

# On the photolysis of chain-chlorinated polystyrene

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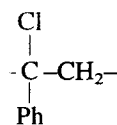
## Abstract

Copolymers of styrene and  $\alpha$ -chlorostyrene containing 19%–95%  $\alpha$ -chlorostyrene, prepared by photochlorination of polystyrene (PSt), were irradiated with UV light at  $\lambda_{\text{inc}} = 254$  nm (continuous irradiation) or at  $\lambda_{\text{inc}} = 266$  nm (flash photolysis). The major photochemical reactions occurring in films of highly chlorinated polymer (CPSt-95,  $\gamma_{\text{Cl}} = 0.95$  Cl atoms per repeating unit) are chlorine release ( $\phi(\text{HCl}) = 2 \times 10^{-2}$ ) and the accompanying formation of carbon–carbon double bonds. Main-chain scission is a minor process of quantum yield  $\phi(\text{S}) \approx 2 \times 10^{-3}$ , but brings about a decrease in the average molar mass of CPSt-95. Flash photolysis studies revealed the existence of singlet excimers ( $\tau \leq 20$  ns), triplets ( $\tau \approx 65$  ns) and benzyl-type radicals ( $\tau \geq 5$  ms). The quantum yields of chlorine release and formation of benzyl-type radicals, measured in tetrahydrofuran solution, are of equal magnitude (about 0.2). By contrast, photochemical reactions in copolymers of low chlorine content resemble those induced in polystyrene, e.g. at  $\gamma_{\text{Cl}} = 0.19$  intermolecular cross-linking dominates over main-chain cleavage and renders the polymer insoluble.

**Keywords:** Photolysis; Chain-chlorinated polystyrene; Copolymers; Styrene;  $\alpha$ -Chlorostyrene

## 1. Introduction

Ring-chlorinated and ring-chloromethylated polystyrene (PSt) have been found to cross-link much faster than unsubstituted PSt upon UV irradiation and have therefore attracted the interest of various researchers developing high performance, negatively working, deep UV resists [1,2]. While in the course of these investigations both the photochemistry and photophysics of ring-chlorinated and ring-chloromethylated polystyrene have been thoroughly studied [3,4], little is known about PSt chlorinated in the polymer backbone. According to McNeill and Coskun [5], a highly chlorinated PSt of  $\gamma_{\text{Cl}} = 1.35$  Cl atoms per repeating unit predominantly cross-linked upon UV irradiation, as was concluded from partial insolubilization of the polymer. Moreover, Nalamasu and Taylor reported [6] that PSt of  $\gamma_{\text{Cl}} = 1.14$ , chlorinated both at the ring and in the  $\alpha$  position, acted as a negative tone resist when exposed to UV light of  $\lambda = 248$  nm. Apart from these small pieces of information, to the best knowledge of the authors, additional more detailed information about the photolysis of chain-chlorinated polystyrene possessing repeating units of the structure



has not been reported in the literature. Therefore, we have recently performed some experiments on the photochemical and photophysical behaviour of this class of polymers and would like to report the results in this paper.

## 2. Experimental details

### 2.1. Preparation of chain-chlorinated PSt

Starting with a polystyrene sample of  $M_w = 3.2 \times 10^5$ , poly(styrene-co- $\alpha$ -chlorostyrene) samples of different comonomer composition were prepared by photochlorination according to a procedure described by Jenkins et al. [7]. Carbon tetrachloride solutions of polystyrene ( $50 \text{ g l}^{-1}$ ) were bubbled with chlorine and irradiated at  $5^\circ\text{C}$  using a medium pressure mercury lamp (TQ 718, 500 W, Original Hanau). The chlorine content of the polymer increased with increasing time of irradiation. In this way various copolymers differing in comonomer composition were prepared. The polymer samples, which were characterized by size exclusion chromatography (SEC), elemental analysis, FTIR and NMR spectroscopy, are listed in Table 1.

The IR and NMR spectra closely resemble those reported in Refs. [7] and [5] respectively. The copolymer CPSt-95, for example, exhibits IR absorption bands (recorded with a

Table 1  
Polymer samples used in this work

Polymer	$M_w^a$	Chlorine content in polymer	
		Wt.% Cl	$\gamma_{Cl}^b$
PSt	$3.2 \times 10^5$	0	0
CPSt-19	$3.0 \times 10^5$	6.4	0.19
CPSt-22	$3.0 \times 10^5$	7.6	0.22
CPSt-40	$5.1 \times 10^4$	12.7	0.40
CPSt-50	$3.0 \times 10^5$	15.4	0.50
CPSt-95	$2.9 \times 10^5^c$	25.6	0.95

<sup>a</sup> Weight average molar mass determined by SEC (calibration on basis of PSt standards).

<sup>b</sup> Number of chlorine atoms per structural repeating unit.

<sup>c</sup> Almost the same value was obtained by the light-scattering method.

Bio-Rad spectrometer, model FTS-7IR) at the following wavenumbers (in  $\text{cm}^{-1}$ ): 547, 700, 760, 840, 920, 1035, 1085, 1460, 1500, 1580, 1605, 1855 (shoulder), 2937, 3006, 3028, 3060 and 3085. The NMR spectrum of CPSt-95 (recorded with a Bruker spectrometer, model AC 200) exhibits signals (chemical shifts  $\delta$  in ppm units) at 1.5 (sharp, due to protons of  $-\text{CH}_2-$  groups) and at 7.0 (broad, due to aromatic protons). Notably, no signal at 1.85 was recorded, indicating the absence of detectable amounts of tertiary protons.

