*e.g.*, ref. 14). However, LC costs far less than MS, and there are probably few MS labs willing or able to dedicate a mass spectrometer to pyrolysis studies.

Py-LC, like HPLC, is of course restricted to substances detectable with available detectors, in particular at present the UV absorption detector. The technique of Py-LC would consequently be of limited use for study of the pyrolysis of for example polyethylene.

EXPERIMENTAL

Sample

The polystyrene samples were taken from a commercially available clear plastic cup. To ascertain purity, infrared (IR) spectra of the polymer were obtained after two different treatments. First, a sample was dissolved in cyclohexane and a film was cast on a watchglass. The IR spectrum was taken on this film in a standard IR film holder with a Perkin-Elmer 252 spectrometer. The second IR spectrum was obtained after dissolving a sample in benzene, precipitating the polymer with methanol, and repeating this three times. The washed sample was then dissolved in dichloromethane and precipitated with methanol, again repeating this process three times. Finally the sample was washed with methanol and dried at ambient temperature, dissolved in cyclohexane, and a film cast as above. The two IR spectra were identical, and matched the standard IR spectrum of polystyrene used to calibrate spectrometers; therefore we believe this polystyrene contains no additives.

In addition, the gel permeation chromatogram (GPC) of the untreated sample shows only the rather symmetrical elution peak of polystyrene, which further confirms the purity of the sample. The molecular weights obtained by GPC are $\bar{M}_w = 2.61 \cdot 10^5$ and $\bar{M}_n = 1.01 \cdot 10^5$.

Stepwise pyrolysis

Pyrolysis was carried out in a stepwise fashion, *i.e.* any given sample was heated at 100°C increments from 200°C to 900°C, using a CDS Pyroprobe 100 pyro-

lyzer with heated interface (Chemical Data Systems, Oxford, PA, U.S.A.). The Pyroprobe is equipped with a Pt coil 15 mm \times 3.0 mm O.D. \times 2.0 mm I.D., heated electrically in a circuit designed to provide accurate temperature control. Samples, generally 5.0 mg, were loaded into a quartz sample tube 15 mm \times 2.0 mm O.D., which fits inside the Pt coil and provides good thermal contact with it. The temperature rise rate of the coil is specified to be 75°C/msec, although the temperature rise rate of the sample no doubt lags considerably behind this. Heating times were 4 min for pyrolysis at 200°C and 300°C, 2 min for 400°C, and 1 min for the higher temperatures; times were varied with temperature to provide comparable quantities of pyrolyzate. In more recent work, samples approximately 50 μ g pyrolyzed for 1–2 sec have been found to give comparable results with less likelihood of secondary reactions occurring.

For pyrolyzate analysis by GC, the outlet of the heated interface was attached with a Swagelok fitting to a pyrolyzate trap consisting of a 5.0 cm \times 3.0 mm O.D. quartz tube filled with 45–90- μ m glass microbeads (Sigma, St. Louis, MO, U.S.A.), held in place with glass wool. The arrangement is depicted in Fig. 1. Use of Tenax rather than glass beads allows greater retention of pyrolyzates but causes severe thermal desorption problems; the glass beads offer a compromise. The pyrolysis products were swept out of the 200°C interface with He at 100 ml/min, and collected separately at each pyrolysis temperature. Before use, the glass beads, glass wool, and quartz tubes were washed with cyclohexane–benzene (1:1) and dried at 300°C. Blank chromatograms showed no detectable organics after this treatment.

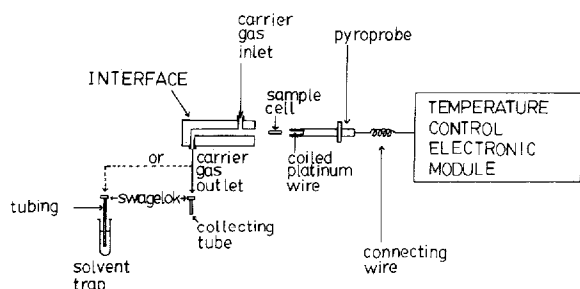


Fig. 1. Schematic diagram of the instrumental arrangement using the CDS Pyroprobe 100 and heated interface with solvent trap or glass microbead collector trap.

For Py-LC, pyrolyzates at each temperature were collected by bubbling the effluent from the pyrolyzer interface through a 1/16 in. O.D. stainless-steel tube into 2.5 ml of cyclohexane, as depicted in Fig. 1. The pyrolysis times at each temperature were the same for Py-LC and Py-GC.

HPLC

Either a Varian Model 8500 liquid chromatograph or a Micromeritics 7500 liquid chromatograph was used with a 25 cm \times 2 mm I.D. Micropak CH-10 column (Varian Instruments), or a 25 cm \times 4.6 mm I.D. Partisil ODS column (Whatman, Clifton, NJ, U.S.A.), respectively. The eluent in either case was acetonitrile–water (90:10) at 25 ml/h. The columns were operated at ambient temperature. The UV

detectors were set at 254 nm. The LC chromatograms were obtained by injecting generally 0.5- μ l aliquots of the collecting solution.

