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THERMAL DEGRADATION OF POLY(*o*-ACETYLSTYRENE)

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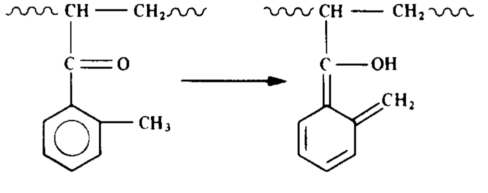
Abstract—The thermal degradation of poly(*o*-acetylstyrene) (POAS) was studied at 390°C under high vacuum. The principal reactions are removal and decomposition of acetyl groups, depolymerization, random chain scission and oligomer formation. The degradation mechanism resembles that of polystyrene (PS) but the presence of methyl radicals increases the number of transfer reactions with the polymer. The resulting chain radicals undergo β-scission (chain scission), one of the two species formed yielding oligomeric products and the other yielding monomer. The ratio of oligomer to monomer concentration is greater than that observed for PS: this effect has been attributed to shorter zip lengths, and to the occurrence of additional transfer reactions in POAS.

INTRODUCTION

Considerable attention has been paid to keto polymers, such as poly(vinylacetophenone) (PVAP) in the context of solar energy transfer and storage [1, 2]. Despite its favourable optical properties, PVAP undergoes simultaneous photodegradation (Norrish Type 1), which reduces the chromophore concentration and the efficiency of energy transfer [3].

A number of studies of *o*-alkylbenzophenones [4] and of poly(*o*-tolylvinylketone) [5, 6] have shown that these molecules undergo photoenolization at the expense of photodegradation, triplets and biradicals being involved, i.e.



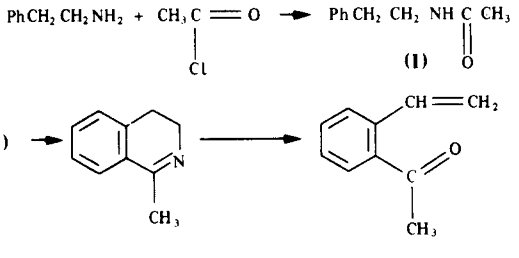
Preliminary studies of the isomeric (to PVAP) polymer, poly(*o*-acetylstyrene) (POAS), indicate that it is considerably more photo-stable than PVAP, [7] and spectroscopic studies of transients formed on irradiation of the polymer with a pulsed N_2 laser indicate the presence of the enol [8]. It thus appears that POAS is a more promising material for solar energy studies.

In their solar energy applications, polymers can be frequently subjected to relatively high temperatures (in excess of T_G). Little is known of the thermal characteristics or of the thermal stability of POAS, and the object of the work described below was to investigate its thermal degradation.

EXPERIMENTAL

Monomer preparation

o-Acetylstyrene was prepared in a three stage synthesis; the first step consisted of the reaction of β-phenylethylamine with acetyl chloride (equimolar quantities) in the presence of 20% NaOH in ethanol. The resulting amide was separated and distilled (reduced pressure), and dried under high vacuum (yield >65%). The second stage involved a modification of the procedure used by Hartung [9, 10]. The amide was refluxed with an excess of P_2O_5 and $POCl_3$ in dry xylene under anhydrous conditions. After reaction and the addition of ice water to remove the dehydrating agents, the aqueous layer was separated, washed and made alkaline (KOH). The 1-methyl 3,4-dihydroisoquinoline, which appeared as an oily material, was extracted (benzene), dried ($MgSO_4$) and pumped under reduced pressure. The monomer, which was prepared from the dihydroisoquinoline by refluxing it with NaOH and dimethylsulphate [11], was vacuum distilled and stored in the dark at −20°C. NMR and i.r. spectra were consistent with the expected chemical structures. The reaction sequence is summarized below.



Polymerization

The monomer was radically polymerized (10^{-3} M AIBN) in bulk at 70°C under high vacuum conditions, the degree of conversion being limited to 10%. The polymer was extracted in pure dichloromethane and precipitated by the addition of methanol. This process was repeated three times, after which the polymer was pumped at 10^{-6} Torr and 60°C, until no traces of monomer, solvent or precipitant were detectable mass spectrometrically.

