

Photolysis of Poly(*p-tert*-butylstyrene)

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Synopsis

The photodegradation of thin films of poly(*p-tert*-butylstyrene) with 254-nm radiation under high vacuum has been studied. The principal gaseous product is hydrogen, but smaller amounts (in decreasing order of yield) of methane, ethane, and isobutane are also formed, indicating that fission of bonds in the *tert*-butyl group is also involved. Ultraviolet and visible spectra of degraded films indicate the presence of unsaturated groups, initial rates of formation of these being considerably higher than those for polystyrene films. Solubility data indicate that crosslinking apparently occurs less readily than in the case of polystyrene, and this is interpreted in terms of the enhanced stability (due to the +I effect of the *tert*-butyl group) of the radicals formed by chain scission and also of the inhibiting steric effect of the *tert*-butyl group, particularly on crosslinking reactions involving the benzene rings. Quantum yields for the gaseous products and for chain scission and crosslinking were determined, and the mechanism of the various reactions are discussed.

INTRODUCTION

The 254-nm UV degradation of polystyrene has been studied in detail by numerous workers, and general mechanisms of the photodegradative reactions have been established.¹⁻⁵ These have been reviewed.⁶ Although the photolysis of the α -substituted polymer, poly(α -methylstyrene), has been studied in detail,⁷ little attention has been directed toward the photodegradation of ring-substituted polystyrenes, with the exception of poly(*p*-methylstyrene), which was found to behave rather similarly to polystyrene. However, there was evidence of participation of the *p*-methyl group, particularly in crosslinking reactions, the rate of crosslinking of the *p*-substituted polymer being approximately twice that of polystyrene.⁸

Otsu⁹ has found that ring substitution in styrene influences the reactivity of styryl radicals in copolymerization reactions, and recently a study of the thermal degradation of ring-substituted polystyrenes has shown that the degradation characteristics are sensitive to ring substitution, in particular, electron-withdrawing groups (Cl, Br) tend to reduce the thermal stability, largely by destabilizing depolymerizing radicals.⁹ Earlier studies of the radiation chemistry of ring-substituted polystyrenes showed some similar correlations with radiation stability.¹⁰ The object of the work described below was to investigate the possible influence of ring substitution on the photochemical reactions of polystyrene. The *tert*-butyl group was chosen as a para substituent largely on account of its electron-repelling characteristics which would be expected to influence the stability of radicals produced, particularly those at the α -position of the polymer.

EXPERIMENTAL

Materials. *p*-*tert*-Butylstyrene was prepared by the thermal depolymerization (under high vacuum) at 340°C of commercial poly(*p*-*tert*-butylstyrene) (Aldrich). Under these conditions, the major product was the monomer. Before polymerization, it was distilled under reduced pressure in the presence of pure nitrogen and stored at -20°C in the dark (bp 75°C at 18 torr). Dichloromethane, toluene, and methanol were analytical-grade reagents and were distilled before use. Pure samples of hydrogen, methane, ethane, and isobutane (Matheson) were used for mass-spectral calibrations.

Polymerization. *p*-*tert*-Butylstyrene was polymerized cationically in dichloromethane solution, using a monomer-solvent ratio of 1:5 by volume. The catalyst was tin tetrachloride, and the temperature was maintained at -5°C by means of an external salt bath. The monomer was distilled into the reaction vessel under high vacuum and was purged with pure nitrogen prior to the introduction of the catalyst, and a nitrogen atmosphere was maintained throughout the reaction. The polymer was isolated by precipitation in methanol, and precipitation was repeated twice, the dichloromethane solution being added to methanol. The polymer was then dried at 40°C under high vacuum (10^{-6} torr) until no residual solvent or precipitant could be detected by mass spectrometry.

