Figure 1. Infrared spectrum of poly(2AEMA) (upper curve) and 2AEMA (lower curve) in Nujol.

poly(N- ethyl-2-vinylcarbazole).[6] A relationship between the degree of shielding and electronic mobilities has been proposed.[6] From the spectrum it appears that poly(1-(2-anthryl)ethyl methacrylate) also exhibits large shielding of one or more aromatic protons.

As anticipated, 1-(2-anthryl)ethyl methacrylate can be copolymerized with other esters of methacrylic acid such as methyl methacrylate (MMA) and dodecyl methacrylate.

For example, 1.0 g (3.5 × 10^{-3} mol) of 2AEMA and 1.25 g (12.5 × 10^{-3} mol) of MMA were copolymerized in 10 ml of xylene at 70° for 20 hr using 0.01 g of benzoyl peroxide as an initiator. The yield was 1.0 g; the percentage composition of 2AEMA units in the copolymer, as determined by the elemental analysis, was 31.6 mol %: $\bar{M}_w$ = 530,000; $\bar{M}_w/\bar{M}_n$ = 3.3. On the other hand, 2AEMA did not copolymerize with, and even inhibited the homopolymerization
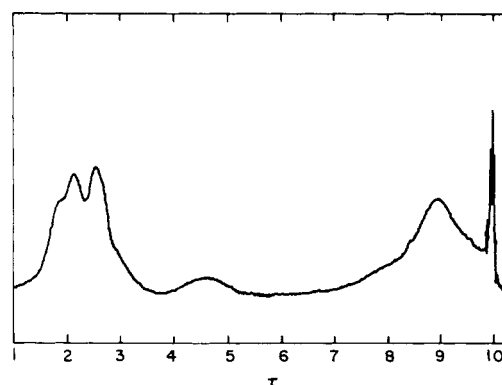

Figure 2. Proton nmr spectrum (60 MHz) of poly(2AEMA) at room temperature in CDCl$_3$.

of, N- vinylcarbazole and vinyl acetate. Thus, by utilizing the unique nonreactivity of the electron defficient methacrylate radical toward anthracene we have been able to synthesize a high molecular weight anthracene-containing polymer. The physical properties of the polymer are under investigation.

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On the Kinetics of Polymer Degradation in Solution. II. Laser Flash Photolysis Studies on Poly(phenyl vinyl ketone) and Butyrophenone

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ABSTRACT: Using the nanosecond flash photolysis technique transient absorption spectra of poly(phenyl vinyl ketone) (PPVK) and butyrophenone (BP) in benzene solution at room temperature were recorded. Samples were irradiated with 347.1-nm light flashes. With both substances the transient spectra decayed by a first-order process with k_1 = 1.0 ± 0.2 × 10^7 sec^{-1}. In PPVK and BP solutions containing naphthalene or biphenyl the established triplet absorption of these compounds is sensitized. It is concluded that the observed transient absorptions are due to triplet states of PPVK and BP, respectively. The quencher studies yielded as an estimate a triplet quantum yield ϕ(^{3}PPVK*) equal to 0.1 to 0.3. k_Q (bimolecular rate constant of energy transfer) is about two times smaller for biphenyl than for naphthalene. For BP k_Q is about two and a half times higher than for PPVK (in the case of naphthalene: k_Q(BP) = 5.0 ± 1.5 × 10^9 M^{-1} sec^{-1} and k_Q(PPVK) = 2 ± 1 × 10^9 M^{-1} sec^{-1}). This result reflects the influence of the diffusion constant of the polymer on k_Q as expected for diffusion-controlled reaction and agrees with earlier findings[10] concerning rate constants of the reaction of scavengers with macroradicals.