GC

A Shimadzu Mini-2 gas chromatograph with flame ionization detector (FID) was used with a 17 m \times 0.25 mm I.D. open tubular glass column wall-coated with OV-101. The carrier gas was helium at 5 ml/min. The column temperature was held initially at 36°C for 5 min after sample introduction, then programmed at 4°C/min to 250°C and held at that temperature for 50 min. To introduce samples, the column was cooled to 36°C, the injector nut removed, the glass bead-filled quartz collector tube inserted directly into the 300°C injection port, and the nut replaced. As indicated in Fig. 2, a 5.0 cm \times 3.0 mm O.D. quartz guard tube packed with glass wool was placed in the injection port between the column and the collecting tube, to prevent any loose glass beads from entering the capillary column. The guard tube, which was left in place while collector tubes were changed, also served to help protect the open tubular column from contamination and blockage by high boiling compounds in the pyrolyzate.

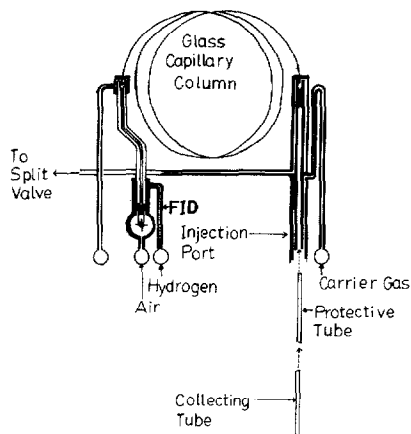


Fig. 2. Schematic diagram of the GC sample inlet system. The quartz guard tube is 5.0 cm \times 0.3 cm packed with glass wool. The quartz collector tube is of the same dimensions, packed with glass microbeads.

Mass spectrometry

Mass spectra were obtained through the courtesy of the Rockefeller University Biotechnology Mass Spectrometric Research Resource. A DuPont 21-492 magnetic deflection mass spectrometer with a chemical ionization source was used. Isobutane was the reagent gas. The total pyrolyzate sample, dissolved in cyclohexane, was analyzed directly using programmed heating of the sample probe. The LC peaks, dissolved in aqueous acetonitrile, were extracted into 1 ml of dichloromethane, condensed to 10 μ l, and analyzed using the heated sample probe.

RESULTS AND DISCUSSION

As shown in Figs. 3-7, the complexity and distribution of pyrolysis products

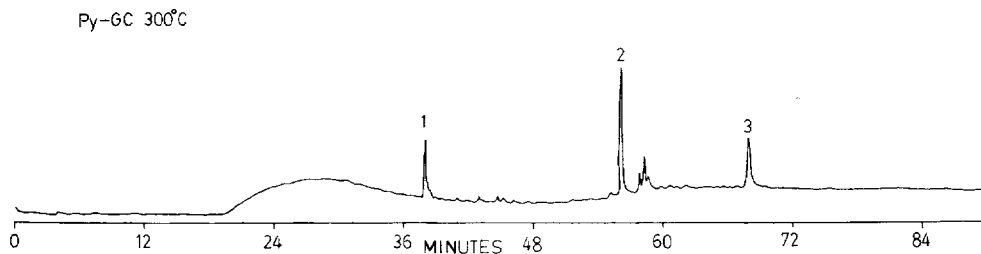


Fig. 3. Py-GC chromatogram of 300°C pyrolysis products of polystyrene. Capillary GC conditions: 17 m \times 0.25 mm I.D. glass column wall-coated with OV-101; 5 ml He/min; temperature programmed after initial 5 min hold at 36°C, at 4°C/min to 250°C with 50 min final hold; FID detector response set at range 10 \times 8; main peaks are (1) styrene, (2) 2,4-diphenyl-1-butene, and (3) 2,4,6-triphenyl-1-hexene.

increases with increasing pyrolysis temperatures, especially above 500–600°C. The capillary GC of the 300°C pyrolyzate is reproduced in Fig. 3. The compounds evolved at the lower temperatures are probably a combination of pyrolysis products and distillates of lower-molecular-weight oligomers. The broad, low peak near the start of the gas chromatograms is a spurious peak associated with the temperature program. Three major peaks, whose identification is discussed below, are observed for the stepwise pyrolyses at 200°, 300°, 400°, and 500°C. The 300°C chromatogram is typical, but as shown in Fig. 4, a plot of relative peak heights of the three major peaks (numbered 1, 2, and 3) at each temperature as a function of stepwise pyrolysis temperature, there are changes in the distribution of these major products; there are some minor differences as well in the minor products. Fig. 5 is the gas chromatogram of the 700°C pyrolysis products, and is typical of the pyrolyses at temperatures higher than 600°C. There are clear differences in the complexity and distribution of both major and minor peaks in the higher temperature pyrolyses.

The HPLC chromatogram of the 300° and 700°C pyrolysis products, representative of the lower and higher temperature chromatograms, respectively, are shown in Fig. 6. Peak identifications are discussed below. As in the gas chromatograms, yield and complexity increase with increasing pyrolysis temperature. The peaks eluting from the LC, however, are of quite higher molecular weight than those from the GC.

In stepwise pyrolysis, which involves heating the same sample sequentially to increasing temperatures, one would expect total chromatographable yield to max-

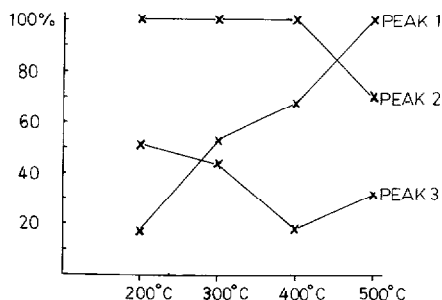


Fig. 4. Relative GC peak heights of monomer, dimer, and trimer as a function of pyrolysis temperature.