Spectral Measurements. Ultraviolet spectra of polymer films were recorded on a Unicam SP800 spectrophotometer. The polymer was cast into films by evaporation of dichloromethane solutions on quartz plates. After removal from the plates, the films were dried at 50 °C under high vacuum, and experiments were not carried out on them until no residual solvent could be detected mass-spectrometrically.

Photochemical Techniques. The polymer was photolyzed in the form of thin films prepared on quartz plates. All reactions were carried out at $20^\circ \pm 1^\circ\text{C}$ under high vacuum (10^{-6} torr). The photochemical techniques and the optical equipment were very similar to those previously described in detail elsewhere,⁸ with the exception that the quartz reaction vessel was joined directly to the inlet of a RMU 7 mass spectrometer and rapid scans of the molecular weight range of 1 to 300 could be made. Alternatively, the mass spectrometer could be tuned to a given mass number, and the progress of formation of a given product could be constantly monitored. Quantitative analyses were performed, the mass spectrometer being calibrated using pure samples. It was established that the Lambert law (i.e., $I = I_0 e^{-\beta L}$ where β is the absorption coefficient, L is the film thickness, and I and I_0 are transmitted and incident intensities, respectively) was obeyed by the polymer, a linear plot of optical density versus film thickness (over the film thickness range 4×10^{-4} - 10^{-3} cm) being observed, and an absorption coefficient of 3300 cm^{-1} for 254-nm radiation was obtained. Film thicknesses were determined by standard interferometric techniques, and the experiments were carried out using films 5×10^{-4} cm thick. Actinometry was carried out using potassium ferrioxalate,¹¹ and the incident intensity of 254 nm radiation was found to be $1.8 \times 10^{-8} \text{ E cm}^{-2} \text{ min}^{-1}$.

Molecular Weight Determination. Number-average molecular weights of the undegraded and the soluble fractions of the irradiated polymers were determined by membrane osmometry (Hewlett-Packard 501 osmometer) at 37°C using toluene as solvent. The undegraded polymer had a \bar{M}_n value of 1.2×10^5 and a \bar{M}_w value (light scattering) of 2.2×10^5 .

Soluble Fraction Determination. After irradiation the films were extracted with toluene at room temperature. The insoluble gel was removed by centrifugation, washed repeatedly with toluene, and dried. The toluene solution was freeze dried to constant weight, and soluble and gel fractions were determined by weighing.

RESULTS AND DISCUSSION

Ultraviolet Spectra

The ultraviolet spectrum of a thin film of poly(*p*-*tert*-butylstyrene) (PTBS) is shown in Figure 1 (curve A). It can be seen that the general absorbance pattern is similar to that for a polystyrene (PS) film. However, the absorbance extends over a wider wavelength range, and the absorption coefficient for 254-nm radiation is higher, presumably the results of the presence of the electron-repelling *tert*-butyl groups, positive inductive effects perturbing the characteristic phenyl group absorption around 260 nm.¹²

Also shown in Figure 1 are the spectral changes associated with irradiation of the film ($\lambda = 254$ nm), and it can be seen that such treatment leads to a general increase in absorption over the entire UV region, extending into the visible region. Most pronounced changes are observed around 225, 280–300, and at 410 nm. In addition, the films undergo a yellowish discoloration on irradiation, and this is related to the absorption at 410 nm.

The general characteristics of increasing absorption at 225 nm are shown in Figure 2 (curve A) along with similar data for PS (curve B) obtained under identical conditions, and it can be seen that while PTBS undergoes more rapid reaction initially, the extents of reaction of both polymers are comparable after about 100 min of reaction. Similarly shaped curves can be obtained for the increasing absorbance in the 290–310 nm region and for the progress of coloration of both polymers, expressed by increased absorption at 410 nm (curves C and D for PTBS and PS, respectively).