I. Introduction

We reported recently[1] on time-resolved measurements of main chain scissions in poly(phenyl vinyl ketone) (PPVK) in benzene solutions. The scissions were induced by flashes from a ruby laser (λ 347 nm, half-width 25 nsec) and were monitored by the light-scattering detection method. During these investigations it was found that the light-scattering intensity decreased after the flash with a half-life of about 20 μsec. The interpretation of this result involved the question of how fast the scission of a C–C bond in the main

chain of PPVK is accomplished. This work concerns kinetic investigations on these questions using the same equipment as before. At present it appears to be well established[2-4] that bond fractures in PPVK occur via base units excited in their triplet states. Therefore, the optical detection method was applied in order to follow the kinetics of triplet decay by observing triplet–triplet absorption and intermolecular energy transfer between excited PPVK molecules and quenchers such as naphthalene and certain dienes.
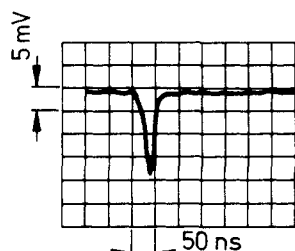
Analogous experiments were carried out with butyrophe-

Figure 1. Oscilloscope trace demonstrating the shape of the flash, obtained by scattering the light of the laser flash into the photomultiplier.
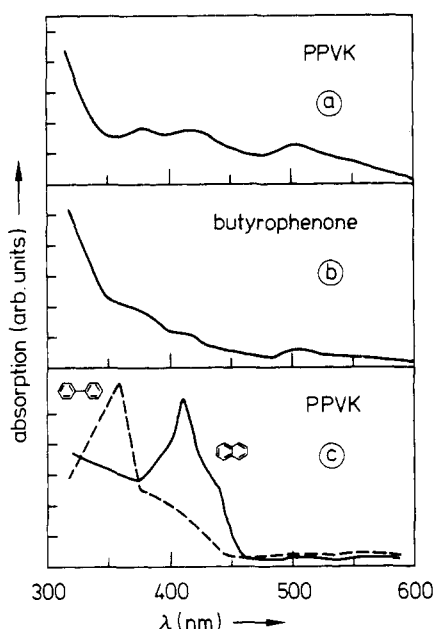

Figure 2. Absorption spectra observed immediately after the flash in benzene solution containing: (a) PPVK, 3.8×10^{-3} base mol/l.; (b) butyrophenone, 4.4×10^{-2} mol/l.; (c) PPVK, 3.8×10^{-3} base mol/l. and 0.2 M naphthalene (solid line) and 0.2 M biphenyl (dotted line).

none (BP). This compound may at least in some way be considered as a model compound of PPVK. Its photochemistry has been extensively studied.[13-16] Results of that research with relevance to our work are that BP undergoes photoelimination (Norrish type II fragmentation) *via* its triplet state with a quantum yield of about 0.4.

II. Experimental Section

(a) **Apparatus.** Sample solutions were irradiated in rectangular cells with light flashes (λ 347.1 nm) from a ruby laser (Korad Model K1QS2) as described before.[1] The half-width of the flashes was about 25 nsec. In order to measure changes of the optical absorption, light of a xenon lamp (Osram, XBO 450 W) passed the cell perpendicular to the ruby laser beam. It was focused to the entrance slit of a high intensity monochromator (33-86-76, Bausch and Lomb) and detected by a photomultiplier (RCA, 1P28). The photomultiplier was operated with only five stages and the rise time of the detection system was 3 nsec when terminated into 50 Ω. Figure 1 shows the signal observed when scattering the light of the laser pulse into the photomultiplier.

To improve the signal-to-noise ratio the current through the xenon lamp was increased for a period of 1.5 msec, resulting in a 10- to 100-fold increase in light intensity, depending on the wavelength.[7] The photomultiplier output was fed into a 7A16A plug-in (Tektronix) and displayed on a storage oscilloscope (Tektronix 7623).

(b) **Actinometry.** Normal laser operation yielded $5 \pm 0.5 \times 10^{16}$ photons per flash as measured with the potassium ferrioxalate actinometer[8] ($\phi[Fe^{2+}] = 1.20$). In order to reduce the incident light
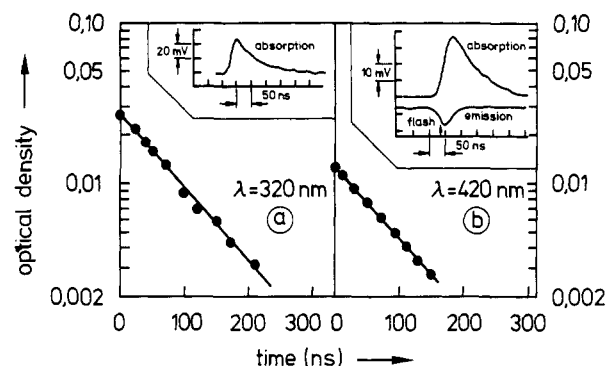

Figure 3. First-order plot of optical density *vs.* time: (a) at λ 320 nm (insert: oscilloscope trace of light absorption), no emission was observed at this wavelength; (b) at λ 420 nm (insert: oscilloscope traces of light absorption and emission), PPVK in benzene solution, 1.9×10^{-3} base mol/l.

intensity filters (Schott BG 23) were used.