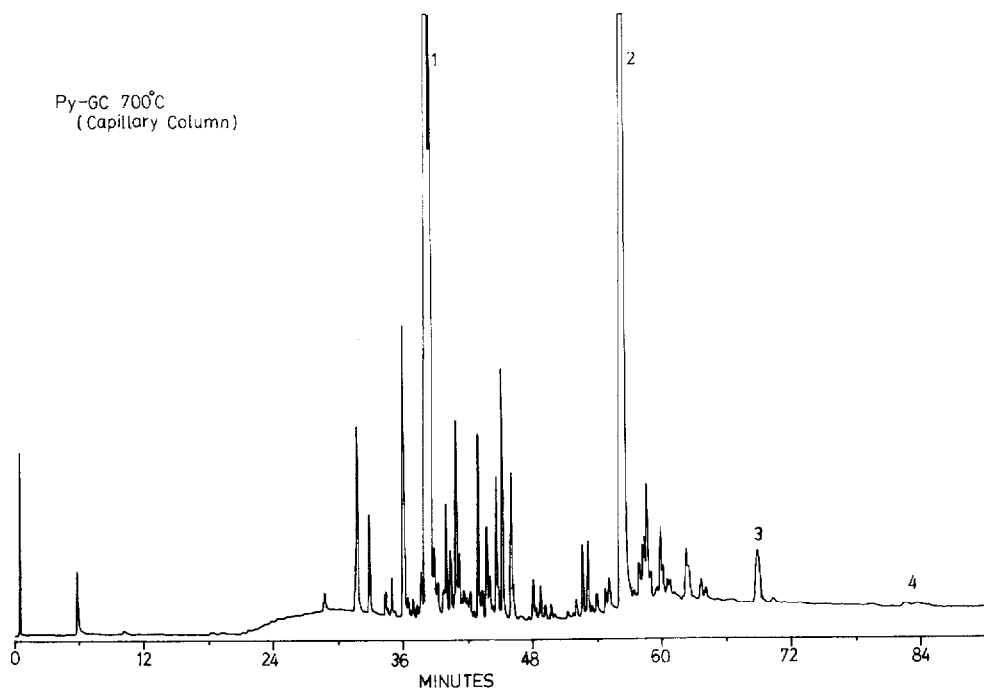


Fig. 5. Py-GC chromatogram of 700°C pyrolysis products of polystyrene. Capillary GC conditions same as Fig. 3. Peak 4 is 2,4,6,8-tetraphenyl-1-octene.

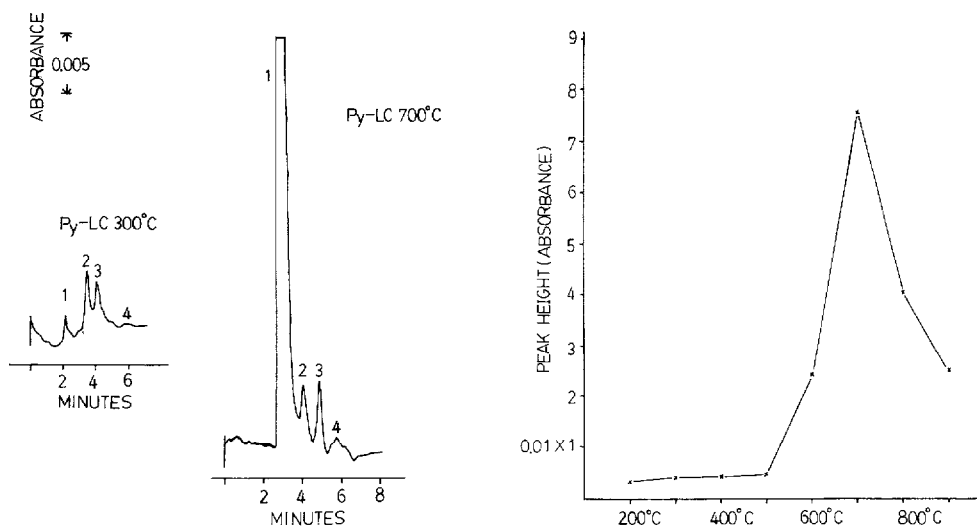


Fig. 6. Py-LC chromatograms of 300°C and 700°C pyrolysis products of polystyrene. HPLC conditions: 25 cm \times 2 mm I.D. Varian Micropak CH-10 reversed-phase column; 25 ml/h of acetonitrile-water (90:10); UV detector set at 254 nm; 0.5- μ l sample injected.

Fig. 7. Total recoverable pyrolyzate yield as a function of pyrolysis temperature. See text for method of determination.

imize at a certain temperature as the polymer is sequentially degraded. This is in fact observed in Fig. 7. Relative total yields of pyrolysis products for each pyrolysis temperature from 200°–900°C at 100°C intervals were determined as follows. Pyrolysis time at each temperature was 10 sec, and pyrolysis products were trapped by bubbling through solvent traps containing 10 ml of cyclohexane. A 1- μ l aliquot of each pyrolyzate solution was injected into the liquid chromatograph with a 2 ft. length of 1/16 in. O.D. stainless-steel tubing replacing the LC column, using 1 ml/min of hexane eluent, and the UV detector set at 254 nm. Relative yield was assumed to be proportional to the peak height of the resulting peak. The results, in Fig. 7, show increased yields above 500°C, with maximum yield near 700°C, which correlates well with the chromatographic results.