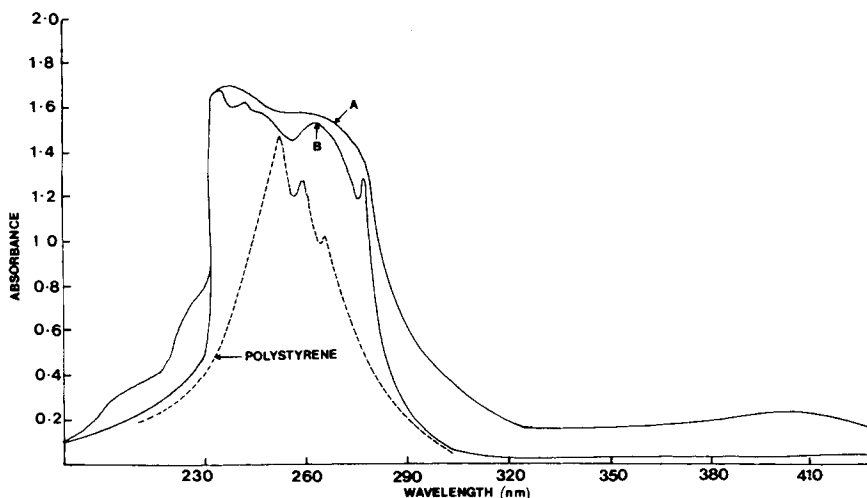


Fig. 1. Ultraviolet spectrum of poly(*p*-*tert*-butylstyrene) films 5×10^{-4} cm thick: A, undegraded; B, irradiated for 20 min under high vacuum ($\lambda = 254$ nm). Data for polystyrene are shown for comparison.

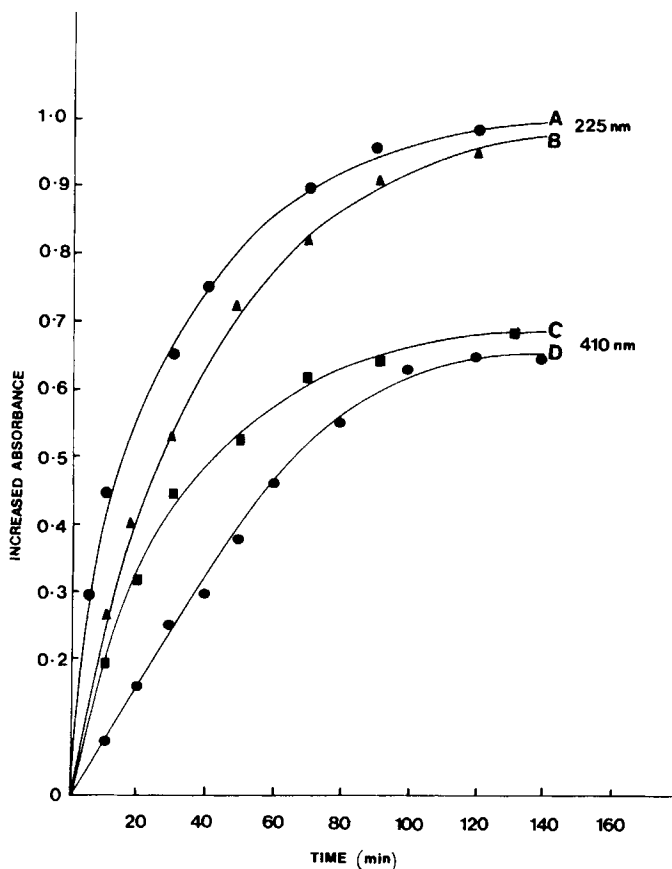


Fig. 2. Spectral changes at 225 and 410 nm as function of time of irradiation under high vacuum ($\lambda = 254$ nm) for: A and C, poly(*p*-*tert*-butylstyrene); B and D, polystyrene.