## 2.2. Preparation of polymer films

Films were prepared by casting  $\text{CH}_2\text{Cl}_2$  solutions of the polymers ( $70 \text{ g l}^{-1}$ ) on quartz plates using a motorized film applicator (Erichson, model 509/1). The films were dried for 3 days in vacuo (0.01 bar) at room temperature.

## 2.3. Irradiations

### 2.3.1. Continuous irradiations

All continuous irradiations were performed in a photo-reactor (Rayonet, model RPR 100), equipped with low pressure mercury lamps (RPR-2537A) emitting essentially (about 80%) light at 253.7 nm, at an exposure dose rate  $D_{r_{\text{exp}}} = 7.2 \times 10^{-3} \text{ einstein l}^{-1} \text{ min}^{-1}$ . The latter was determined with the aid of a potassium ferrioxalate actinometer.

Irradiations of polymer solutions were performed in quartz ampoules. For the sake of deaeration the solutions were purged with argon prior to irradiation. Polymer films deposited on quartz substrates were irradiated in evacuated quartz vessels.

### 2.3.2. Flash photolysis

Polymer solutions of appropriate concentrations and polymer films (about  $1.2 \mu\text{m}$  thick) were irradiated with single 15 ns flashes of 266 nm light produced by an Nd-YAG laser system operated in conjunction with two frequency doublers.  $\text{K}_4\text{Fe}(\text{CN})_6$  actinometry yielded exposure doses per flash of about  $5 \times 10^{-5} \text{ einstein l}^{-1}$ . Transient absorption measure-

ments were performed under conditions similar to those described earlier [4].

## 2.4. Determination of HCl

Determinations were performed both with deaerated tetrahydrofuran (THF) solutions of the polymers and with polymer films. To the irradiated solutions equal volumes of water were added and the pH value of the resulting solutions was measured potentiometrically with the aid of a glass electrode.

In the case of films the irradiation vessel containing the sample was immersed in liquid nitrogen after irradiation in order to condense HCl. Subsequently THF was added to dissolve both polymer and HCl, and prior to the potentiometric measurement water was added.

## 2.5. Detection of unsaturations

Dichloromethane solutions of the irradiated copolymers were treated with bromine ( $\text{Br}_2$ ). The reaction of  $\text{Br}_2$  with carbon-carbon double bonds was followed via luminescence measurements. After the treatment, surplus bromine and solvent were removed from the polymer by evaporation. Subsequent emission measurements with the redissolved polymer showed that bromination resulted in a decrease in the fluorescence intensity provided that unsaturations were present. Absorption measurements turned out to be less appropriate for the detection of the progress of the bromination, because both  $\text{Br}_2$  and the irradiated polymers absorb light in the same wavelength range. In spite of this obstacle, a bromination-related discoloration of the polymer solution in the wavelength range between 300 and 350 nm was recorded.

## 2.6. Molar mass characterization of the copolymers

Size exclusion chromatography was applied using two systems. System I was used for molar mass determinations based on polystyrene calibration. It consisted of four columns (Waters, Ultrastyrigel 500,  $10^3$ ,  $10^4$  and  $10^5 \text{ \AA}$ ) operated in conjunction with an RI detector (Waters 410). System II was used to attribute luminescing groups. It consisted of two columns (Shodex A-803 and Ultrastyrigel  $10^5 \text{ \AA}$ ) operated in conjunction with an emission detector (Merck-Hitachi, model F-410). Absolute molar mass determinations were performed with the aid of the light-scattering method.

## 3. Results and discussion

### 3.1. Continuous irradiations

#### 3.1.1. Molar mass changes

When films of the various copolymers ( $d = 1.2 \mu\text{m}$ ) were irradiated under argon, the average molar mass decreased apart from the case of CPSt-19, the copolymer with the lowest

Table 2  
Irradiation of CPSt-95 at  $\lambda_{inc} = 254$  nm. Quantum yields  $\phi(S)$ , of main-chain scission, and  $\phi(HCl)$ , of hydrogen chloride formation

Solvent	Atmosphere	$\phi(S)$	$\phi(HCl)$
None (film)	Ar	$2.2 \times 10^{-3}$	$2.3 \times 10^{-2}$
THF	Ar	$5.7 \times 10^{-3}$	$2.0 \times 10^{-1}$
$CH_2Cl_2$	Ar	$5.8 \times 10^{-3}$	
$CH_2Cl_2$	O <sub>2</sub>	$7.2 \times 10^{-3}$	

chlorine content. This polymer became insoluble upon UV irradiation, indicating predominant intermolecular cross-linking. However, cross-linking was less efficient than in the case of PSt, as revealed from a comparison of the gel doses:  $D_{gel} = 2.4 \times 10^{-6}$  einstein  $cm^{-2}$  (CPSt-19) and  $D_{gel} = 0.7 \times 10^{-6}$  einstein  $cm^{-2}$  (PSt).