To determine whether pyrolyzate was left in the interface, 2.5 ml of cyclohexane was used to rinse out the interface and connecting tubing, following sequential pyrolysis of a polystyrene sample in the usual manner. A 0.5- μ l aliquot was injected into the liquid chromatograph, giving rise to the chromatogram in Fig. 8. As might be expected, there is condensation of considerable amounts of pyrolyzate in the interface. Clearly a redesign of the interface between pyrolyzer and collector is indicated. In addition, for Py-GC, the interface should be cleaned regularly to prevent artifacts in the pyrogram and to avoid loss of volatile pyrolyzate by dissolution into or adsorption onto the condensate.

To test for quantitative transfer of pyrolyzate from the collector tube and guard tube in the GC inlet to the GC column, after a normal GC run of a 700°C pyrolyzate, the collector tube and guard tube were removed and rinsed with 10 ml of

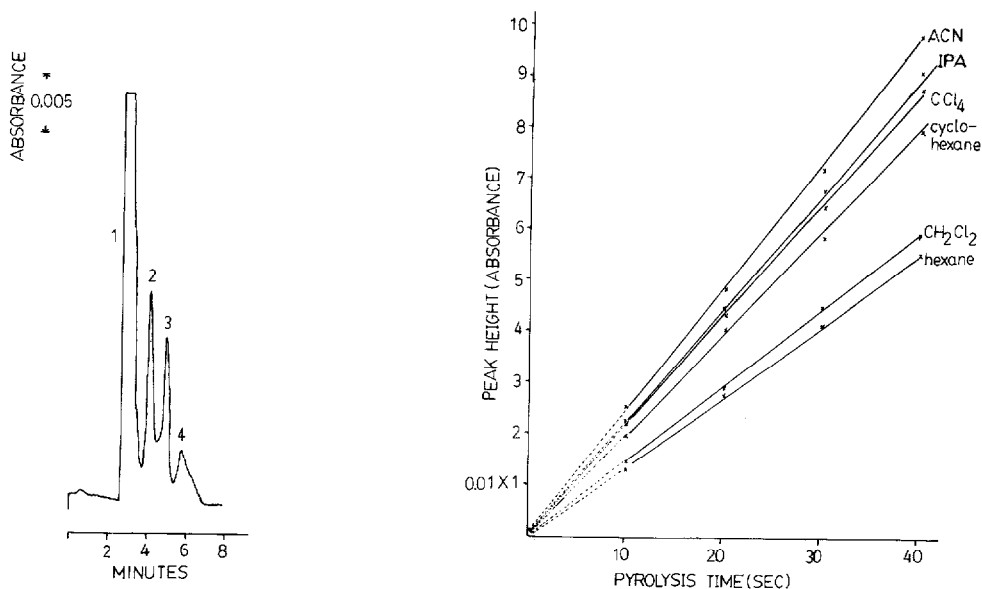


Fig. 8. LC chromatogram of rinsings of heated interface after pyrolysis. Solvent: 10 ml cyclohexane. HPLC conditions as for Fig. 6.

Fig. 9. Trapping efficiencies of several solvents.

cyclohexane. A 1.0- μ l aliquot was analyzed in the same fashion as described above for the determination of total pyrolysis yield as a function of temperature. About 12% of the pyrolyzate is in fact retained in the collector tube, and about 1–2% in the guard tube. This further confirms that the LC provides access to the study of the higher-molecular-weight, less volatile portion of the pyrolyzates.

Although most of the solvent-trapping results reported here were obtained using cyclohexane, several solvents were recently evaluated for efficiency of trapping. The efficiency is the ratio of the weight trapped to the weight loss on pyrolysis. The latter was determined gravimetrically. The weight trapped was determined spectrophotometrically at 254 nm in the trapping solution, assuming the molar absorptivity of the pyrolyzate equals that for styrene. For cyclohexane, the trapping efficiency is 67%; one-third of the pyrolysis products never reach the trap from the interface, or are not condensed in the solvent trap. Fig. 9 shows the amount of 700°C pyrolyzate trapped, determined using the no-column chromatographic method described above, increases linearly with pyrolysis time; the trapping efficiency increases in the order *n*-hexane, dichloromethane, cyclohexane, carbon tetrachloride, 2-propanol (IPA), and acetonitrile (ACN). The % efficiency of each solvent can be calculated from this plot and the known efficiency of cyclohexane, *e.g.* ACN is 80% efficient. In similar fashion, the trapping efficiencies of the glass microbead trap and a trap packed with glass wool were determined to be 15% and 3%, respectively. Again, trapping efficiency must be balanced against desorption efficiency.

GC peaks were identified using retention data. The three main peaks in Figs. 3 and 5 were identified by comparison with literature data^{15,16} as styrene, 2,4-diphenyl-1-butene, and 2,4,6-triphenyl-1-hexene; the styrene identification was confirmed by chromatographing pure styrene. In addition to the main peaks in the higher temperature pyrograms, compounds such as ethyl benzene and 3-phenyl-1-propene elute near styrene; 1,4-diphenyl-1-butene and 1,4-diphenyl-butane near 2,4-diphenyl-1-butene, *etc.*¹⁵. At the highest pyrolysis temperatures a small peak (numbered 4 in Fig. 5) appears, probably corresponding to a tetramer, *e.g.* 2,4,6,8-tetraphenyl-1-octene, but the volatility of this compound is close to or less than the limit that GC can handle.