(c) **Material.** Synthesis and characterization of PPVK have been already described. Butyrophenone (Fluka AG) was distilled over a spinning band column (E. Haage, Mülheim). Benzene (Merck, p.a.) was purified by shaking with concentrated H_2SO_4 and drying over $CaCl_2$ and CaH_2. It was distilled over a splitting tube column (Fischer, Bonn).

Ar-saturated samples yielded the same results as oxygen-saturated samples. Therefore, oxygen was not excluded in most experiments.

III. Results and Discussion

(a) **Determination of Transient Lifetime.** Laser excitation of PPVK and butyrophenone in benzene solution lead to a transient absorption as well as to an emission of light. The absorption spectra of the transients observed immediately after the pulse are shown in Figures 2a and 2b. Between λ 600 and 370 nm several minor peaks were detected. Below λ 400 nm the absorption increases with decreasing wavelength. The emission was very short lasting and decayed within the duration of the flash. Typical oscilloscope traces are shown in the inserts of Figure 3. The absorption was formed during the flash. It decayed at all monitored wavelengths according to a first-order rate law, indicating that the absorption is due to single transient species. Typical examples of first-order plots are shown in Figures 3a and 3b. Within the error limit the same rate constant was found for PPVK and BP. It amounts to $\Sigma k_1 = 1.0 \pm 0.2 \times 10^7$ sec^{-1}. Corresponding values of Σk_1 reported by other authors (obtained in benzene solution under stationary conditions using the quencher method with the assumption of $k_Q = 5 \times 10^9$ M^{-1} sec^{-1}) are for BP 2.7 $\times 10^6$ sec^{-1},[13] 6.6 $\times 10^6$ sec^{-1},[16] 7.6 $\times 10^6$ sec^{-1},[15] and for PPVK 5.9 $\times 10^7$ sec^{-1}.[17] Since rate constants of singlet decay of ketone compounds of 10^8 to 10^9 sec^{-1} have been reported,[19] it may be excluded that the spectra shown in Figures 2a and 2b are due to singlet transients.

In the presence of biphenyl and naphthalene, which do not absorb light at 347 nm, the spectra shown in Figure 2c appeared immediately after the flash. Other authors[5,11,12] reported triplet–triplet (T–T) absorption spectra of excited naphthalene and biphenyl. The spectra of Figure 2c are identical with those. Together with the measured lifetime this finding may be considered as evidence that the absorption spectra demonstrated in Figures 2a and 2b are pertaining to the T–T absorption of excited PPVK and butyrophenone, respectively. Another evidence for this assignment is the fact that the olefinic triplet quenchers 1,3-pentadiene and α-methylstyrene suppressed the absorption of the transients of PPVK and butyrophenone completely when present at concentrations higher than 1 M. 1,3-Pen-
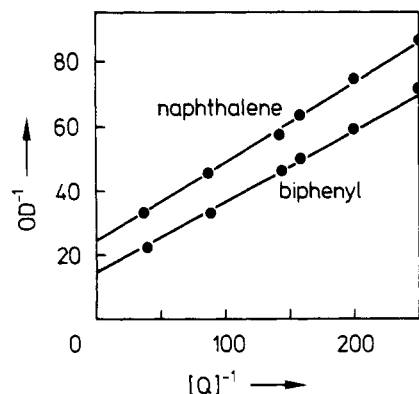
Figure 4. Plots of reciprocal optical density vs. reciprocal quencher concentration according to eq 2. PPVK in benzene solution, 1.9 × 10⁻³ base mol/l.

