Cleavage of the α carbon–carbon bond via the Norrish I process also occurs to some extent in these ketones.[18]

The formation of biphenyl may be explained on the basis of a Norrish I process followed by elimination of carbon monoxide and subsequent hydrogen atom abstraction. Benzophenone formation could occur via hydrogen abstraction by a $^3(n,\pi^*)$ carbonyl of a backbone C–H bond, scission of the five-membered ring, and subsequent free radical hydrogen atom abstraction. These reactions must, of course, occur from a higher lying $^3(n,\pi^*)$ state in order to explain the emissions from the triplet levels of biphenyl and benzophenone.

In conclusion, dilute solutions and thin films of P2VF exhibit normal and excimer fluorescence when excited in the lowest excited $^1(\pi,\pi^*)$ states. No phosphorescence from the lowest lying $^3(\pi,\pi^*)$ state is observed. Excitation of P2VF to higher excited singlet states results in photochemical reactions and possible formation of benzophenone and biphenyl, presumably from a higher lying $^3(n,\pi^*)$ state in P2VF.

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Laser Flash Photolysis Studies on Homo- and Copolymers of Phenyl Vinyl Ketone in Solution

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Received March 20, 1975

ABSTRACT: Triplet lifetimes τ of copolymers (CP) of methyl methacrylate (MMA), vinyl acetate (VAc), and styrene (St) with phenyl vinyl ketone (PVK) were determined as a function of PVK content in benzene solution at room temperature. Samples were irradiated with 347.1 nm light flashes. T–T spectra were recorded. With all three CP systems τ was found to increase with decreasing PVK content. The effect is most strongly pronounced with CP-MMA-PVK, where τ amounts to several microseconds at PVK contents of about 1 mol % (for homo PVK: $\tau = 0.1$ μsec). In the system St/PVK τ increases only by a factor of ca. 2. The results are discussed in terms of triplet deactivation via 1,4 biradical formation and energy migration along the polymer chain. τ depends on CP concentration indicating self-quenching. Detailed kinetic studies performed with CP-MMA-PVK yielded the following results: assuming homogeneous distribution of PVK units in the solution the rate constant of intermolecular self-quenching amounts to $k_{\mathrm{s,inter}} = 7 \pm 1 \times 10^7$ l./base mol sec. Decay rate constants extrapolated to infinite dilution and determined for CP's with varying number of PVK units per chain yielded evidence for intramolecular self-quenching. τ decreases with increasing intensity of incident light, indicating triplet–triplet annihilation ($k_{\mathrm{T-T}} = 9.7 \times 10^9$ M^{-1} sec^{-1}). Triplet quenching with 2,5-dimethylhexadiene-2,4 yielded rate constant values k_q between 7.5×10^8 and 9.5×10^8 M^{-1} sec^{-1} for CP's of all three systems studied. Oxygen also acted as a quencher. A fairly low rate constant $k_{O_2} = 4.2 \pm 0.4 \times 10^8$ M^{-1} sec^{-1} was estimated for CP-MMA-PVK (14.1 mol %).

Poly(phenyl vinyl ketone) (PPVK)[1-3,5] and copolymers of phenyl vinyl ketone (PVK) with styrene (St)[2,4] and methyl methacrylate (MMA)[4] are degraded in the main chain upon irradiation with uv light in solution. Generally, it is assumed that main chain rupture occurs in these cases via photoelimination according to a Norrish type II process involving essentially excited triplet states. A triplet state lifetime of about 100 nsec for homo-PPVK in benzene solution was determined in our laboratory recently.[6]

Golemba and Guillet[2] reported that on irradiating at λ 313 nm a copolymer of PVK and St (containing 9% PVK) a curved Stern-Volmer plot was obtained during the quenching of photoscissioning with 1,3-cyclooctadiene. This phenomenon was explained by assuming that either the triplet lifetimes of isolated PVK units are longer than those of excited PVK units neighbored by other PVK units or that the efficiency of quenching is greater for the copolymer than for the homopolymer. Lukáč et al.[4] also investigated the main chain degradation of copolymers of MMA and PVK and of St and PVK. They also assumed that triplet lifetimes of copolymers were longer than that of homo-PPVK and thought that the increase of triplet lifetime is responsible for the oxygen effect observed during the degradation of MMA/PVK copolymer.