In the case of CPSt-95 the decrease in the weight average molar mass  $M_w$  was measured as a function of the irradiation time.  $1/M_w$  was found to increase linearly and the quantum yield of main-chain scission  $\phi(S) = 2.2 \times 10^{-3}$  was obtained on the basis that intermolecular cross-linking can be neglected. As is seen from Table 2, quantum yields of the same order of magnitude were found when CPSt-95 was irradiated in dilute solutions of dichloromethane or tetrahydrofuran. Actually,  $\phi(S)_{solution}$  is about three times larger than  $\phi(S)_{film}$ . Oxygen seems to influence the yield only slightly. From these experiments it is concluded that chain chlorination of polystyrene brings about a tendency of increased photocleavage of C–C bonds in the main-chains.

### 3.1.2. C–Cl bond scission

**Irradiation of polymers in solution.** Since chlorine atoms released in THF solution rapidly abstract hydrogen from the solvent to form HCl, C–Cl bond cleavage can be conveniently monitored by determining the amount of HCl formed. Actually, the amount of HCl increased with increasing irradiation time and approached a limiting value which corresponded exactly to the chlorine content of the polymer under investigation. This implies complete photochemical chlorine release from the polymer. No HCl was formed upon irradiation of PSt. The quantum yields of HCl formation obtained from the initial slopes of the HCl formation curves are plotted in Fig. 1 as a function of  $\gamma_{Cl}$ . Since the extinction coefficients of both monomer units at 254 nm are equal ( $\epsilon_{254\text{ nm}} = 205 \text{ l mol}^{-1} \text{ cm}^{-1}$ ), both copolymer components absorb light at ratios corresponding to the composition ratio. Therefore, from the linear dependence of  $\phi(HCl)$  on  $\gamma_{Cl}$  it is concluded that energy transfer from styrene to  $\alpha$ -chlorostyrene units and vice versa does not occur. Notably, the quantum yield  $\phi(HCl) = 0.20$  determined in the case of CPSt-95 is of a magnitude similar to the quantum yield of C–Cl bond rupture (0.26) reported in the literature for benzyl chloride [8]. The latter value was substantiated in this work:  $\phi(HCl) = 0.30$ . Obviously, regarding the HCl release, a polymer effect does not exist in the case of chain-chlorinated polystyrene, which contrasts with the case of poly(*p*-chlorostyrene) where the

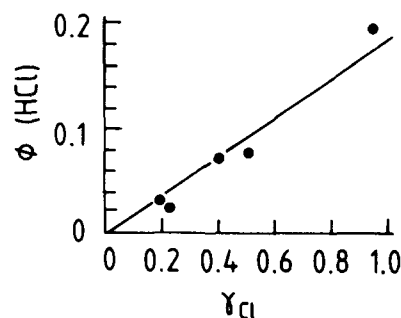


Fig. 1. Continuous irradiation of chlorinated polystyrenes at  $\lambda_{inc} = 254$  nm in Ar-saturated THF solution. The quantum yield of HCl formation vs.  $\gamma_{Cl}$ , the number of chlorine atoms per repeating unit.

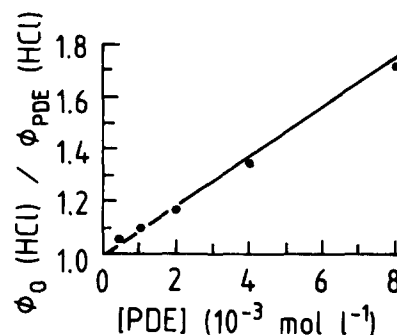


Fig. 2. Stern–Volmer plot of HCl quenching by PDE.  $\phi_0(HCl)$  and  $\phi_{PDE}(HCl)$  denote values obtained in the absence and presence of PDE respectively.

$\phi(HCl)$  value for the polymer is about 20 times lower than that for the low molecular model [3].

Regarding the mechanism of C–Cl bond cleavage, it is interesting to note that penta-1,2-diene (PDE) acted as a quencher with respect to HCl formation. The extent of quenching increased with increasing PDE concentration as can be seen from Fig. 2, which shows a typical Stern–Volmer plot. The linearity of the plot suggests that only one kind of excited species is quenched by PDE and the magnitude of PDE concentrations causing effective quenching indicates that PDE acts as triplet quencher in this case. Therefore, it is concluded that C–Cl bond cleavage originates essentially from the decay of excited triplet states. From the slope of the straight line in Fig. 2 the bimolecular rate constant  $k_q = 1.4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  is obtained.

**Irradiation of polymer films.** Chlorine radicals generated in the neat polymer can either abstract backbone H atoms or add to benzene rings. In the former case HCl is formed. In the case of CPSt-95 rather little HCl was found:  $\phi(HCl) = 0.023$ , i.e. about one order of magnitude less than in solution. Since addition to the benzene ring does not occur faster than hydrogen abstraction, the low quantum yield of HCl is indicative of a low yield of C–Cl bond cleavage in films. This can be explained in terms of cage recombinations occurring in films with a much higher probability than in polymer solutions. Notably, prolonged irradiation of polymer films resulted in HCl yields corresponding to an almost complete conversion of chlorine into HCl, thus demonstrating

that chlorine addition to the benzene ring is negligible. Regarding the low quantum yield of HCl found for films, it is interesting to note that poly(vinyl chloride) (PVC) exhibits quite a similar behaviour: for PVC films  $\phi(\text{HCl})$  is about one order of magnitude lower than for THF solution [9].