Table I
Values of the Rate Constant of Triplet–Triplet Transfer from Ketones to Quenchers

Ketone	Quencher	k_Q, M^{-1} sec^{-1}
PPVK	Naphthalene	$2 \pm 1 \times 10^9$
	Biphenyl	$0.8 \pm 0.4 \times 10^9$
Butyrophenone	Naphthalene	$5.0 \pm 1.5 \times 10^9$
	Biphenyl	$2 \pm 1 \times 10^9$

tadiene is known to quench the photoelimination of butyrophenone.[13] An optical absorption between 300 and 600 nm originating from transients formed by energy transfer from excited ketone molecules to molecules of these two compounds was not observed.

Quantum yields $\phi(T)$ of naphthalene and biphenyl triplet formation were estimated using ϵ_{T-T}^{413} (naphth) = 2 × 10⁴ M^{-1} cm^{-1} and ϵ_{T-T}^{370}.(biph) = 3.5 × 10⁴ M^{-1} cm^{-1} [5,8] as 0.1 to 0.3 for solutions containing PPVK or butyrophenone. Based on the assumption that all ketone triplets formed initially are converted to naphthalene and the respective biphenyl triplets this value should be equal to $\phi(^3PPVK^*)$. The quantum yield for main-chain scissions $\phi(S)$ for PPVK in benzene solution (determined at stationary irradiations with light of λ 313 nm) amounts to 0.25.[2,3] Our own estimate[1] yielded $\phi(S)$ equal to 0.4 to 0.6. The error limit in the determination of both quantum yields is relatively high. Therefore, a comparison of $\phi(S)$ and $\phi(T)$ allows only the conclusion that at least a fraction of main-chain scissioning in PPVK occurs via excited triplet states.

(b) Rate Constants of Triplet Energy Transfer from PPVK and Butyrophenone to Naphthalene and Biphenyl. In order to determine the rate constant k_Q of the reaction

$$^3\text{ketone*} + {}^1\text{Q} \xrightarrow{k_Q} {}^1\text{ketone} + {}^3\text{Q*} \tag{1}$$
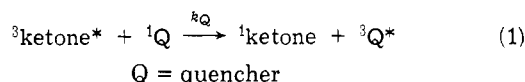
$$Q = \text{quencher}$$

the absorption immediately after the flash was measured at λ 413 nm (naphthalene) and λ 361 nm (biphenyl) at various quencher concentrations. At these experiments the average number of photons (λ 347 nm) absorbed per macromolecule was less than one. Figure 4 shows typical examples of plots of the reciprocal optical density vs. the reciprocal quencher concentration.

In all cases straight lines were obtained. Therefore, it appears that the following relationship holds.

$$\frac{1}{\text{OD}} = \frac{1}{\text{OD}_L} + \frac{\Sigma k_1}{\text{OD}_L k_Q [Q]} \tag{2}$$

OD denotes the optical density at scavenger concentration [Q]. OD$_L$ is the limiting value obtained by extrapolation of the straight lines (compare Figure 4) to [Q]$^{-1}$ = 0. The rate constant k_Q was calculated from the slopes of the straight lines using the Σk_1 values given above. The results are shown in Table I. One recognizes that k_Q is about two times smaller for biphenyl than for naphthalene. This cor-

roborates earlier measurements of Stern–Volmer constants.[1,18] Furthermore it is found that k_Q is about two and a half times greater for BP than for PPVK. This effect may be explained by considering that the quenching reaction is an (almost) encounter-controlled process. For a homologous series of compounds it is expected that k_Q decreases with increasing chain length according to the Smoluchowski equation

$$k_Q = 4\pi N_A \times 10^{-3} r(D_Q + D_T) \tag{3}$$

Here N_A denotes Avogadros number; D_Q and D_T are the diffusion coefficients of quencher and triplet excited molecules; r is the reaction distance. The decrease of k_Q results mainly from the fact that D_T decreases with increasing chain length. D values for the compounds used during this work are not known. However, the comparison with D values of compounds of other homologous series shows that the observed decrease of k_Q corresponds to the presumable decrease of D for PPVK with molecular weight.

It may be pointed out that detailed analogous studies have been carried out in our laboratory on the almost encounter-controlled reaction of macroradicals with radical scavengers like tetranitromethane and p-nitrosodimethylaniline.[10] Then, it was found that the dependency of the rate constant of the reaction of macroradicals with scavenger molecules upon the diffusion constant follows the Smoluchowski equation.

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