Spectroscopy

The high molecular weight products of degradation were analyzed using u.v. spectrophotometry (Perkin–Elmer 1320), the products being dissolved in $CHCl_3$. Proton and ^{13}C-NMR spectra (80 MHz in $CDCl_3$) of the high molecular weight products were obtained using a Bruker WP80 spectrometer. In order to determine the identities of the various C-atoms, spectral editing was carried out using a DEPT (Distortionless Enhancement by Polarization Transfer) sequence and a Bruker AM300 spectrometer.

Differential scanning calorimetry (DSC)

DSC data were obtained using a duPont 990 thermal analyzer, equipped with a standard DSC cell. Samples (5 mg) were sealed in Al pans and heated (at 10°C per min) in an atmosphere of pure N_2. An empty Al pan was used as reference. All samples were heated to 200°C, quenched, and reheated (5°C per min). The glass transition temperature, T_G, was obtained from the intersection of the baseline prior to the transition with the tangent drawn to the ΔT vs T curve associated with the transition.

Differential thermal analysis (DTA)

DTA data were obtained using a duPont thermobalance. Samples (5 mg) were heated to 500°C in a silica crucible at a programmed rate (10°C/min) in a dynamic N_2 atmosphere (50 cm^3/min).

Thermal degradations

Degradations were carried out under high vacuum (10^{-6} Torr) at 390 ± 2°C. Polymer samples (*ca* 100 mg) were heated in a glass reaction vessel, which was placed in a coaxial furnace. The volatile products of degradation, which were continuously removed by pumping, were separated into a number of fractions on passing through three traps arranged in series. The first trap (at 10°C), in which the high boiling components were collected, was placed immediately outside the furnace, and others were maintained at −45°C and at liquid N_2 temperature. The presence of non-considerable products was indicated by an in-line Pirani gauge placed at the exit of the liquid N_2 trap.

Thermal volatilization analyses (TVA)

Samples (100 mg) were pyrolyzed at 10^{-6} Torr in a standard TVA apparatus [12]. The heating rate was 10°/min, and the final temperature was 450°C. The traps were maintained at 0°C, −45°C, −75°C, −100°C and at liquid N_2 temperature.

Product analyses

(*a*) *Gaseous products.* A Toepler pump was used to transfer the gases which were not condensed in the liquid N_2 trap into a small reservoir which was connected to the inlet system of a gas chromatograph (Hewlett–Packard 5750). They were then transferred directly and quantitatively onto the column by the carrier gas. The analytical system consisted of a 2 m stainless steel column (5 mm diameter), packed with Poropak N (80–100 mesh) and operated at 60°C with He carrier gas. A thermal conductivity detector was used. The system was calibrated using known amounts of authentic samples of various gases (Matheson).

(*b*) *Liquid products.* The contents of the traps at −45°C and at −196°C were also analyzed by gas chromatography.

The liquid N_2 trap was warmed to 20°C, and the contents were swept by carrier gas (He) directly onto the column used in (a) above. The −45°C trap was warmed to 50°C, and the contents, transferred by carrier gas (N_2), reached the columns via the heated inlet system. Two columns were used, since the sensitivity of each was not sufficient to measure all the products; (a) a 6 m × 5 mm stainless steel column packed with 10% OV-351 (dimethyl silicone) (Chromatographic Specialities) on Chromosorb 80/100 operated at 100°C and programmed to 160°C, and (b) a 2 m × 5 mm stainless steel column with 5% DIDP (diisodecylphthalate) + 1.75% Bentone 34 (Chromatographic Specialities) on Chromosorb W-HP 80/100 operated at 90°C. In both cases, N_2 was the carrier gas.

The identities of the liquids were confirmed by mass spectrometry, the products exiting from the columns being trapped and subsequently transferred to the heated inlet of a Perkin-Elmer RMU7 mass spectrometer. Only qualitative analyses were undertaken but approximate relative amounts of each were estimated.

(*c*) *High molecular weight fraction.* The high boiling liquid fraction and the cold ring fraction from TVA were analyzed by mass spectrometry and by NMR. Mixtures were introduced into the mass spectrometer via the heated inlet system. Detection limits were critically influenced by the volatilities of the various components; thus not all of the products were necessarily analyzed.

Proton NMR spectra (80 MHz in CDl_3) and ^{13}C-NMR (20.1 MHz in $CDCl_3$) were obtained and spectral editing was carried out using a DEPT sequence.

While it was possible to distinguish the various environments of the carbon atoms present, (i.e. CH, CH_2, etc.) using DEPT, it was not possible to identify all the compounds unequivocally.