Those considerations[2,4] appeared to become very important recently for our investigations on time-resolved measurements of chain scissioning using the light-scattering detection method[5] (data pertaining to the copolymers studied during this work will be reported later). We, therefore, started a quantitative study aimed at the determination of triplet lifetimes as a function of copolymer composition with three copolymer systems (MMA/PVK, St/PVK, and vinyl acetate (VAc)/PVK). In addition rate constants of inter- and intramolecular self-quenching, of triplet–triplet annihilation, and of reactions with certain quenchers were measured. These determinations became possible since the triplet lifetimes of copolymers were found being significantly longer than in the case of homo-PPVK.

Table I
Characterization of Copolymer Samples

Series	Polymer sample	PVK content, mol %	No. av mol wt $\bar{M}_n \times 10^{-6}$
Methyl methacrylate/phenyl vinyl ketone (MMA/PVK)	CP-MMA-PVK-0.8	0.82	0.49
	CP-MMA-PVK-1.2	1.22	0.23
	CP-MMA-PVK-1.8	1.83	0.70
	CP-MMA-PVK-2.8	2.75	1.10
	CP-MMA-PVK-4.8	4.80	0.37
	CP-MMA-PVK-7.8	7.80	1.50
	CP-MMA-PVK-14.1	14.10	1.10
Vinyl acetate/phenyl vinyl ketone (VAc/PVK)	CP-VAc-PVK-0.08	0.075	0.29
	CP-VAc-PVK-0.14	0.14	0.35
	CP-VAc-PVK-0.34	0.34	0.18
	CP-VAc-PVK-1.51	1.51	0.10
	CP-VAc-PVK-3.42	3.42	0.41
Styrene/phenyl vinyl ketone (St/PVK)	CP-St-PVK-0.6	0.6	0.51
	CP-St-PVK-3.5	3.5	0.65
	CP-St-PVK-9.0	9.0	0.78
	CP-St-PVK-11.5	11.5	0.51
	CP-St-PVK-13.6	13.6	0.15
	CP-St-PVK-18.2	18.2	0.39

Experimental Section

(a) Apparatus. Sample solutions were irradiated in rectangular cells with flashes (λ 347.1 nm) with a ruby laser (Korad Model K1QS2). The half-width of the flashes was about 25 nsec. Details have been reported before.[6]

(b) Actinometry. Normal laser operations yielded 5.0 ± 0.5 × 10^{16} photons per flash as measured with the potassium ferrioxalate actinometer[9] ($\Phi[Fe^{2+}] = 1.20$). In order to reduce the incident light intensity filters (Schott BG 23) were used.

(c) Materials. PVK was prepared by Hofmann degradation of β-dimethylaminopropiophenone hydrochloride (Aldrich). MMA (Ferak), St (Ferak), and VAc (Ferak) were freed from stabilizer by washing several times with aqueous NaOH solution. This procedure was followed by washing with water, drying, and fractionated distillation.

The polymerization of monomer mixtures was initiated by ^{60}Co γ-rays at room temperature. The conversion was in all cases less than 10%. The copolymers were reprecipitated several times (CP-St-PVK from benzene solutions with methanol, CP-MMA-PVK from acetone solution with methanol, CP-VAc-PVK from chloroform solution with petroleum ether) and dried at the vacuum line (10^{-5} Torr). The copolymer samples were characterized by gel permeation chromatography. Number average molecular weights were determined by membrane osmometry in toluene at 37° using a Mechrolab osmometer. The composition of the copolymers was determined spectrophotometrically in benzene solution (extinction coefficients for PVK units $\epsilon_{290\ nm} = 924\ M^{-1}\ cm^{-1}$). Table I contains a compilation of all polymer samples used during this work.

The synthesis of the copolymer samples was selected to give macromolecules with a high fraction of isolated PVK units in the chain. The polymerization occurred via a radical mechanism and a distribution of PVK sequences of various lengths was expected. An estimate of the sequence distribution is possible if the copolymerization parameters r_1 and r_2 are known. Values pertaining to PVK were not available from the literature. Our own experiments[23] showed that all three systems studied can be assigned to the case of nonazeotropic ideal copolymerization with $r_1 = r_2^{-1}$. Therefore, high contents of isolated PVK units should be obtained by polymerizing monomer mixtures containing small amounts of PVK. In the MMA-co-PVK system, e.g., it was estimated that a polymer with 14 mol % PVK units contains about 89% isolated PVK units. The latter fraction increases to about 98% when the PVK fraction in the copolymer amounts to 0.82 mol %.