For the LC chromatograms, GC and MS were used for peak identification. Peak 1 in Fig. 6 was studied as follows. The 700°C pyrolyzate was collected in 2.5 ml of cyclohexane, a 0.5- μ l aliquot injected into a glass microbead-packed collector tube, and the cyclohexane evaporated in a stream of nitrogen. The tube was inserted into the GC inlet as described above to produce the chromatogram in Fig. 10A. A 0.5- μ l aliquot of the same cyclohexane solution of pyrolyzate was injected into the liquid chromatograph, the first peak collected, injected into a glass microbead collector tube, and following the same procedure, the chromatogram in Fig. 10B was obtained. It is clear that the first LC peak corresponds primarily to the first three GC peaks. Figs. 5 and 10A differ in apparent sensitivity only because a smaller portion of the pyrolyzate was analyzed in the latter case.

CI-MS was applied to the four LC peaks and also to a sample of the total 700°C pyrolyzate collected in cyclohexane. CI-MS with isobutane yields strong peaks at *m/z* values of *M* - 1, *M*, and *M* + 1, and relatively little fragmentation. For the total pyrolyzate, MS peaks with intensities less than 3% of the base peak were subtracted manually, and the remaining peaks plausibly identified using the *M* - 1, *M*,

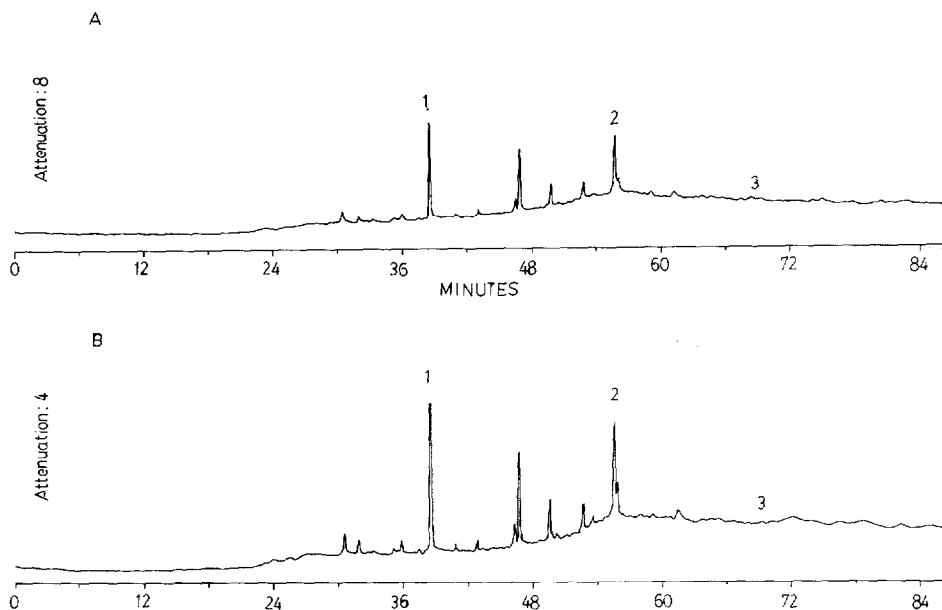


Fig. 10. Pyrolysis-GC chromatogram of pyrolyzate at 700°C collected by bubbling pyrolyzer effluent through cyclohexane. (A) GC of cyclohexane solution. GC conditions as for Fig. 3. (B) GC of first HPLC peak of same cyclohexane solution.

and $M + 1$ peaks. Table I lists the compounds identified tentatively in this manner. Only one of several possible isomers are listed, e.g. the peak at $m/z = 208$ could be 2,4-diphenyl-1-butene and/or 1,4-diphenyl-1-butene and/or the 1,3- and/or the 2,3-isomer, etc. About one-third of these were identified previously^{15,16}. Compounds heavier than hexaphenylundecene (mol.wt. = 613) were not observed, probably because the maximum sample probe temperature was 240°C, and in any case the mass spectral scan stopped at $m/z = 700$.

The mass spectra of the compounds in the LC peaks were simplified by subtracting manually peaks smaller than 15% of the base peak. These are presented in Fig. 11. Compounds up to the tetramer (mol.wt. = 416) were found in the first LC peak, confirming the GC analysis. The pentamer (mol.wt. = 520) was found in the later peaks, and hexaphenylundecene in the third LC peak. Absence of the higher oligomers is probably accountable in terms of the reasons above, and in addition the total amounts of pyrolyzates diminish with increasing molecular weight; the concentration of the higher oligomers in the later peaks may be below the mass spectral sensitivity. In any case it is clear in Fig. 11 that the distribution of products shifts to higher m/z values with increasing LC retention time.