Molecular weights

Number-average molecular weights of the undegraded polymer and those of polymers undergoing degradation were obtained by membrane osmometry (Hewlett–Packard 501) using toluene as solvent at 37°C. The initial $\bar{M}_n$ was 9×10^4 (polydispersity index = 1.9).

RESULTS

Thermal analyses

(*a*) *DSC.* The DSC curve for POAS is shown in Fig. 1. The lower temperature endotherm is associated with the glass transition, and the higher temperature one with thermal degradation. Although the results qualitatively resemble those obtained for PS, [13] the T_G is about 30°C above that of PS, and this can be attributed to the higher energy barriers to segmental rotation brought about by dipole–dipole interactions of the CO groups, and by the steric effect

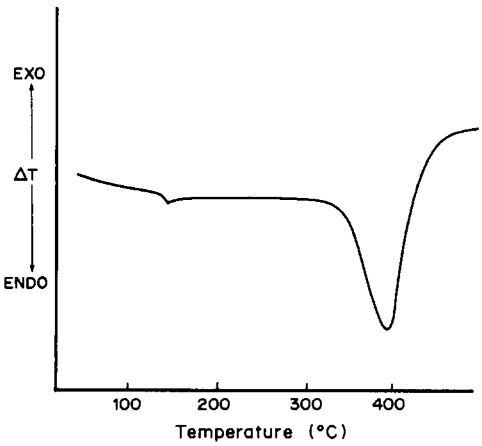


Fig. 1. DSC data for POAS. Heating rate 10%/min in N_2.

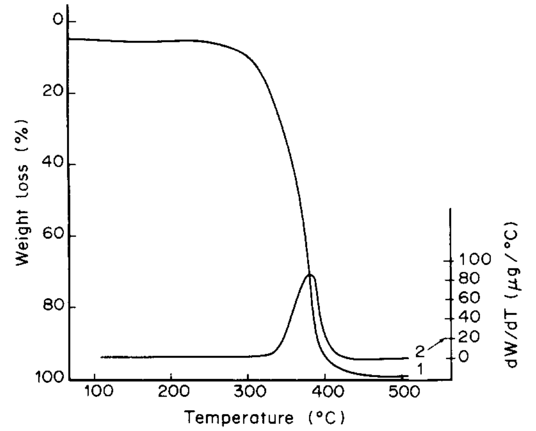


Fig. 2. Thermogravimetric data for POAS-dynamic N_2. (1) Weight loss curve; (2) differential weight loss.

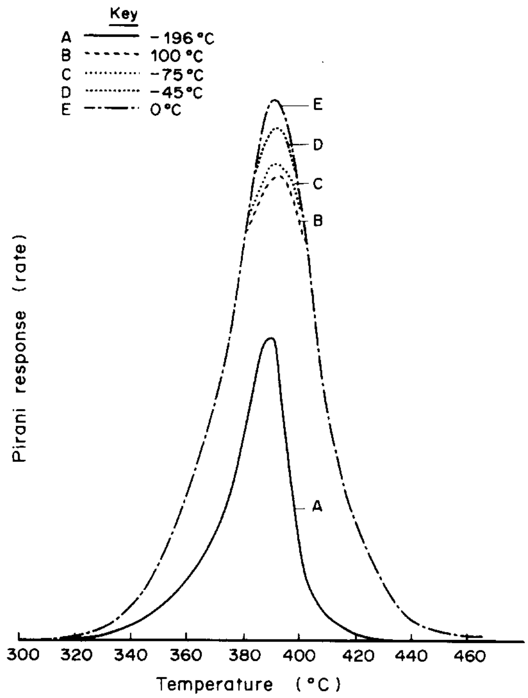


Fig. 3. TVA trace for POAS. Heating rate 10%/min. Trap temperatures shown in the key.

of the *o*-acetyl substituents. While the onset of degradation of POAS occurs at a similar temperature (to PS) (approximately 320°C), the temperature of maximum degradation is increased by about 30°C, and the endothermicity is higher than for PS, indicating that more reactions are involved in the overall process.

(*b*) *Thermogravimetric analysis*. Thermogravimetric data are shown in Fig. 2. The temperature of maximum weight loss coincides with the larger endotherm in Fig. 1, and it appears that the thermal degradation, as indicated by weight loss, occurs in a one stage process. No measurable amount of residue remains. The differential weight loss curve is superimposed on the above data (Fig. 2); it not only confirms the DSC data but indicates that POAS is thermally more stable than PS.