Special care was taken to purify benzene (Merck, p.a.) which served as solvent for all irradiation experiments. It was shaken with concentrated H_2SO_4 several times, washed with water, dried over $CaCl_2$ and CaH_2, and distilled over a splitting tube column (Fischer, Bonn). 2,5-Dimethylhexadiene-2,4 was also distilled over the splitting tube column. The fraction boiling at 135° at 760 Torr was used.

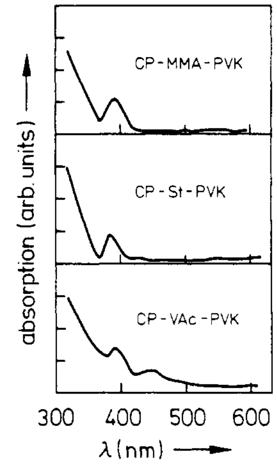

Figure 1. Typical absorption spectra observed at the end of the flash in benzene solutions containing copolymer.

(d) Sample Preparation. Irradiations were carried out at room temperature and, unless otherwise stated, in the absence of oxygen. For the latter purpose, Ar containing 0.01% O_2 (corresponding to $[O_2] = 7 \times 10^{-7}\ M$ in benzene at 25°) was bubbled through the samples. In order to establish well-defined O_2 concentrations, samples were bubbled with argon-oxygen mixtures which were obtained by combining the two gases in a mixing device containing an endOmess instrument (Friedrichsfeld) for continuous O_2 analysis in front of the exit. O_2 concentrations were calculated on the basis of a solubility of $7.1 \times 10^{-3}\ M$[16,17] at an O_2 pressure of 1 atm at 25°.

Results

(a) Transient Spectra and Lifetime. Optical absorption spectra observed immediately after the flash in copolymer containing benzene solutions are shown in Figure 1. No absorption could be detected in pure benzene. Within the error limit the PVK content did not influence the spectra. Except for a slight red shift in the case of the VAc-co-PVK system the spectra are very similar to the transient spectra observed with homo-PPVK. Therefore, it is assumed that the absorption is due to the same species, namely the excit-

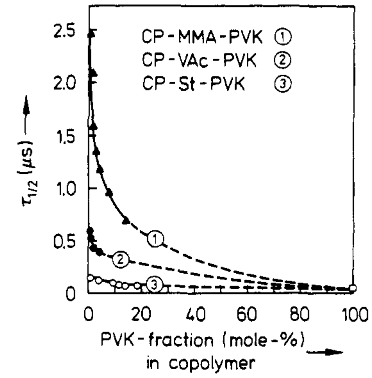

Figure 2. Transient half-life monitored at λ 390 nm as a function of PVK content of copolymers. Solvent: Ar-saturated benzene.

ed PVK unit in its lowest triplet state. As found with homo-PPVK the rate of decay of the transient spectra of the copolymers is independent of wavelength. However, it depends strongly on copolymer composition. This is demonstrated in Figure 2, where first-order half-lifes monitored at λ 390 nm are plotted vs. the PVK content. During these experiments the copolymer concentration was chosen to contain the average concentration of PVK units of about 2 $\times 10^{-3}$ base mol/l. which corresponds to concentrations on a weight per volume basis between 2 and 47 g of copolymer/l. depending on the PVK content. In all cases first-order behavior was observed over at least 2 half-lifetimes. For homo-PPVK $\tau_{1/2}$ is about 70 nsec. As is shown in Figure 2 $\tau_{1/2}$ increases significantly with decreasing PVK content. This effect is most strongly pronounced with copolymers of MMA and PVK where $\tau_{1/2} \approx 2.5$ μsec was found for the copolymer with the lowest PVK content (0.8 mol %). With copolymers of VAc and PVK the effect is less strongly pronounced than with the MMA copolymers. At the lowest PVK content of 0.08 mol % $\tau_{1/2}$ is 630 nsec, i.e., still nine times higher than in the case of homo-PPVK. In the system St/PVK only a relatively small increase of $\tau_{1/2}$ with decreasing PVK content was observed. The half-life increased here only by a factor of 2.