Absorption in the 225-nm region is associated with the presence of unsaturated hydrocarbon groups in conjugation with phenyl groups,¹³ and it has been suggested that the chromophores responsible for such absorptions in irradiated polystyrene¹ and poly(*p*-methylstyrene) (PPMS)⁸ are main-chain double bonds conjugated with the phenyl groups of these polymers, and also that extension of such conjugation ultimately leads to changes in the visible spectrum and to coloration. An alternative view has been taken by Rabek and Rånby,^{5,6} who have attributed the coloration and also spectral changes in the 280–300 nm region to the presence of fulvene and benzvalene derivatives, formed by the photoisomerization of the benzene rings in the polymers. So far it has not been established unequivocally that either of the above mechanisms is alone responsible for the formation of unsaturated centers in PS and PPMS, and it is suggested that the observed UV and visible spectral changes associated with irradiation of PTBS could be explained in terms of a combination of main-chain unsaturation and the presence of fulvene or benzvalene derivatives.

It is interesting to note that substituted fulvenes (as would be formed in this case) are generally more stable, and it is possible that the more rapid coloration of PTBS is in part the result of formation of such substituted fulvenes. One prerequisite for main-chain unsaturation is the formation of hydrogen atoms

by the fission of the C—H bond on the C atom in the position α to the phenyl group or abstraction of hydrogen from the same C atom, both reactions also yielding a radical center on the α -C atom. By analogy with previous findings,¹³ it can be predicted that such a radical formed on PTBS would be stabilized to some extent by the positive inductive (+I) effect of the *tert*-butyl group in the para position, hence formation of unsaturated centers (and hence possibly also coloration) may be facilitated and the more rapid reactions shown in Figure 2 would occur. The general shapes of the curves in Figure 2 can probably be explained in terms of self-inhibition, the initially formed chromophores acting as internal filters of the incident radiation (absorption at 254 nm is enhanced after a short period or reaction, Fig. 1), the effect being more marked in the more rapidly changing PTBS.

Volatile Products

Both qualitative and quantitative mass-spectroscopic analyses were carried out during the irradiations, and hydrogen was found to be the main product. Smaller amounts of methane, ethane, and isobutane were also formed. Figure 3 shows the characteristics of volatile product formation and the relative rates of formation of the above molecules. Although the rate of H₂ evolution is con-

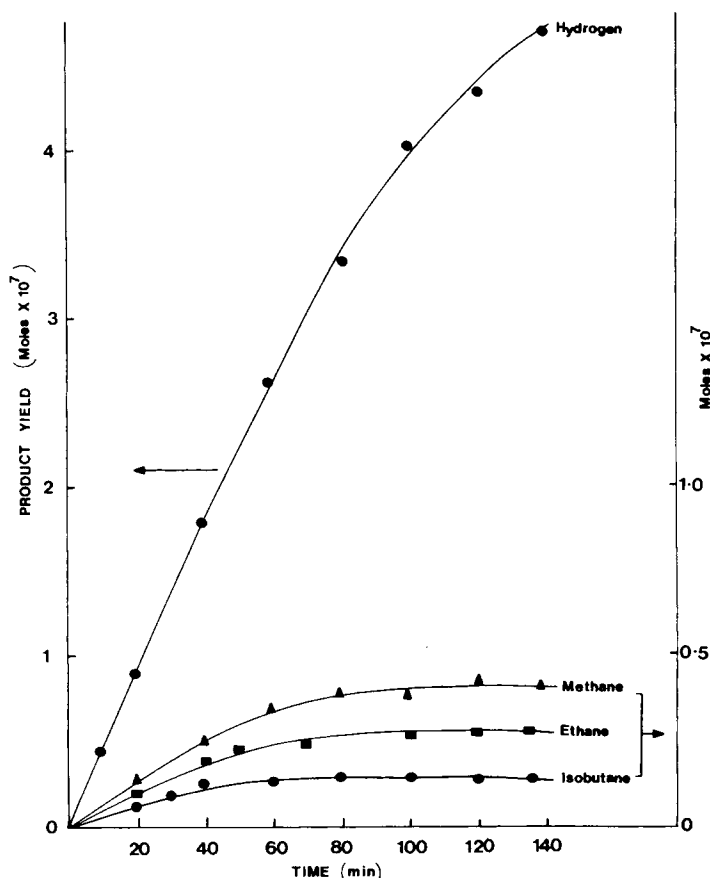


Fig. 3. Product evolution from poly(*p*-*tert*-butylstyrene) as function of time of irradiation ($\lambda = 254$ nm) under high vacuum.