(*c*) *TVA*. The TVA trace is shown in Fig. 4; it can be seen that the single rate maximum at 390°C coincides with the larger endotherm shown in Fig. 1. Although the most abundant products are low molecular weight species, i.e. non-condensables and those volatile at −100°C, a range of other products having a wide range of volatilities is also formed. In all cases, the rate maxima occur at 390°C. No residue was detected but a significant cold ring fraction was formed.

Molecular weight changes

Number-average molecular weights are shown as a function of time of heating at 390°C (Fig. 3), and it can be seen $\bar{M}_n$ decreases rapidly in the early stages of the degradation. This behaviour is reminiscent of that shown by PS, in which case the initial rapid drop in molecular weight has been attributed to random chain scission [14, 15]. Also shown in Fig. 3 is a plot of reciprocal molecular weight vs time. The linearity implies that, at least in the early stages of the reaction, random chain scission occurs.

Reaction products

(*a*) *Gaseous products*. The results of quantitative analyses of the low molecular weight gaseous products are shown in Table 1.

(*b*) *Liquid products*. Results of the gas chromatographic and mass spectrophotometric analyses of the liquid fractions are summarized in Table 2. Monomer is by far the most abundant product but it comprises a smaller fraction (*ca* 23%) of the total products than does styrene in the PS degradation (i.e. about 40%). It is also obvious that the acetyl groups are removed from the *ortho* ring substituents, products such as styrene and toluene being formed in substantial yields. It is possible that the liquid mixture contains additional (and similar) species. However, only molecules which have been positively identified are shown in Table 2.

(*c*) *High molecular weight products*. The compositions of the cold ring fraction (TVA) and the mixture trapped at 10°C were qualitatively very similar. ^{1}H-NMR spectra gave broad peaks characteristic of oligomers and these were difficult to resolve.

Table 1. Yields of low molecular weight products. Degradation of POAS (100 mg) at 390°C in vacuum

Product	$10^4 \times$ Yield (mol)
CO	1.2
CH_4	0.5
C_2H_6	2.0

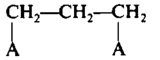
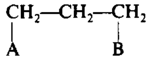
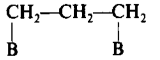
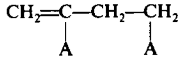
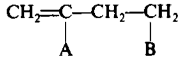
Table 2. Liquid products formed from POAS (390°C under vacuum). Approximate abundances; monomer = 100

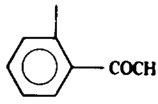
Product	Relative abundance
2-Acetylstyrene	100
2-Acetyltoluene	6.5
Styrene	8.5
Toluene	2.5
α-Methyl styrene	0.2
α-Methyl 2-acetylstyrene	0.1

Table 3. ^1H and ^{13}C-NMR signals from the high molecular weight fractions

^{13}C signal (ppm)	^1H signal (ppm)	Assignment
22–26	1.0–1.3	$-CH_3$
40	2.7–3.0	$-CH_2-$
42–46	5.4–5.8	$=CH_2$
48–50	6.8–7.1	$-\underset{\vert}{C}H$
130–150	7.0–8.1	$-CH$(aromatic)

Table 4. Partial analysis of the high molecular weight fraction from the degradation of POAS at 390°C under vacuum

Molecular weight (*m*/*e* value)	Possible structure
186	 $\underset{A}{\underset{\vert}{C}H_2}-CH_2-\underset{A}{\underset{\vert}{C}H_2}$
238	 $\underset{A}{\underset{\vert}{C}H_2}-CH_2-\underset{B}{\underset{\vert}{C}H_2}$
290	 $\underset{B}{\underset{\vert}{C}H_2}-CH_2-\underset{B}{\underset{\vert}{C}H_2}$
198	 $CH_2=\underset{A}{\underset{\vert}{C}}-CH_2-\underset{A}{\underset{\vert}{C}H_2}$
250	 $CH_2=\underset{A}{\underset{\vert}{C}}-CH_2-\underset{B}{\underset{\vert}{C}H_2}$