(b) Characterization of Transient Species. The first-order decay kinetics observed in all cases are interpretable in terms of an excited state rather than a radical which should decay according to a second-order process. The long lifetimes observed indicate a triplet rather than a singlet state. Further evidence for the triplet state was obtained from quenching and sensitization experiments. In the presence of 2,5-dimethylhexadiene-2,4 (DMHD) (E_T = 58 kcal/mol[9]) and piperylene (E_T = 59 kcal/mol[11]) a marked decrease of lifetimes was observed. Oxygen also acted as a quencher. Its quenching ability has been reviewed recently.[10] Copolymer solutions containing naphthalene exhibited the characteristic T–T absorption spectrum of naphthalene which indicates that triplet states were generated in the copolymer beforehand. Naphthalene itself does not absorb light of λ 347.1 nm. Benzene solutions containing 0.1 *M* naphthalene and no copolymer possessed an absorption of 0.03% at λ 413 nm (maximum of T–T absorption of naphthalene). On the other hand a solution containing in addition 10^{-2} base mol CP-MMA-PVK-14.1 per liter yielded under the same conditions an absorption of about 5%. A triplet quantum yield $\Phi(T) \approx 0.2$ was estimated for the copolymers on the basis of the absorption at 413 nm with $\epsilon_{T-T}(413) = 2 \times 10^4\ M^{-1}\ cm^{-1}$. Further details of the investigations mentioned in this section will be reported below.

(c) Dependence of Lifetime on Copolymer Concentration. The aim of these experiments was to obtain knowledge on self-quenching, i.e., the deactivation of excited carbonyl groups by carbonyl groups in the ground state. Self-quenching studies on low molecular weight ketones have been reported in the literature.[21,22] To the knowledge of the authors no kinetic work on polymers has been published yet. With polymers one may distinguish between inter- and intramolecular self-quenching, i.e., in our case the deactivation of triplet excited PVK units may proceed by the reactions

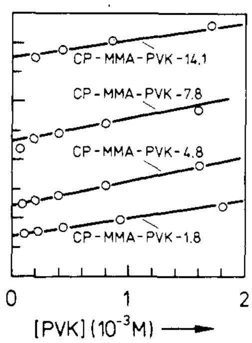

Figure 3. Reciprocal lifetime monitored at λ 390 nm as a function of concentration of PVK units. Intensity of incident light: 1.2 $\times 10^{16}$ photons/flash.

$$\begin{array}{c} \text{—PVK*—} \\ \text{—PVK—} \end{array} \xrightarrow{k_{s,\text{inter}}} \begin{array}{c} \text{—PVK—} \\ \text{—PVK—} \end{array} + \text{energy} \qquad \text{(I)}$$

and

$$\left[\begin{array}{c} \text{PVK*—} \\ \text{PVK—} \end{array}\right. \xrightarrow{k_{s,\text{intra}}} \left[\begin{array}{c} \text{PVK—} \\ \text{PVK—} \end{array}\right. + \text{energy} \qquad \text{(II)}$$

Test experiments with CP-MMA-PVK-14.1 proved the existence of process I. At constant incident intensity of about 1×10^{16} photons/flash the lifetime decreased with increasing polymer concentration in the investigated range from 2 $\times 10^{-5}$ to 3.4×10^{-3} base mol/l. Therefore, analogous runs were carried out with other copolymers of this series. In Figure 3 reciprocal lifetimes observed during these experiments are plotted vs. the concentration of PVK units. It turns out that a linear dependence exists between τ^{-1} and PVK which formally leads to the expression

$$1/\tau_{\text{obsd}} = k' + k_{s,\text{inter}}[\text{PVK}] \qquad (1)$$

where k' designates the first-order rate constant obtained by extrapolation of [PVK] to 0. k' concerns deactivation processes other than intermolecular self-quenching. The slopes of the straight lines in Figure 3 yield $k_{s,\text{inter}} = 7 \pm 1 \times 10^7$ l./base mol sec. It may be pointed out that this treatment of data neglects the fact of unhomogeneous distribution of PVK units in the solution. $k_{s,\text{inter}}$ may, therefore, only serve to describe reaction I in a quantitative manner without having the usual kinetic meaning. At infinite dilution no intermolecular self-quenching is possible. However, the occurrence of reaction II is feasible under this condition as long as the number Z_{PVK} of PVK units per macromolecule is greater than 2. The rate of reaction II should depend on Z_{PVK}. k' may, therefore, be expressed as