Mechanisms of pyrolytic polymer degradation have been studied extensively. For vinyl polymers, three major processes are involved: unzipping of the chain to yield sequential monomer units¹⁷⁻¹⁹; elimination of small neutral molecules (e.g. HCl from polyvinylchloride) prior to further decomposition²⁰; and random chain cleavage²¹. Plausible mechanisms for the pyrolytic formation of the products listed in Table I are presented in Figs. 12-16. Homolytic cleavage of the polystyrene chain (Fig. 12) results in formation of two terminal radicals (RI and RII in Fig. 12) and

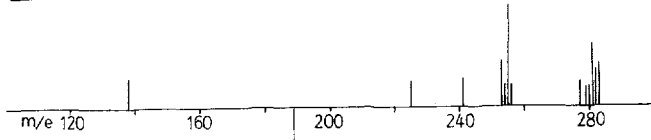
TABLE I
TENTATIVE IDENTIFICATION OF COMPOUNDS IN 700°C PYROLYZATE OF POLY-
STYRENE USING CI-MS

<i>Mol.wt.</i> <i>M</i>	<i>% of base peak</i>			<i>Tentative identification</i>
	<i>M - 1</i>	<i>M</i>	<i>M + 1</i>	
92	18	—	6	Toluene
104	—	—	19	Styrene
106	19	—	7	Ethylbenzene
118	41	9	8	2-Phenyl-1-propene
120	8	7	7	Cumene
132	11	—	9	1-Phenyl-1-butene
146	—	—	5	1-Phenyl-1-pentene
160	9	—	15	1-Phenyl-1-hexene
174	4	—	6	1-Phenyl-1-heptene
180	7	—	4	1,2-Diphenyl ethylene
192	6	—	12	1,3-Diphenylallene
194	12	6	73	1,3-Diphenyl-1-propene
196	73	21	4	1,3-Diphenylpropane
202	—	—	7	1-Phenyl-1-nonene
206	—	7	30	1,3-Diphenyl-1,3-butadiene
208	30	10	17	2,4-Diphenyl-1-butene (dimer)
210	17	7	11	2,4-Diphenylbutane
216	7	—	6	1-Phenyl-1-decene
220	16	—	26	2,4-Diphenyl-1,4-pentadiene
222	26	9	9	2,4-Diphenyl-1-pentene
224	9	4	9	2,4-Diphenylpentane
234	27	4	59	2,5-Diphenyl-1,5-hexadiene
236	59	13	16	2,5-Diphenyl-1-hexene
244	5	—	—	1-Phenyl-1-dodecene
250	9	—	14	1,2-Diphenyl-1-heptene
258	19	4	5	1-Phenyl-1-tridecene
264	7	11	13	1,2-Diphenyl-1-octene
270	—	—	19	1,2,3-Triphenylpropene
272	19	4	30	1,2,3-Triphenylpropane
278	6	4	9	1,2-Diphenyl-1-nonene
284	29	9	19	1,2,3-Triphenyl-1-butene
286	19	9	5	1,2,3-Triphenylbutane
292	12	—	5	1,2-Diphenyl-1-decene
296	—	—	11	1,3,5-Triphenyl-1,4-pentadiene
298	11	7	15	1,3,5-Triphenyl-1-pentene
300	15	6	9	1,3,5-Triphenylpentane
306	—	—	8	1,2-Diphenyl-1-undecene
310	11	10	43	1,3,5-Triphenyl-1,5-hexadiene
312	43	39	36	2,4,6-Triphenyl-1-hexene (trimer)
314	36	14	35	1,3,5-Triphenylhexane
320	4	6	—	1,2-Diphenyl-1-dodecene
324	7	4	20	2,4,6-Triphenyl-1,6-heptadiene
326	20	6	13	2,4,6-Triphenyl-1-heptene
328	13	10	16	2,4,6-Triphenylheptane
334	6	—	16	1,2-Diphenyl-1-tridecene
338	10	—	9	2,5,7-Triphenyl-1,7-octadiene

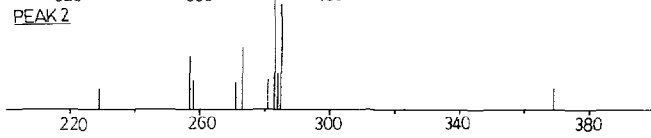
TABLE I (continued)