### 3.1.3. Polyene formation

Irradiation of the chlorinated polystyrenes both in the form of films and in solution resulted in the formation of a broad unstructured optical absorption in the wavelength range between 230 and 500 nm.

*Irradiation of polymers in solution.* Typical results are presented in Fig. 3, where optical absorption spectra of unirradiated and irradiated Ar-saturated dichloromethane solutions of CPSt-95 are depicted. The increase in the optical density (OD) becomes slower with increasing irradiation time and approaches a limiting value, the latter being larger the higher the chlorine content of the polymer is. This can be seen from Fig. 4, where time profiles of the OD at  $\lambda_{\text{obs}} = 300$

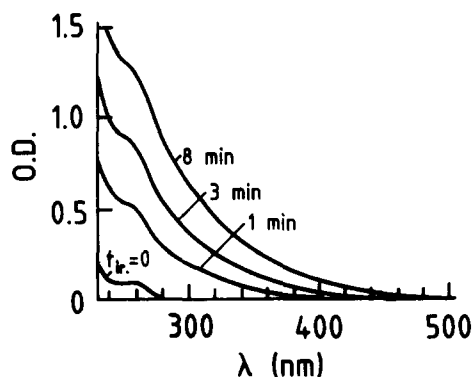


Fig. 3. Continuous irradiation of CPSt-95 at  $\lambda_{\text{inc}} = 254$  nm in Ar-saturated  $\text{CH}_2\text{Cl}_2$  solution. Optical absorption spectra recorded after various times of irradiation (as indicated).

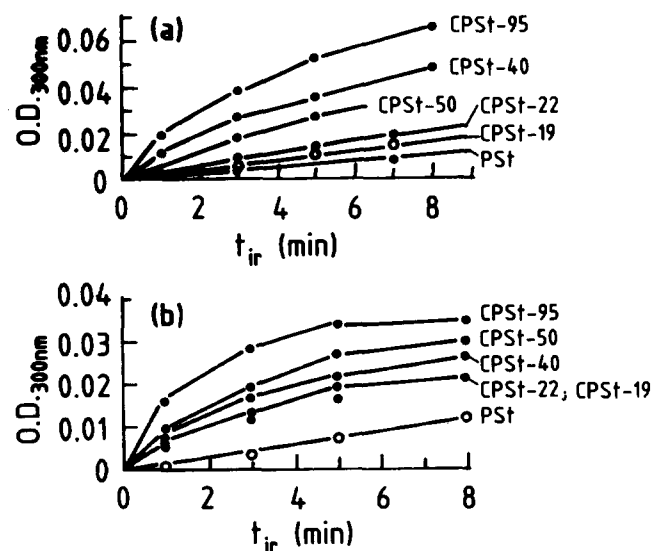


Fig. 4. Continuous irradiation of PSt and CPSt samples 19, 22, 40, 50 and 95 at  $\lambda_{\text{inc}} = 254$  nm in (a) Ar-saturated and (b)  $\text{O}_2$ -saturated  $\text{CH}_2\text{Cl}_2$  solution. Plots of the optical density at 300 nm vs. the time of irradiation.

nm obtained for the various copolymers are shown. A comparison of the plots in Figs. 4(a) and 4(b) reveals that  $\text{O}_2$  retards the build-up of the new absorption. In connection with these results it is notable that poly(vinyl chloride) exhibits quite a similar behaviour when exposed to UV irradiation [10–14], i.e. also in this case a new absorption extending up to the visible wavelength range is formed. Since this absorption is due to polyene formation, it was suggested that conjugated double bonds are also generated in the CPSt samples. Actually, convincing evidence for this suggestion was obtained by bromination tests in conjunction with emission measurements (see Section 3.1.4). Therefore it is concluded that the formation of HCl is accompanied by the generation of C=C bonds in the polymer backbone.

*Irradiation of polymer films.* When films of CPSt-95 were irradiated, changes in the optical absorption spectrum quite similar to those caused by irradiation of the polymer in solution, but considerably less pronounced, were observed. At constant absorbed dose the extent of the OD increase at  $\lambda = 300$  nm is about two times lower than in solution. This is in accordance with the lower probability of C–Cl bond rupture in films and also indicates the connection between double-bond formation and chlorine release.

### 3.1.4. Emission measurements

*Irradiation of polymers in solution.* Upon recording fluorescence spectra of the copolymers dissolved in dichloromethane solution, the following observations were made (see Fig. 5). (a) The shape of the spectra of the copolymers possessing maxima at 280 nm and 330 nm resembles that of the spectrum of PSt, where the peaks are attributed to monomer and excimer emission respectively. The intensity ratio  $I_{\text{dim}}/I_{\text{mon}}$  decreases with increasing chlorine content from 2.1 (PSt) to 1.3 (CPSt-95) thus indicating that the copolymers are less prone to excimer formation than PSt. (b) The overall emission intensity decreases with increasing chlorine content of the polymers suggesting that deactivation paths different from light emission become operative in the case of chlorinated polystyrenes. Interestingly, as can be seen from Fig.