$$k' = k'' + k_s' Z_{\text{PVK}} \qquad (2)$$

where k'' is a first-order rate constant at infinite dilution of all deactivation processes except intramolecular self-quenching (reaction II). k_s' should be proportional to $k_{s,\text{intra}}$; $k_s' = y k_{s,\text{intra}}$, where y denotes a constant concerning steric factors, unit distribution along the chains, etc. Figure 4 shows a plot of k' vs. Z_{PVK}. The slope of the straight line obtained yields $k_s' \simeq 300\ \text{sec}^{-1}$.

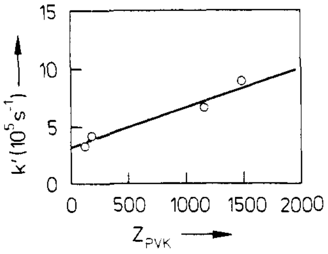

Figure 4. Plot of k' (reciprocal lifetime extrapolated to [PVK] → 0) vs. Z_{PVK} (number of PVK units per macromolecule) according to eq 2.

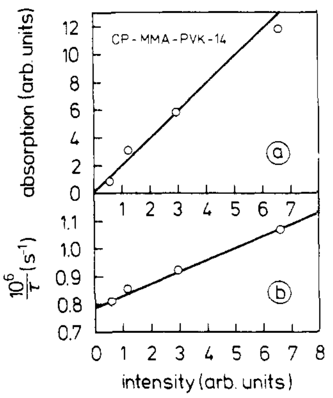

Figure 5. Influence of intensity of incident light. (a) Triplet absorption monitored at λ 390 nm vs. intensity; (b) reciprocal lifetime as a function of intensity. Polymer sample: CP-MMA-PVK-14.1 at 2.4 × 10^{-2} base mol/l.

It may be noted that the intensity of incident light applied during this series of experiments was low enough in order to neglect T–T deactivation. Furthermore, it may be mentioned that in the case of a low molecular weight aromatic ketone (n-butyrophenone) no concentration effect could be detected. The decay lifetime was found to be constant (100 nsec) at butyrophenone concentrations between 6.7 × 10^{-4} and 4.4 × 10^{-2} mol/l. In the case of homo-PPVK ($\bar{M}_w$ = 1.1 × 10^6) the triplet lifetime was found to be independent of polymer concentration in the range of 1.0 × 10^{-4} to 1.6 × 10^{-3} base mol/l.

(d) Dependence of Lifetime on the Intensity of Incident Light. The influence of intensity was investigated in the case of sample CP-MMA-PVK-14.1 dissolved in Ar-saturated benzene. The copolymer concentration of 2.5 g/l. corresponded to a light absorption of 37% at 347.1 nm due to PVK units. Triplet absorption was monitored at 390.0 nm. As shown in Figure 5a the triplet absorption depends linearly on the intensity of incident light indicating that the triplet concentration at the end of the flash is proportional to the intensity. The lifetime increases with decreasing intensity thus indicating triplet–triplet annihilation. The results in Figure 5b demonstrate that the relationship

$$k_{obsd} = \Sigma k_i + k_T[T] \qquad (3)$$

holds, where Σk_i denotes the sum of all first-order deactivation reactions and k_T is the bimolecular rate constant of deactivation via triplet–triplet interaction. Taking $\Phi(T)$ = 0.2 it is estimated from the slope of the straight line in Figure 5b that k_T = 9.7 × 10^9 M^{-1} sec^{-1}. The available experimental data do not yet allow one to discriminate between inter- and intramolecular triplet–triplet annihilation. Since at the highest intensity used the average number of triplets per macromolecule was about 12 it is believed that the k_T value given above is essentially determined by intramolecular T–T interaction.