A = Ph, B = 

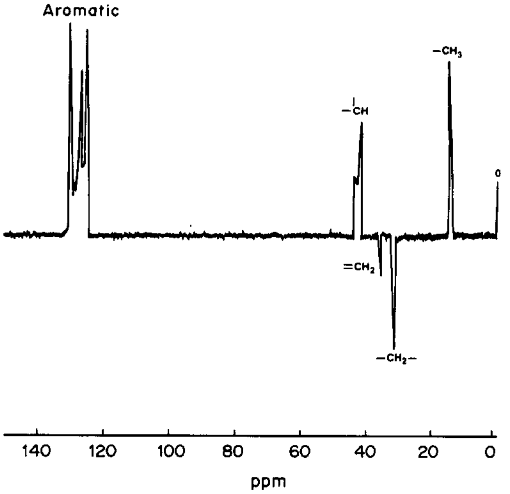


Fig. 5. Edited ^{13}C-NMR spectrum of high molecular weight products of degradation of POAS (CD_3Cl at 74.47 MHz).

^{13}C-signals were of low intensity. It was possible, however, to distinguish a number of different carbon atom environments using the DEPT sequence for spectral editing, and it can be concluded that the high boiling mixture consists of dimers and trimers, signals characteristic of bonded monomer units being present (Fig. 5). Other NMR data are summarized in Table 3, along with possible assignments.

Mass spectral analyses confirmed that some dimeric species were formed, and the presence of trimers was also indicated. However, their volatilities were insufficient to permit any conclusive identification. Analyses also indicated the presence of both phenyl and CO groups.

On the basis of the above analyses, a number of plausible structures are given in Table 4. (It is appreciated that this list is not necessarily complete, lower concentrations of other molecules not being detected.)

DISCUSSION

It is clear from the nature of both gaseous and liquid products that acetyl groups are removed from the benzene rings. Previous work indicates that their removal precedes monomer production [17]. However, such a sequence is inconsistent with the TVA data (Fig. 4), which clearly show that non-condensable gases and monomer (and other liquid products) are formed in concurrent processes. The lifetime of the acetyl radical at temperatures above about 150°C is very short, decomposing quantitatively to CO and $\dot{C}H_3$ [18]. If indeed CO, CH_4 and

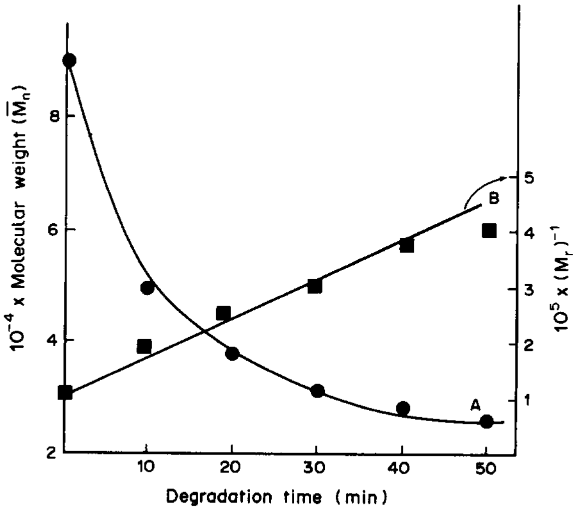
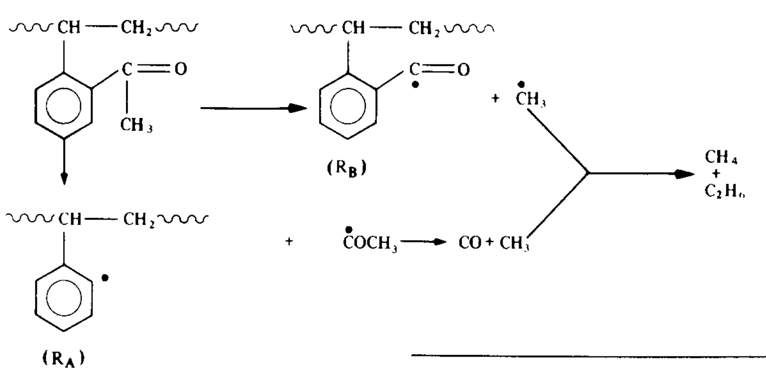
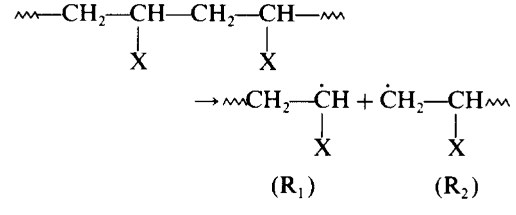


Fig. 4. Number-average molecular weight changes on degradation of POAS at 390°C under vacuum. (A) Molecular weight curve; (B) reciprocal $\bar{M}_n$ values.