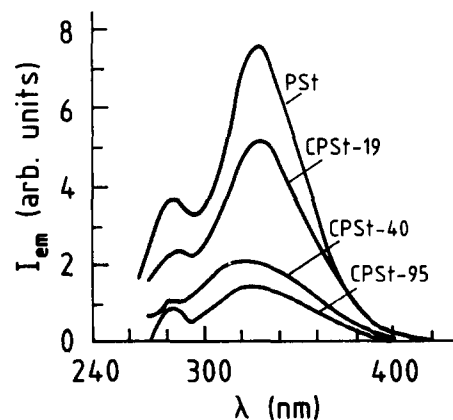


Fig. 5. Fluorescence spectra of PSt and CPSt samples 19, 40 and 95 recorded with Ar-saturated  $\text{CH}_2\text{Cl}_2$  solutions;  $\lambda_{\text{exc}} = 266$  nm. Polymer concentrations were adjusted to  $\text{OD}_{266 \text{ nm}} = 0.2$ .

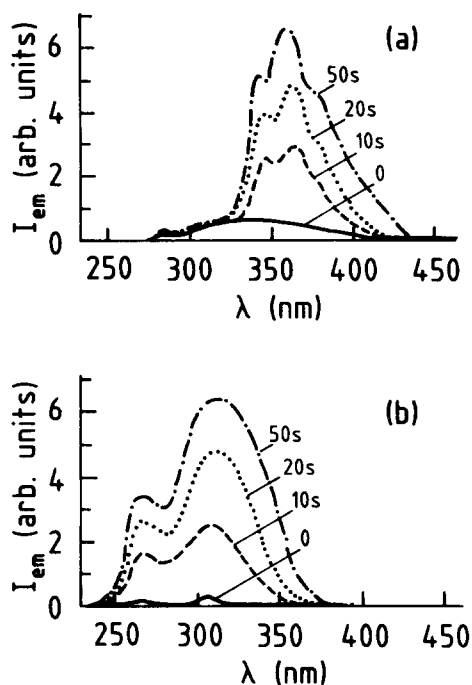


Fig. 6. Continuous irradiation of CPSt-95 at  $\lambda_{\text{inc}}=254$  nm in Ar-saturated  $\text{CH}_2\text{Cl}_2$  solution. (a) Fluorescence spectra,  $\lambda_{\text{exc}}=260$  nm, and (b) excitation spectra,  $\lambda_{\text{obs}}=360$  nm, recorded after various times of irradiation (as indicated).

6(a), irradiation of the copolymers at  $\lambda_{\text{inc}}=254$  nm gave rise to the formation of a new, quite intense, structured fluorescence spectrum with maxima at 345, 365 and 380 nm. The light-emitting chromophores possess absorption bands at 270 and 310 nm, as can be seen from the excitation spectrum shown in Fig. 6(b). By SEC in conjunction with fluorescence detection it was proved that the fluorescing groups are attached to the polymer. Moreover, it turned out that at constant absorbed dose the intensity of the new emission increased with increasing chlorine content of the copolymer. Therefore, it seems feasible to assume that the emission originates from the newly formed chromophores consisting of conjugated systems which include aromatic side-groups and double bonds in the main-chain. Actually, bromination of irradiated CPSt-95 resulted in a significant decrease in the intensity of the radiation-induced luminescence, which substantiates the conclusion arrived at above.

**Irradiation of polymer films.** Findings quite similar to those made with solutions were observed with polymer films. Moreover, as in the case of the optical absorption measurements, the intensities of the newly formed emission bands were lower with films than with solutions. This result again leads to the conclusion that in polymer films polyene formation is much less pronounced than in polymer solutions.

### 3.2. Flash photolysis studies

Transient absorption spectra taken with THF and  $\text{CH}_2\text{Cl}_2$  solutions of CPSt-95 are presented in Figs. 7(a) and 7(b) respectively. Quite similar spectra exhibiting two broad

absorption bands with maxima around 300 and 500 nm were recorded during or shortly after the 15 ns flash in solutions of both solvents. Notably, at  $\lambda_{\text{obs}} < 400$  nm the absorption change during the flash was not measurable because of the superposition of the absorption signal by a strong emission.

#### 3.2.1. Transient absorption spectra recorded in THF solution

As can be seen from the left inset in Fig. 7(a), the absorption formed around 300 nm during the flash decayed according to two modes. A rather rapid mode with a lifetime  $\tau \approx 65$  ns is followed by a slow mode ( $\tau \geq 5$  ms). The rapid mode could be quenched by  $\text{O}_2$  and penta-1,3-diene and is therefore assigned to excited triplet states. The long-lived absorption is probably due to free benzyl-type radicals which are generated by C–Cl bond cleavage. This assignment is based on the fact that benzyl radicals absorb relatively strongly in the wavelength range between 300 and 320 nm ( $\epsilon_{316\text{nm}} = 8.8 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$  [15]). A rough estimate based on the initial transient absorption at 316 nm yielded  $\phi(\text{benzyl}) \approx 0.2 \pm 0.1$ , a value of the same order of magni-