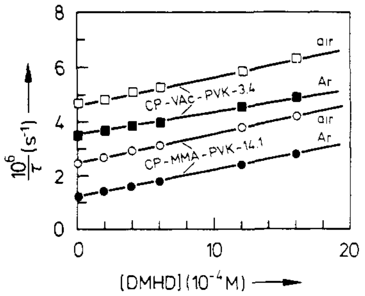

Figure 6. The reciprocal lifetime monitored at λ 390 nm vs. the concentration of 2,5-dimethylhexadiene-2,4 (DMHD). Polymer sample designation in figure. Copolymer concentration: 1 g/l. Intensity of incident light: 1.2 × 10^{16} photons per flash.

Table II
Triplet Quenching with DMHD in Benzene Solution

Polymer sample	Atmosphere	Polymer concn, g/l.	k_{DMHD}, M^{-1} sec^{-1}
CP-VAc-PVK-0.14	Argon	10	9.5 × 10^8
CP-VAc-PVK-3.4	Argon	1	9.3 × 10^8
	Air	1	9.3 × 10^8
CP-MMA-PVK-14.1	Argon	1	7.5 × 10^8
	Air	1	7.5 × 10^8

(e) Quenching Experiments with 2,5-Dimethylhexadiene-2,4 (DMHD). Provided the absorption spectra shown in Figure 1 correspond to triplet–triplet absorption their decay rate should be influenced by triplet quenchers. Lukáč et al.[4] studied the main chain degradation of one copolymer sample consisting of MMA and PVK (29.6 wt %) in the presence of numerous quenchers, the most efficient of them being DMHD (E_T = 58 kcal/mol[11]). We also used DMHD and found a decrease of lifetime with increasing quencher concentration. As shown in Figure 6 plots of the reciprocal lifetime vs. DMHD concentration yield straight lines according to the relationship

$$1/\tau = \Sigma k_1 + k_{DMHD}[DMHD] \qquad (4)$$

Σk_1 is the reciprocal lifetime found in the absence of DMHD. T–T interaction could be neglected during this series of experiments since the intensity of incident light was relatively low. Several values of bimolecular rate constants k_{DMHD} are given in Table II, which may be considered as being equal within the error limit. It is interesting to note that experiments carried out with air-saturated solutions yielded shorter triplet lifetimes than runs with Ar-saturated solutions, but the same k_{DMHD} values were calculated from straight lines of τ^{-1} vs. DMHD plots. The quenching ability of O_2 was thus indicated.

(f) Quenching Experiments with Oxygen. All experiments concerning the influence of PVK content on triplet lifetime (compare Figure 2) were also carried out with air-saturated solutions. In all cases except homo-PPVK oxygen reduced the lifetime drastically. Typical data are given in Table III. In order to determine the rate constant k_{O_2} of the reaction of O_2 with triplet excited PVK units a series of experiments was carried out with solutions of CP-MMA-PVK-14.1 saturated with well-defined mixtures of Ar and O_2. The results are shown in Figure 7 where τ^{-1} is plotted as a function of oxygen concentration. From the slope of the straight line which follows the relationship

$$1/\tau = k_0 + k_{O_2}[O_2] \qquad (5)$$

Table III
Triplet Lifetimes in Air- and Argon-Saturated Benzene Solutions

Polymer sample	Atmosphere	Polymer concn, g/l.	Lifetime monitored at λ 390 nm, nsec
CP-MMA-PVK-1.22	Argon	17	2900
	Air	17	1770
CP-MMA-PVK-14.10	Argon	2	990
	Air	2	480
CP-VAc-PVK-0.08	Argon	1	960
	Air	1	360
CP-VAc-PVK-3.42	Argon	1	640
	Air	1	400
CP-St-PVK-0.6	Argon	26.6	180
	Air	26.6	110
CP-St-PVK-13.6	Argon	1.2	120
	Air	1.2	90

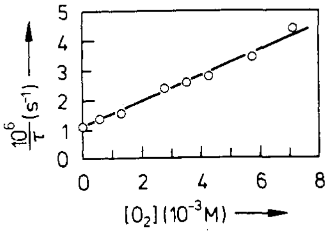

Figure 7. Reciprocal lifetime monitored at λ 390 nm as a function of oxygen concentration. Polymer sample: CP-MMA-PVK-14.1 at 2.4 × 10^{-2} base mol/l.

(k_0 is the reciprocal lifetime measured with Ar-saturated solution) $k_{O_2} = 4.2 \pm 0.4 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ was estimated. The oxygen content in Ar-saturated solutions was 7×10^{-7} mol/l. and could therefore be neglected during the determination of k_0.