Mol.wt. M	% of base peak			Tentative identification
	M - 1	M	M + 1	
340	9	—	9	2,5,7-Triphenyl-1-octene
348	—	—	7	1,2-Diphenyl-1-tetradecene
354	6	—	12	1,2,3-Triphenyl-1-nonene
358	—	7	5	1,2,3,4-Tetraphenyl-1,3-butadiene
360	5	4	—	1,2,3,4-Tetraphenyl-1-butene
362	—	—	10	1,2,3,4-Tetraphenylbutane
368	16	13	100	1,2,3-Triphenyl-1-decene
374	10	7	4	1,2,3,4-Tetraphenyl-1-pentene
382	7	4	13	1,2,3-Triphenyl-1-undecene
386	14	—	—	1,2,4,6-Tetraphenyl-1,5-hexadiene
388	—	4	9	1,2,4,6-Tetraphenyl-1-hexene
396	11	—	—	1,2,3-Triphenyl-1-dodecene
400	9	11	8	1,3,5,7-Tetraphenyl-1,6-heptadiene
402	8	—	7	1,3,5,7-Tetraphenyl-1-heptene
404	7	—	6	1,3,5,7-Tetraphenylheptane
410	20	4	33	1,2,3-Triphenyl-1-tridecene
414	7	10	9	1,3,5,7-Tetraphenyl-1,7-octadiene
416	9	—	11	2,4,6,8-Tetraphenyl-1-octene (tetramer)
418	11	—	—	1,3,5,7-Tetraphenyloctane
424	7	—	14	1,2,3-Triphenyl-1-tetradecene
428	55	12	14	2,4,6,8-Tetraphenyl-1,8-nonadiene
430	14	—	14	2,4,6,8-Tetraphenyl-1-nonene
432	14	—	15	2,4,6,8-Tetraphenylnonane
438	—	4	11	1,2,3-Triphenyl-1-pentadecene
442	—	4	7	2,4,7,9-Tetraphenyl-1,9-decadiene
444	7	—	17	2,4,7,9-Tetraphenyl-1-decene
448	14	7	14	1,2,3,4,5-Pentaphenyl-1,4-pentadiene
450	14	14	14	1,2,3,4,5-Pentaphenyl-1-pentene
452	14	—	—	1,2,3,4,5-Pentaphenylpentane
458	5	—	7	1,2,3,4-Tetraphenyl-1-undecene
472	5	5	5	1,2,3,4-Tetraphenyl-1-dodecene
478	23	16	32	1,2,3,4,5-Pentaphenyl-1-heptene
486	9	—	5	1,2,3,4-Tetraphenyl-1-tridecene
490	9	—	25	1,2,4,6,8-Pentaphenyl-1,7-octadiene
492	25	9	19	1,3,5,7,8-Pentaphenyl-1-octene
500	—	—	9	1,2,3,4-Tetraphenyl-1-tetradecene
504	10	4	26	1,3,5,7,9-Pentaphenyl-1,8-nonadiene
506	26	9	27	1,3,5,7,9-Pentaphenyl-1-nonene
508	27	19	11	1,3,5,7,9-Pentaphenylnonane
518	6	—	13	1,3,5,7,9-Pentaphenyl-1,9-decadiene
520	13	10	19	2,4,6,8,10-Pentaphenyl-1-decene (pentamer)
522	19	—	—	1,3,5,7,9-Pentaphenyldecane
532	24	10	20	2,4,6,8,10-Pentaphenyl-1,10-undecadiene
534	20	14	23	2,4,6,8,10-Pentaphenyl-1-undecene
536	23	14	14	2,4,6,8,10-Pentaphenylundecane
546	7	—	15	2,4,6,8,11-Pentaphenyl-1,11-dodecadiene
548	15	13	16	2,4,6,8,11-Pentaphenyl-1-dodecene
554	—	9	—	1,2,3,4,5,6-Hexaphenyl-1-heptene
562	17	7	11	1,2,3,4,5-Pentaphenyl-1-tridecene
576	—	—	13	1,2,3,4,5-Pentaphenyl-1-tetradecene
582	—	—	12	1,2,3,4,5,6-Hexaphenyl-1-nonene
590	—	8	—	1,2,3,4,5-Pentaphenyl-1-pentadecene

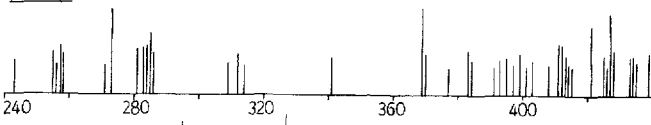
PEAK 1



PEAK 2



PEAK 3



PEAK 4

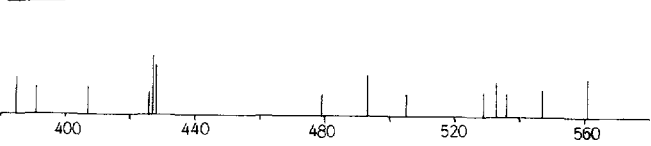


Fig. 11. Simplified mass spectra of four LC peaks of 700°C pyrolysis of polystyrene.

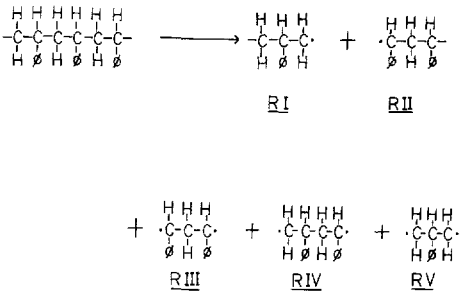


Fig. 12. Homolytic cleavage of polystyrene chain to terminal radicals and diradicals.

and diradicals can be used to account for the appearance of the compounds in the chromatograms identified by CI-MS.

For example, compounds formed from RI terminal radical reactions include 2-phenyl-1-propene, 1,3-diphenyl-1-butene, 2,4-diphenyl-1-pentene, 1,3,5-triphenyl-1-hexene, 2,4,6-triphenyl-1-heptene, and 1,3,5,7-tetraphenyl-1-octene. Those from RII terminal radical reactions include 1,3-diphenyl-1-propene, 2,4-diphenyl-1-butene, 1,3,5-triphenyl-1-pentene, 2,4,6-triphenyl-1-hexene, 1,3,5,7-tetraphenyl-1-heptene, and 2,4,6,8-tetraphenyl-1-octene. The higher mass fragments formed from RI and RII terminal radicals are listed in Table II. These compounds in the 700°C pyrolyzate have been identified for the first time here.

As indicated in Fig. 13, intramolecular C-4 and C-5 proton transfer give rise to 1,3,5-triphenyl-1-pentene, 2,4-diphenyl-1-pentene, and 2,4,6-triphenyl-1-hexene. Although left-handed intramolecular proton transfer in RIV diradicals produces α -olefin isomers, styrene oligomers are formed via right-handed intramolecular proton transfer in these diradicals. The α -olefins and styrene oligomers found are listed in Table III. Other possible paths to formation of the styrene oligomers are suggested in Fig. 14A. Other types of homologues formed from RIII and RV diradicals are listed in Table IV.