stant over the first 80 min, rates of formation of the other products decrease rapidly after about 40 min. While it is possible that the decreasing rate of H₂ formation (after 80 min) is related to the decreased intensity of UV radiation penetrating the polymer (due to the filtering effects of the chromophores), it is most unlikely that such an effect could directly reduce rates of formation of the other products at a comparatively early stage in the reaction. It is more likely that the rates of formation of the products are governed by their rates of diffusion out of an increasingly crosslinked polymer matrix¹⁴ (the polymer rapidly becomes insoluble on irradiation). On account of its small volume, the H₂ molecule will be relatively unaffected, particularly when the crosslink density is not high. Heating of irradiated films leads to further liberation of these gases, but the quantities were not sufficient to conclude that the decreasing rates were totally the result of decreased diffusion coefficients due to crosslinking. It is possible that crosslinking also inhibits the separation of methyl and *tert*-butyl radicals (precursors of these gaseous products) from the cages in which they are initially formed by photolysis. Hence, radical mobilities and ultimately product yields are reduced. It is also possible that the various chromophores act indirectly by accepting some of the energy from the excited phenyl groups, a process which would compete with energy transfer to the bonds which dissociate to yield the products.

Quantum Yields

Quantum yields for formation of the four products were determined by standard methods.¹⁵

Because of the high extinction coefficient, 253.7 nm, radiation is nonuniformly absorbed through the films. The treatment used to calculate the quantum yield is modified as follows: If the light absorbed in an elementary layer of polymer of thickness dl and distance l from the surface on which the light is incident is dI (quanta $\text{cm}^{-2} \text{sec}^{-1}$) and I_0 is the incident intensity, then

$$dI/dl = I_0\beta \exp(-\beta l) \quad (\text{from the Beer-Lambert law})$$

where β is the absorption coefficient. The rate of light absorption in the elementary layer, in quanta $\text{cm}^{-1} \text{sec}^{-1}$, is I' , where

$$I' = dI/dt = I_0\beta \exp(-\beta l)$$

Integrating over the whole film thickness L , the total mean number of quanta absorbed, I_a , is given by the relation

$$I_a = \frac{\int_0^L [I_0\beta \exp(-\beta l)] dl}{\int_0^L dl} = \frac{I_0[1 - \exp(-\beta L)]}{L}$$

The quantum yield for Φ_l for formation of a species X in the elementary layer is

$$\Phi_l = \left(\frac{dX}{dt} \right) \frac{1}{I'}$$

where dX/dt is the local rate of formation of product X . The experimentally determined quantum yield is Φ , and this is given by the relation

$$\Phi = \frac{\text{net rate of product formation in the film}}{\text{mean rate of absorption of quanta by the film}}$$

From the above relations,

$$\Phi = \left(\frac{dX}{dt} \right)' \left\{ \frac{L}{I_0 [1 - \exp(-\beta L)]} \right\}$$

where $(dX/dt)'$ is the net rate of formation of X . Quantum yields using this equation were found to be as follows ($\pm 7\%$):

$$\Phi_{\text{H}_2} = 10^{-3}, \quad \Phi_{\text{CH}_4} = 2 \times 10^{-4}, \quad \Phi_{\text{C}_2\text{H}_6} = 10^{-4}, \quad \text{and} \quad \Phi_{\text{C}_4\text{H}_{10}} = 5 \times 10^{-5}$$

It is interesting to compare Φ_{H_2} with that obtained under identical conditions for polystyrene photolysis, i.e., $\Phi_{\text{H}_2} = 6 \times 10^{-4}$, a value in good agreement with previous data.¹ The greater H_2 yield can be attributed to the photolysis of the *tert*-butyl group, which has been shown to occur in *tert*-butylbenzene^{16,17} and perhaps also to a greater extent (relative to PS) of fission of the C—H bond in the α -position to the benzene ring, the resulting radicals being stabilized to some extent by the + I effect of the *p*-*tert*-butyl group.