Discussion

As mentioned in the Experimental Section, the copolymers investigated during this work contain a high fraction of isolated PVK units. The results, therefore, appear to demonstrate that the triplet lifetime of a PVK unit which is adjacent to units other than PVK is much longer than that of a triplet PVK unit in a PPVK chain. This effect is explained by the assumption that intramolecular γ-hydrogen abstraction leading to the formation of a biradical[13,14] is the most rapid pathway for triplet deactivation of homo-PPVK in benzene solution. This assumption is confirmed by the following comparison; in the system MMA/PVK the longest lifetimes (determined at lowest PVK contents) amount to about 4 μsec. They are almost equal to triplet lifetimes of low molecular weight aromatic ketones that do not contain abstractable hydrogen atoms in γ position to the carbonyl group. Lutz et al.[8] reported, e.g., for acetophenone a triplet lifetime of 3 μsec in benzene at room temperature. On the other hand, the lifetime of butyrophenone triplets is only 0.1 μsec,[6] i.e., equal to the value determined for PPVK.[6]

If the MMA content in the copolymer system MMA/PVK increases, γ-hydrogen atoms are successively substituted by methyl groups. Thus, this pathway of deactivation becomes less possible and the triplet lifetime and the probability of different modes of triplet deactivation increase. However, a comparison of the three copolymer systems investigated during this work demonstrates that the availability of γ-hydrogen atoms is not the sole criterion which has to be considered. In both other systems, namely the St-PVK and the VAc-PVK system, the number of γ-hydrogen atoms remains unaltered during the variation of copolymer composition. The long lifetime may here be due to a greater bond strength of the γ-hydrogen atom, thus reducing its reactivity toward the excited carbonyl group. It may be noted that according to the work of Lukáč et al.[4] the quantum yield for main chain scissions Φ(S) was found to be reduced by a factor of about 2 in comparison with homo-PPVK when copolymer samples of MMA with PVK (29.6 wt %) and St with PVK (12.0 wt %) were irradiated. Those results appear to be corroborated by our triplet lifetime measurements.

Another factor determining triplet lifetime turns out to be intramolecular self-quenching. The existence of this process was evidenced in Results section c. If the data in Figure 4 are extrapolated to homo-PPVK ($\bar{M}_n = 7 \times 10^5$) a lifetime due to intramolecular self-quenching of 600 nsec is obtained. Since the observed lifetime is 100 nsec this estimate yields that in homo-PPVK a portion of triplet decay could be due to self-quenching.

Besides the consideration of availability and reactivity of γ-hydrogen atoms the dependence of triplet lifetime might also be discussed in terms of energy migration along the polymer chain, a process which has been referred to frequently.[17,20] Indications of energy migration via proximate carbonyl units in ketone polymers have already been reported.[18] If such a process would occur with high velocity in homo-PPVK the reaction probability for biradical formation would be optimum. Inasmuch as PVK units are substituted by other units energy migration would be retarded or respectively restricted to limited portions of the macromolecule. The fact that styrene-containing copolymers exhibit only a weak influence of copolymer composition on triplet lifetime could be explained on this basis by the assumption that migration of excitation energy is still possible in this system. On the other hand energy migration in polymer chains consisting of PVK and VAc units does not appear to be feasible.

Concerning the oxygen effect described above, it may be noted that the rate constant k_{O_2} is relatively low ($4.2 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$). The triplet energy E_T of PVK units was estimated to be about 70 kcal/mol.[12] According to Porter et al.[7] the rate constant k_{O_2} decreases with E_T for aromatic hydrocarbons when $E_T > 46$ kcal/mol. It might be that aromatic carbonyl compounds behave analogously. The low value of k_{O_2} could, on the other hand, indicate a polymer effect, a point which has to be clarified with low molecular weight model compounds. In any case, the low value of k_{O_2} explains why main chain scissioning of homo-PPVK is not influenced by air in benzene solution. In this case $[O_2] = 1.5 \times 10^{-3}\ M$ and therefore $k_{O_2}[O_2] = 6.3 \times 10^5\ \mathrm{sec}^{-1}$. Since the triplet lifetime of homo-PPVK in the absence of oxygen is ca. 10^{-7} sec the fraction of triplets which is deactivated by O_2 quenching amounts only to about 6%. This small portion is certainly within the error limit of experimental observations.