Proton transfers at positions other than C-4 and C-5 will be followed by right or left β -scission, as shown in Fig. 14A. Diradicals can abstract a proton from other

TABLE III

 α -OLEFINS AND STYRENE OLIGOMERS FORMED VIA PROTON TRANSFER

RIV Diradicals	Proton transfer	Products
$\begin{array}{c} \text{H H} \\ \cdot \text{C} \cdot \text{C} \cdot \\ \text{H } \phi \end{array}$	—	C=C (Styrene) ϕ
$\begin{array}{c} \text{H H H H} \\ \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \\ \text{H } \phi \text{H } \phi \end{array}$	C-3-Right	G-C-C-C (DIMER) $\phi \phi$
	C-3-Left	C-C-C-C $\phi \phi \phi$ 1,3-diphenyl-1-butene
$\begin{array}{c} \text{H H H H H H} \\ \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \\ \text{H } \phi \text{H } \phi \text{H } \phi \end{array}$	C-5-Right	G-C-C-C-G-C $\phi \phi \phi \phi$ (TRIMER)
	C-5-Left	G-C-C-G-C-C $\phi \phi \phi \phi$ 1,3,5-triphenyl-1-pentene
$\begin{array}{c} \text{H H H H H H H H} \\ \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \\ \text{H } \phi \text{H } \phi \text{H } \phi \text{H } \phi \end{array}$	C-7-Right	G-C-C-C-G-C-G-C $\phi \phi \phi \phi \phi$ (TETRAMER)
	C-7-Left	C-C-C-C-C-C-C $\phi \phi \phi \phi \phi$ 1,3,5,7-tetraphenyl-1-octene
$\begin{array}{c} \text{H H H H H H H H H H} \\ \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \\ \text{H } \phi \text{H } \phi \text{H } \phi \text{H } \phi \text{H } \phi \end{array}$	C-9-Right	G-C-C-C-G-C-G-C-G-C $\phi \phi \phi \phi \phi \phi$ (PENTAMER)
	C-9-Left	C-C-C-C-G-C-C-C $\phi \phi \phi \phi \phi \phi$ 1,3,5,7,9-pentaphenyl-1-decene (HEXAMER)
$\begin{array}{c} \text{H H H H H H H H H H H H} \\ \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \\ \text{H } \phi \text{H } \phi \text{H } \phi \text{H } \phi \text{H } \phi \text{H } \phi \end{array}$	C-11-Right	G-C-G-G-C-C-G-C-G-C $\phi \phi \phi \phi \phi \phi \phi$
	C-11-Left	G-C-C-C-G-C-G-C-C-C $\phi \phi \phi \phi \phi \phi \phi$ 1,3,5,7,9,11-hexaphenyl-1-dodecene

TABLE IV
HOMOLOGS FORMED VIA RIII AND RV DIRADICALS

<i>Diradicals</i>	<i>Proton transfer</i>	<i>Products</i>
<i>RIII</i>		
$\begin{array}{c} \text{H H H} \\ \cdot \text{C} - \text{C} - \text{C} \cdot \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	C-2	$\begin{array}{c} \text{C} - \text{C} - \text{C} \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ 1,3-diphenyl-1-propene
$\begin{array}{c} \text{H H H H H} \\ \cdot \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \cdot \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	C-4	$\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$ 1,3,5-triphenyl-1-pentene
$\begin{array}{c} \text{H H H H H H H} \\ \cdot \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \cdot \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	C-6	$\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$ 1,3,5,7-tetraphenyl-1-heptene
$\begin{array}{c} \text{H H H H H H H H H} \\ \cdot \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \cdot \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	C-8	$\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$ 1,3,5,7,9-pentaphenyl-1-nonene
$\begin{array}{c} \text{H H H H H H H H H H H} \\ \cdot \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \cdot \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	C-10	$\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$ 1,3,5,7,9,11-hexaphenyl-1-undecene
<i>RV</i>		
$\begin{array}{c} \text{H H H} \\ \cdot \text{C} - \text{C} - \text{C} \cdot \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	C-2	$\begin{array}{c} \text{C} - \text{C} - \text{C} \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ 2-phenyl-1-propene
$\begin{array}{c} \text{H H H H H} \\ \cdot \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \cdot \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	C-4	$\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$ 2,4-diphenyl-1-pentene
$\begin{array}{c} \text{H H H H H H H} \\ \cdot \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \cdot \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	C-6	$\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$ 2,4,6-triphenyl-1-heptene
$\begin{array}{c} \text{H H H H H H H H H} \\ \cdot \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \cdot \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	C-8	$\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$ 2,4,6,8-tetraphenyl-1-nonene
$\begin{array}{c} \text{H H H H H H H H H H H} \\ \cdot \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \cdot \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	C-10	$\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$ 2,4,6,8,10-pentaphenyl-1-undecene

chain fragments or radicals to produce terminal radicals as indicated in Fig. 14B, which react further via known reactions¹⁶. Dienes and α -olefins such as 2,4-diphenyl-1,4-pentadiene and 2,4-diphenyl-1-pentene can be produced via disproportionation reactions as shown in Fig. 15. Finally, tail-to-tail and head-to-head diradicals can be formed from smaller diradical combinations, giving rise to products with different arrangements of the phenyl groups, as depicted in Fig. 16. The mechanisms proposed here not only agree with earlier studies (ref. 16 and references cited therein), but also can account for the formation of the dienes identified by CI-MS.

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