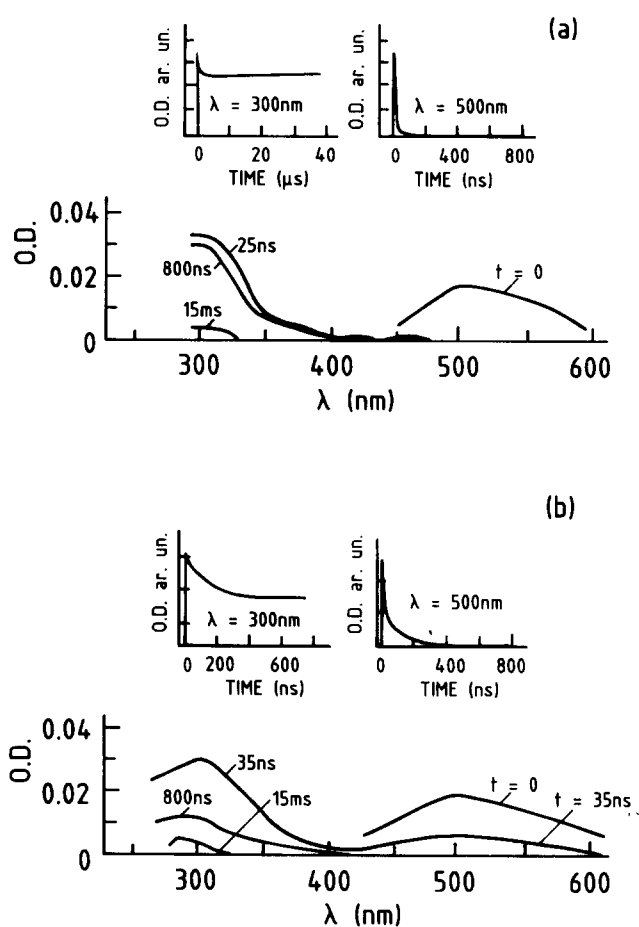


Fig. 7. Flash photolysis of CPSt-95 at  $\lambda_{\text{inc}}=266$  nm in (a) Ar-saturated THF and (b) Ar-saturated  $\text{CH}_2\text{Cl}_2$  solution. The spectra were recorded during and at various times after the flash (as indicated; the maximum of the flash was chosen as the origin of the time scale).  $D_{\text{abs}} =$  (a)  $2.9 \times 10^{-5}$  and (b)  $3.1 \times 10^{-5}$  einstein  $\text{l}^{-1}$  per flash. Insets: kinetic traces recorded at 300 and 500 nm.

tude as  $\phi(\text{HCl}) \approx 0.2$ . The absorption signals observed at wavelengths between 450 and 600 nm had the shape of the flash, as can be seen from the right inset in Fig. 7(a). The broad and rather intense absorption band originates most likely from short-lived intramolecular singlet excimers ( $\tau \leq 20$  ns). A very similar absorption band has been found in the case of PSt [16].

### 3.2.2. Transient absorption spectra recorded in $\text{CH}_2\text{Cl}_2$ solution

In  $\text{CH}_2\text{Cl}_2$  solutions the transient absorptions in both wavelength ranges, around 300 and 500 nm, decayed according to two modes, which is demonstrated by the kinetic traces shown in the insets of Fig. 7(b). At 300 nm a rapid mode ( $\tau \approx 140$  ns) is followed by a slow mode ( $\tau \geq 5$  ms). At 500 nm one portion of the absorption formed during the flash decayed very fast ( $\tau < 20$  ns) and is assigned to singlet excimers. The remainder lived longer ( $\tau \approx 140$  ns). Formerly, a transient absorption spectrum quite similar to that decaying with  $\tau \approx 140$  ns was found upon irradiation of polystyrene in chloroform solution [16]. In that case the transient spectrum had been assigned to charge transfer (CT) complexes formed between the aromatic rings of the polymer and the Cl atoms of the solvent. Therefore in the present case the transient spectrum decaying with  $\tau \approx 140$  ns is also tentatively assigned to CT complexes.

Qualitatively, quite similar transient absorption spectra were obtained with all copolymers under investigation. However, there are quantitative differences reflecting the composition of the copolymers. This can be seen from Fig. 8, where data obtained with  $\text{CH}_2\text{Cl}_2$  solutions are presented. The transient absorption of singlet excimers (short-lived absorption mode at  $\lambda = 500$  nm) decreases with increasing chlorine content as shown in Fig. 8(a). This is in accordance with the decrease in the fluorescence intensity ratio  $I_{\text{dim}}/I_{\text{mon}}$  with increasing  $\gamma_{\text{Cl}}$  values and again indicates that  $\alpha$ -chlorostyrene moieties in CPSt-95 are less prone to excimer formation than are the repeating units of PSt. Also, the absorption attributed to CT complexes (long-lived absorption mode at  $\lambda = 500$  nm) decreases with increasing chlorine content of the polymers (see Fig. 8(b)). This is very likely due to the drop in the electronegativity of the aromatic ring caused by the chlorine in the  $\alpha$  position of the main-chain and the ensuing reduced tendency to form CT complexes. The absorption assigned to benzyl-type radicals (long-lived absorption mode at  $\lambda = 300$  nm), on the other hand, increases with growing Cl content, as can be seen from Fig. 8(c). This reflects higher yields of benzyl radicals when copolymers of higher Cl content are photolysed.