C_2H_6 are derived from acetyl radical decomposition the combined yields of CH_4 and C_2H_6 should be comparable with that of CO. It can be seen, however, (Table 1) that the yields of hydrocarbons are about twice that of CO, and it is concluded that methyl radicals are formed additionally by scission of the CH_3–CO bond, a process which can be rationalized on the basis of the stabilization (due to delocalization) of the incipient radical (R_B) [19]. Ethane is formed by combination of two CH_3 (in presence of a "third" body) and methane by abstraction reactions involving the methyl radicals and most probably (on energetic grounds), α–C atoms of the polymer [20, 21]. Production of low molecular weight products is summarized as follows.



It has been established that both PS and poly(α-methyl-styrene) (PAMS) undergo random chain scission at temperatures in excess of 300°C [14, 15, 22, 23], and the molecular weight data shown in Fig. 3 imply that similar chain scission occurs in POAS. It may be represented as follows.

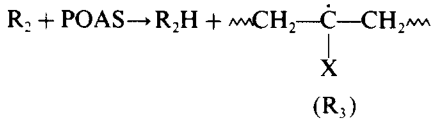


$$\sim\!CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}-\sim\ \rightarrow \underset{(R_1)}{\sim\!CH_2-\underset{X}{\dot{C}H}} + \underset{(R_2)}{\dot{C}H_2-\underset{X}{CH}\sim}$$

in which X = ($PhCOCH_3$).

R_1 then unzips to monomer, and R_2 undergoes abstraction reactions with the polymer [14, 15, 22], the radical centres being formed preferentially on the α–C-atoms [20].

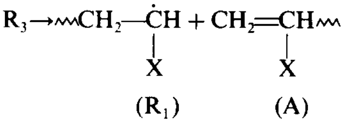
i.e.



$$R_2 + POAS \rightarrow R_2H + \underset{(R_3)}{\sim\!CH_2-\underset{X}{\dot{C}}-CH_2\sim}$$

R_3 may also be formed by intramolecular transfer reactions (back-biting) involving R_1 [14, 15, 22], a reaction which competes directly with depolymerization from R_1.

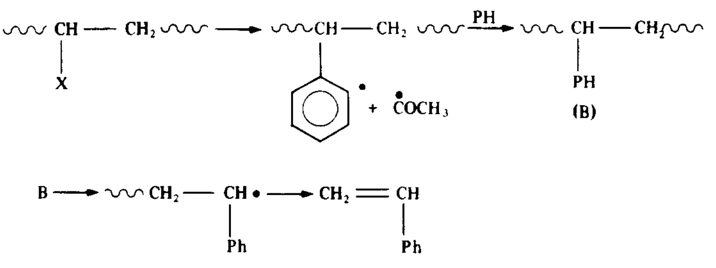
Recent studies have shown that the contribution to degradation from the initial random chain scission is relatively minor, the reaction contributing predominantly to molecular weight decreases being the subsequent decomposition of R_3 to produce an R_1 radical and a terminally unsaturated species [15]. It is likely that POAS undergoes similar β-scission, i.e.



$$R_3 \rightarrow \underset{(R_1)}{\sim\!CH_2-\underset{X}{\dot{C}H}} + \underset{(A)}{CH_2{=}\underset{X}{CH}\sim}$$

The monomer yield from POAS is lower than that from PS or PAMS, which suggests that abstractions involving R_1 compete favourably with depolymerization. However, methyl radical abstraction with the polymer also occurs [20, 21], thus the concentration of R_3 radicals is increased, and with it the possibilities for both intramolecular transfer and decomposition (to R_1 and A). In such circumstances, the effective zip length is decreased, and with it the monomer yield [15].