Solubility Measurements

Insolubilization is concomitant with volatile product formation, the rate of formation of insoluble gel increasing with exposure for about 2.5 hr, after which it decreases rapidly. At this stage, the polymer is highly crosslinked, and the macroradicals have little mobility; however, volatile formation is still possible on account of the greater mobilities of the small-radical precursors.

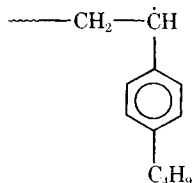
The data were analyzed using Charlesby's¹⁸ equation which is applicable to simultaneous chain scission and crosslinking of a polymer having an initial random molecular weight distribution (in this case $\overline{M}_w/\overline{M}_n \approx 2$):

$$S + S^{1/2} = \frac{\alpha}{\gamma} + \frac{1}{\gamma P_0 D}$$

in which S is the weight of the soluble portion after absorbance of a radiation dose D , P_0 is the initial number-average degree of polymerization, and α and γ are constants proportional to the probabilities of chain scission and crosslinking, respectively. This equation has been found to represent photochemical degradation adequately¹⁸⁻²⁰ when modified to

$$S + S^{1/2} = \frac{\alpha}{\gamma} + \frac{1}{P_0 \gamma_0 t}$$

where I_0 is the incident intensity and t is the time of irradiation. Figure 4 is a typical plot of $(S + S^{1/2})$ versus t^{-1} . It can be seen, then, that as the reaction proceeds, there is progressive departure from linearity; however, extrapolation of the linear portion to zero dose gives an intercept of $\alpha/\gamma = 0.49 \pm 5\%$, indicating that crosslinking is almost two times more probable than chain scission. This ratio is higher than that observed (under identical conditions) for PS, i.e., $0.4 \pm 5\%$,²¹ and it reflects the more facile chain scission in PTBS. This is perhaps a consequence of the inhibiting effect of the bulky *tert*-butyl groups on crosslinking reactions. Reactions involving crosslinking through the benzene rings, in particular, would be susceptible to such steric effects. On the other hand, one of the radicals formed on chain scission, i.e.,