Regarding double-bond formation in the main-chain, this process was expected to lower the segment mobility and at higher conversion to significantly augment the chain stiffness. Consequently, the probability of singlet excimer formation should be decreased. Actually, this conjecture was substantiated by the following experiment. CPSt-95 was continuously irradiated in argon-saturated  $\text{CH}_2\text{Cl}_2$  solution at

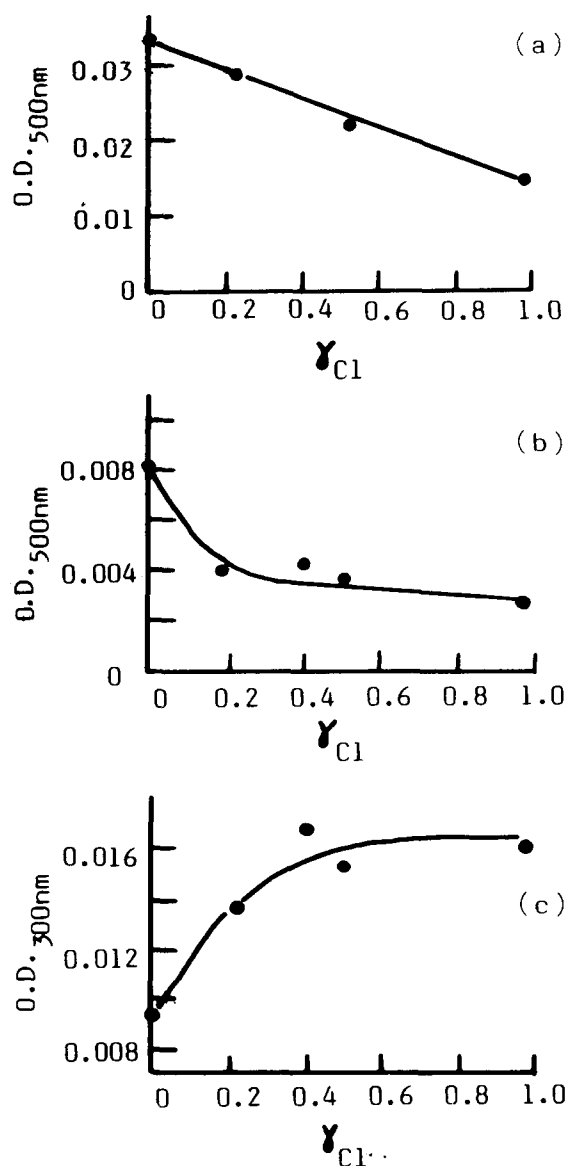


Fig. 8. Flash photolysis of CPSt-95 at  $\lambda_{\text{inc}} = 266$  nm in Ar-saturated  $\text{CH}_2\text{Cl}_2$  solution. (a) Short-lived portion of the OD at 500 nm and (b, c) long-lived portions of the OD at (b) 500 and (c) 300 nm vs.  $\gamma_{\text{Cl}}$ , the number of chlorine atoms per repeating unit. The OD values were normalized to constant absorbed dose per flash.

$\lambda_{\text{inc}} = 254$  nm. Subsequently the solution was subjected to flash photolysis. It turned out that the transient optical absorption due to excimers (the rapidly decaying absorption mode around 500 nm) was affected by the pre-irradiation. As can be seen from Fig. 9, the OD formed during the flash decreased with increasing pre-irradiation time, indicating a decrease in the excimer yield.

### 3.2.3. Transient absorption spectra of CPSt-95 films

Since the samples reflected rather strongly part of the analysing light, it was not possible to perform measurements during and shortly after the flash. The spectral changes measured 30 ns after the flash are quite similar to those observed with THF solutions. This can be seen from Fig. 10, which

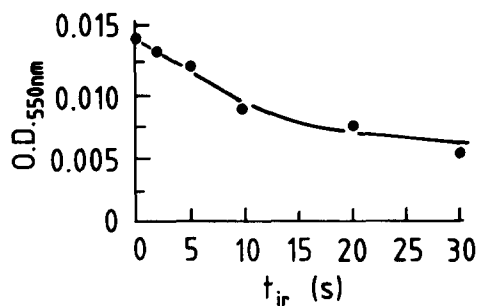


Fig. 9. Flash photolysis of pre-irradiated CPSt-95 at  $\lambda_{inc}=266$  nm in Ar-saturated  $\text{CH}_2\text{Cl}_2$  solution ( $c=0.18$  g  $\text{l}^{-1}$ ). Short-lived portion of the OD at 500 nm (ascribed to excimers) vs. the time of pre-irradiation at 254 nm ( $D r_{exp}=7.2 \times 10^{-3}$  einstein  $\text{l}^{-1} \text{min}^{-1}$ ). The  $\text{OD}_{500 \text{ nm}}$  values were normalized to constant absorbed dose per flash.

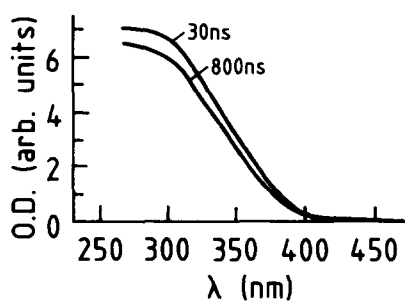


Fig. 10. Flash photolysis of a CPSt-95 film ( $d \approx 1$   $\mu\text{m}$ ) at  $\lambda_{inc}=266$  nm in Ar atmosphere. Transient absorption spectra recorded 30 and 800 ns after the flash (origin of time scale: maximum of flash).