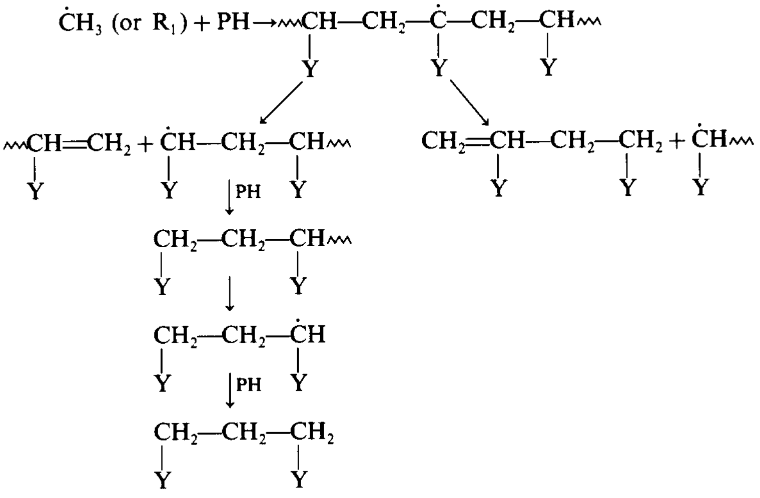
Styrene can be formed by a similar unzipping process, the acetyl group having been previously eliminated, i.e.



(PH = polymer)

The relatively large styrene yield is consistent with acetyl group removal, the extent of which is estimated to be 20% (based on CO yield).

The origin of dimeric species (Table 4) can be summarized as follows, [15] the group Y being either Ph or $PhCOCH_3$. (Prior removal of the CH_3CO groups yields the diphenyl compounds, and partial removal the mixed phenyl and ketonic species



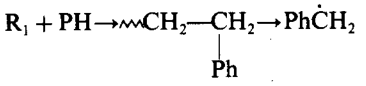
$$\dot{C}H_3 \text{ (or } R_1) + PH \rightarrow \sim\underset{Y}{CH}{-}CH_2{-}\underset{Y}{\dot{C}}{-}CH_2{-}\underset{Y}{CH}\sim$$

$$\sim\underset{Y}{CH}{=}CH_2 + \underset{Y}{\dot{C}H}{-}CH_2{-}\underset{Y}{CH}\sim \qquad CH_2{=}\underset{Y}{CH}{-}CH_2{-}\underset{Y}{CH_2} + \underset{Y}{\dot{C}H}\sim$$

$$\xrightarrow{PH} \underset{Y}{CH_2}{-}CH_2{-}\underset{Y}{CH}\sim \rightarrow \underset{Y}{CH_2}{-}CH_2{-}\underset{Y}{\dot{C}H} \xrightarrow{PH} \underset{Y}{CH_2}{-}CH_2{-}\underset{Y}{CH_2}$$

That the yields of dimeric and oligomeric species are greater (by about 50%) than the corresponding yields from PS [24], confirms the involvement of the methyl radicals in the above abstraction reaction. These results are in qualitative agreement with the observations of McNeill [25] and Camino [26] who showed that the presence of small free radicals during thermal degradation of a polymer, like PS, not only influences the rate, but also modifies the course of the degradation, more frequent transfer reactions, as above, producing the precursors of the oligomeric species at the expense of monomer.

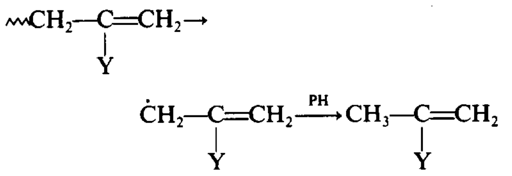
The formation of toluene from PS has been attributed to the decomposition of a benzylic chain end, it in turn being formed by abstraction involving R_1 [26], i.e.



$$R_1 + PH \rightarrow \sim\sim CH_2{-}\underset{Ph}{\dot{C}H_2} \rightarrow Ph\dot{C}H_2$$

$$Ph\dot{C}H_2 + PH \rightarrow PhCH_3$$

Analogous reactions with R_1 type radicals derived from POAS will yield toluene and 2-acetyltoluene. The relatively larger yields of these compounds (cf. PS) (Table 3) reflect the higher concentration of R_1 radicals formed (by abstraction) from POAS. The reactions of styryl radicals, following decomposition of unsaturated chain ends, are associated with the production of α-methylstyrene from PS, [14, 24, 26] i.e.



$$\sim\sim CH_2{-}\underset{Y}{C}{=}CH_2 \rightarrow$$

$$\dot{C}H_2{-}\underset{Y}{C}{=}CH_2 \xrightarrow{PH} CH_3{-}\underset{Y}{C}{=}CH_2$$

It can be seen that when Y = Ph and $PhCOCH_3$ respectively, α-methylstyrene and α-methyl-2-acetyl styrene are formed.

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