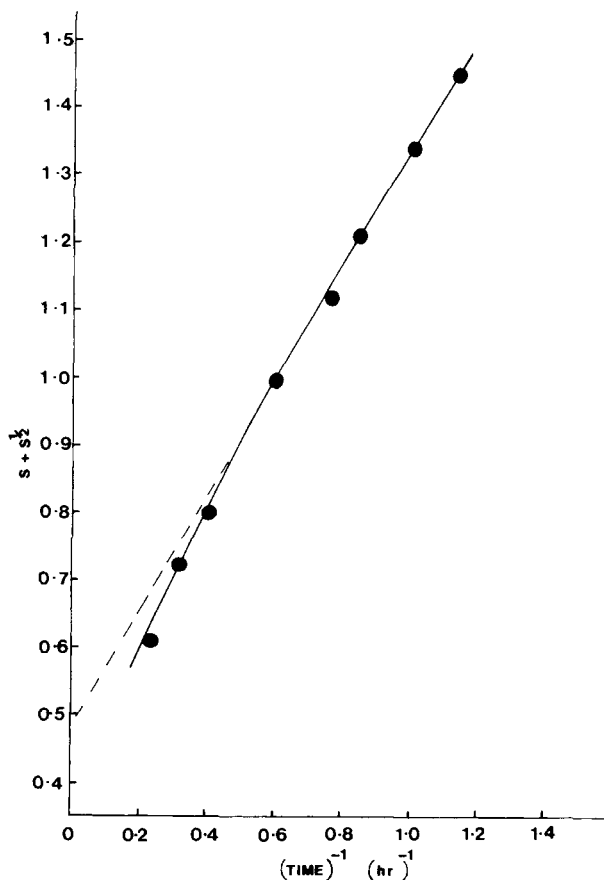


Fig. 4. Pinner-Charlesby plot for the photolysis of poly(*p*-*tert*-butylstyrene) under high vacuum ($\lambda = 254$ nm). Soluble fraction S as a function of reciprocal irradiation time.

is likely to be more stabilized than the corresponding radical formed on PS on account of the $+I$ effect of the *tert*-butyl group, hence chain scission would be relatively more probable.

Quantum yields for chain scission and for crosslinking were estimated from the Charlesby-Pinner data using the method of Geuskens.²² The equation may be rewritten²²

$$S + S^{1/2} = \frac{\alpha}{\gamma} + \frac{2R'_{\text{gel}}}{R}$$

where R'_{gel} is the dose for incipient gel formation and R is the dose absorbed. The quantum yield for crosslinking Φ_{CL} was calculated from the gelling dose R_{gel} , since this corresponds to one crosslinked unit per macromolecule.^{22,23} The crosslinking quantum yield Φ'_{CL} that would be observed in the absence of chain scission can be obtained from the R'_{gel} , i.e., the gelling dose that would be observed in the absence of main-chain scission,²³ and the quantum yield for chain scission Φ_{CS} is obtained from the relation²²

$$\alpha/\gamma = \Phi_{CS}/2\Phi'_{CL}$$

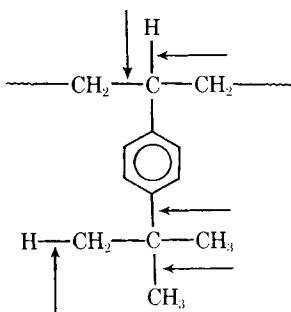
Values of these parameters are summarized in Table I.

The Reaction Mechanism

Primary Reactions

The chromophores for 254-nm radiation in PTBS are the phenyl moieties, the initially formed excited species being the first singlet states (monomer fluorescence can be observed²¹). However, in order to account for the reaction products, bonds adjacent to the phenyl groups have to be ruptured. Electronic energy transfer into the various vibrational modes (by internal conversion) presumably takes place.

Previous studies^{16,17} of the photolysis of *p*-disubstituted benzenes (plausible model compounds) have shown that fission of bonds occurs in the positions α , β , and γ to the benzene rings, the order of fission being approximately related to the bond dissociation energies. The initial bond fissions required to account for the present products are indicated on the following formula, and quantum, i.e.,



yields for gaseous product formation reflect the various bond dissociation energies. H_2 , CH_4 , and C_2H_6 have previously been obtained from the photolysis of *p*-*tert*-butylbenzene.^{16,17} However, there appears to be some difference of opinion regarding the exact extent of γ_{C-H} bond fission,^{16,17} and the absence of C_4H_{10} could be due to analytic limitations, the present technique being much more sensitive. It has previously been established^{1,4} that α_{C-H} bond fission occurs in PS and that this is the origin of the H_2 . It is likely that such fission also occurs in PTBS, the resulting radical being stabilized by the $+I$ effect of the *tert*-butyl group, and it is possible that the enhanced rate of H_2 formation (relative to PS) is related to this. Fission of the γ_{C-H} bond as a primary source of H_2 would, on the basis of bond dissociation energies, be much less favorable (approximate values of 75 and 87 kcal/mole for α - and γ -bonds, respectively, can be calculated using Benson's method²⁴), but in the light of previous findings¹⁶ it cannot be excluded.