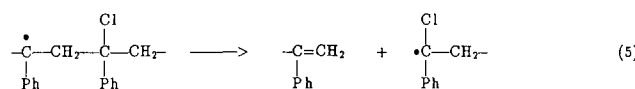
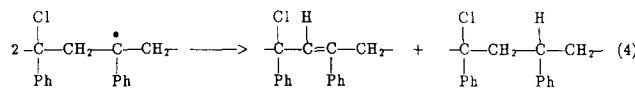
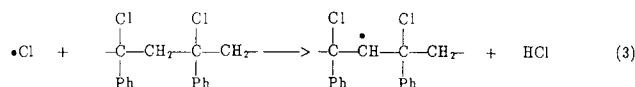
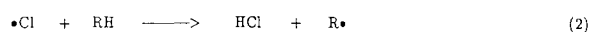
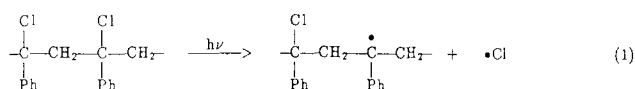
depicts transient absorption spectra recorded with a CPSt-95 film 30 and 800 ns after the flash. A small portion of the absorption decaying with a lifetime of about 60 ns is assigned to excited triplet states. The remainder decayed rather slowly with a lifetime  $\tau > 5$  ms and is assigned to free radicals, mainly of the benzyl type. The quantum yield of benzyl-type radical formation  $\phi(\text{benzyl}) \approx 0.03 \pm 0.01$  is lower than that found in dilute THF solution. This value is in accordance with  $\phi(\text{HCl})$  in polymer films.

#### 4. Conclusions

Poly( $\alpha$ -chlorostyrene) undergoes predominantly main-chain cleavage upon UV irradiation in the absence of  $\text{O}_2$  and does not form an insoluble gel. This contrasts with the behaviour of polystyrene, which predominantly cross-links and becomes partially insoluble. Expectations based on the previously reported [5,6] predominant photo-cross-linking of highly chlorinated polystyrenes of  $\gamma_{\text{Cl}} > 1.0$  were not substantiated with less chlorinated polystyrenes ( $\gamma_{\text{Cl}} \leq 1.0$ ) in his work. The seeming discrepancy might be explained in terms of partial ring chlorination during the preparation of the formerly investigated polystyrenes. Partially ring-chlorinated polymers might undergo to some extent photoreactions different from those observed in the present work.

Although of great importance for the retention of the solubility, main-chain scission is a minor photochemical process

in the case of CPSt-95, as follows from the comparatively low quantum yield  $\phi(S) \approx 2 \times 10^{-3}$ . The major photochemical process in poly( $\alpha$ -chlorostyrene) is the cleavage of C–Cl bonds according to reaction (1) (see Scheme 1), which results in the formation of benzyl-type free radicals and chlorine atoms. As can be seen from Table 2, the quantum yield of C–Cl bond rupture in dilute THF solution is rather high, of the order of 0.2 Cl atoms released per photon according to estimates based on the quantum yields of the formation of both hydrochloride and benzyl-type radicals in THF solution. In polymer films the quantum yield of C–Cl bond rupture is about one order of magnitude lower than that found in dilute solution, which is attributed to the cage effect, i.e. to a high probability of recombination of radical pairs formed by C–Cl bond rupture in the polymer matrix. Notably, benzyl-type radicals generated according to reaction (1) are neither very likely to undergo main-chain cleavage, as indicated by the low quantum yield  $\phi(S)$ , nor to combine and form cross-links, as indicated by the lack of observation of gel formation. A reaction mechanism concerning the photolysis of poly( $\alpha$ -chlorostyrene) in THF solution is presented in Scheme 1. In THF solution chlorine radicals are very likely to abstract hydrogen from solvent molecules rather than from polymer molecules according to reaction (3). However, the latter process should play an important role in the photolysis of the neat polymer. Regarding the fate of benzyl-type radicals, the results indicate that combination resulting in cross-link formation is very unlikely in contrast to disproportionation according to reaction (4), which would explain the formation of carbon–carbon double bonds in the main-chain. In this way conjugated double bonds will be generated with increasing release of chlorine atoms. Instead of reacting with other radicals via disproportionation, a certain portion of the benzyl-type radicals might induce  $\beta$  scission, thus giving rise to main-chain cleavage according to reaction (5). Alternative reaction routes ending up in main-chain cleavage cannot be excluded. Attempts to gain further information on this aspect



Scheme 1.

via the use of the light-scattering detection method in conjunction with flash photolysis experiments were futile because of the low quantum yield  $\phi(S)$ .

It is noticeable that the photochemical behaviour of poly( $\alpha$ -chlorostyrene) strongly resembles that of poly(vinyl chloride). The photolysis of PVC also results in the release of HCl and the simultaneous formation of polyene structures and it has been postulated that this process occurs by a chain reaction [9]. Regarding both HCl release and polyene formation during the photolysis of poly( $\alpha$ -chlorostyrene), evidence for the occurrence of a chain reaction has not been obtained, at least as far as the photolysis in solution is concerned. The quantum yield of hydrochloride formation determined by continuous irradiation equals the quantum yield of the formation of benzyl-type radicals determined by flash photolysis experiments. Therefore each benzyl-type radical initially formed corresponds to one Cl atom released from the polymer. An increase in the transient absorption due to benzyl-type radicals after the flash would be indicative of a chain reaction, but it was not observed.

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