Acknowledgment. The authors are grateful to Mrs. U. Fehrmann who synthesized the polymer samples and to Fonds der Chemischen Industrie for partial support of this work. The help of Dr. G. Beck concerning the operation of the electronic equipment was greatly appreciated.

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Topochemical Effects in Polymerization of Vinylsulfonate Attached to an Ionene Matrix

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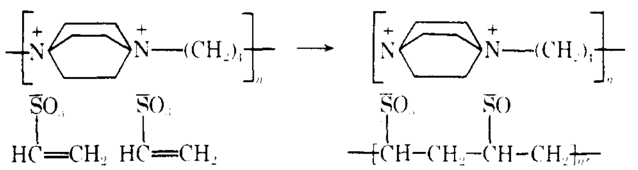
ABSTRACT: Proton and ^{13}C NMR spectra of sodium poly(vinylsulfonate) separated from ionene matrix (PVS-1) are compared with the spectra of sodium poly(vinylsulfonate) prepared in aqueous solution (PVS-2). X-Ray diffraction patterns of polyelectrolyte complexes between ionene and PVS-1 and PVS-2, respectively, are shown. Influence of the ionene matrix on the tacticity of PVS-1 is discussed.

We have recently reported the results of our study of the kinetics of free-radical polymerization of styrenesulfonic acid on ionene matrices[2] and the formation of highly ordered polyelectrolyte complexes which result from such polymerization in the case of vinylsulfonic acid and the poly(diazabicyclo[2.2.2]octyl-1-butane) or ionene.[3] We have also described the separation of the poly(vinylsulfonic acid) from its matrix.[2b,4] We would like to report here the results of preliminary NMR investigations of the tacticity of a "reference" and of a matrix-prepared poly(vinylsulfonic acid).



The reference poly(vinylsulfonic acid) (PVS-2) was prepared by free-radical polymerization in concentrated aqueous solution at 55°. The conversion was 35% and the M_n = 30,000. The poly(vinylsulfonic acid) prepared on the matrix (PVS-1) was obtained by complexing the acidic monomer with a stoichiometric amount of ionene hydroxide (mol wt = 4000). The polymerization was carried out in aqueous solution at 70° with a free-radical initiator. The detailed procedure for polymerization and separation of polymer and matrix has been reported elsewhere.[2b,4] The matrix polymer used here was as obtained after one separation step. Elementary analysis indicated the presence of some 2–3% unseparated ionene matrix, possibly fragments permanently attached to the poly(vinylsulfonate) through covalent bonding. The proton magnetic resonance spectra were obtained at room temperature in D_2O with a HR-300 MHz spectrometer, using sodium trimethylsilylpropanoate-d_5 as internal standard. The ^{13}C spectra were run using a JEOLCO NMR spectrometer and 50% (by weight) solutions of sodium poly(vinylsulfonate) in D_2O with tetramethylsilane as standard at room temperature. Each spectrum is an accumulation of 7,000 scans obtained at 25.14 MHz at room temperature. Figure 1a gives the proton magnetic resonance spectrum of PVS-2; the methine protons appear in the 3.5–4.0 ppm region and the methylene in the 1.5–2.6 ppm area. Figure 1b gives the PMR spectrum of the matrix-polymerized and separated poly(vinylsulfonate), PVS-1. Here a group of peaks appear between 1.6 and 2.6 ppm and another between 2.9 and 3.8 ppm. Determination of the ratio of the methine to methyne peak areas for PVS-1 indicates some contamination by unseparated matrix. Assuming that 16 of the 20 ionene protons will contribute to the methine peak area of PVS-1, the spectra indicate that approximately three monomeric ionene fragments remain, per 100 monomeric vinylsulfonate units. Neglecting the contribution of ionene contamination to the methylene area (approximately 6% of the total) and assuming that the ionene contribution in the methine area is in the 2.8–3.2 ppm range (shaded region), one can see a drastic difference between the spectra of the two polymers.

Figures 2a and 2b give the ^{13}C spectra of PVS-2 and PVS-1, respectively. The methine area of the reference polymer shows two approximately equal peaks at 55.769 and 54.941 ppm. The methylene area is more complicated. For the matrix-separated polymer the relative peak intensities in the methine and methylene areas increase with in-