Photoisomerization of the excited phenyl groups to substituted fulvenes and benzvalenes could presumably also occur, and such species could account in part for the coloration that is observed.

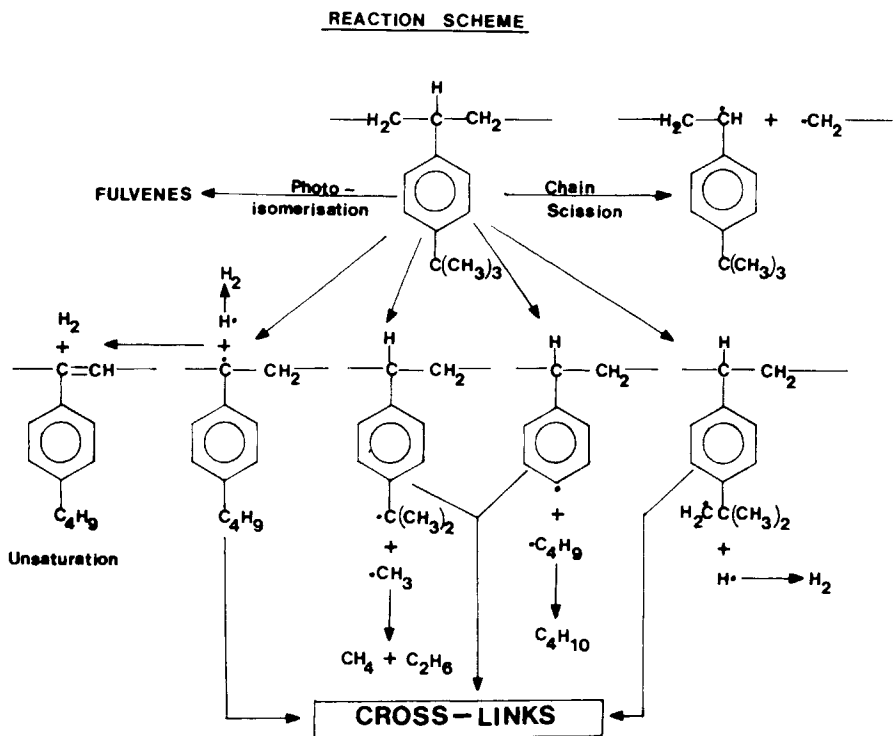
Secondary Reactions

These are the results of the interactions of the micro and macro radicals with each other and with the polymer. H_2 may be formed by combination of H atoms (in the presence of a third body), but on account of the reactivity of H atoms, it

is likely that most of the H_2 will result from inter- and intramolecular abstraction reactions. It is conceivable that abstraction from the β -C atom in the main chain (i.e., the atom adjacent to the initial α -C-H fission) will lead to main-chain unsaturation²⁵ and hence account in part for some of the UV spectral changes observed. The other gaseous products can be accounted for by methyl radical combination (in the presence of a third body) and by abstraction by both methyl and *tert*-butyl radicals from the polymer, or perhaps by combination of these radicals with H atoms.

Crosslinking may be achieved by the interaction of a variety of macroradicals, produced by abstractions and by α -C-H fission. As pointed out above, the participation of the benzene rings in crosslinking may be reduced by the steric effect of the *tert*-butyl groups.

The most important reactions are summarized in the following scheme:



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TABLE I
Photolysis of PTBS Film ($\lambda = 254$ nm) Under High Vacuum. Estimation of Quantum Yields for Chain Scission and Crosslinking

Parameter	Value ($\pm 7\%$)
R_{gel}	$8.5 \times 10^{-6} \text{ E mg}^{-1}$
R'_{gel}	$6 \times 10^{-6} \text{ E mg}^{-1}$
α/γ	0.49
Φ_{CL}	6×10^{-4}
Φ'_{CL}	9×10^{-4}
Φ_{CS}	8.8×10^{-4}

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