PHOTOCHEMICAL TRANSFORMATIONS ON POLYMERS - INVESTIGATIONS OF RAPID REACTIONS

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Abstract - Applications of modern techniques for the study of fast photo-induced reactions in polymers are reported. So far such studies served mainly the purpose of elucidating reaction mechanisms, i.e. they were devoted for the identification of transient species and the detection of rates of elementary reactions. With respect to polymeric systems it is possible to include into the aims of photochemical and photophysical investigations the elucidation of polymer specific problems pertaining e.g. to intramolecular reactions or dynamic aspects (interpenetration and disentanglement of coiled macromolecules). Typical examples are presented concerning the various techniques based on luminescence, triplet-triplet absorption and time resolved light scattering measurements.

INTRODUCTION

Thanks to the recent progress concerning the development of new techniques or the improvement of older techniques it has become possible to investigate photochemical transformations of polymers at ambient temperature in rather sophisticated ways. This progress was essentially based on the fact that various powerful lasers and certain highly refined electronic devices became available. With respect to the investigation of rapid reactions, this paper is dealing with the improvement of the time resolution of several detection methods contributed essentially to the advances.

Since it is now possible to record molecular changes in the time range from minutes or hours down to picoseconds the elucidation of the complete course of a photo-induced process leading to a permanent chemical change can be followed. Thus, physical as well as chemical reactions can be recognized and analyzed. There is no strict discrimination with respect to the importance of those two modes of reactions for the polymer chemist, because in principle electronically excited molecules can undergo chemical reactions with unexcited intact molecules if the lifetime of the excited state is long enough. Some important physical and chemical reactions of excited molecules are listed in Table 1.

The primary aim of the investigations, which shall be dealt with here, is the elucidation of the mechanism of photochemical reactions of macromolecules (see Table 2). Relevant experimental work usually concerns the identification of transient species as well as the detection and measurement of rates of elementary reactions.

Obviously, optical detection methods are highly appropriate for the investigation of rapid reactions. Therefore, most frequently luminescence (fluorescence, phosphorescence) measurements were carried out. Since even rather weak luminescence signals can be detected relatively accurately, low intensity photolyzing light sources are in many cases sufficient for fluorescence or phosphorescence studies. In other cases sampling techniques can be used in order to improve the sensitivity of detecting systems. A different situation is normally met with optical absorption measurements, where powerful photolyzing light sources have to be applied in order to achieve sufficiently high signal changes. In this field a breakthrough was achieved with the advent of powerful lasers which can be used as photolyzing light sources for flash photolysis studies. The latter have been devoted to photophysical and photochemical investigations of polymers in combination with optical absorption, light scattering and most recently also with electrical conductivity measurements.

The application of these methods to polymeric systems not only served the purpose of elucidating reaction mechanisms. As is indicated in Table 2, the modern photophysical and

TABLE 1. Some important reactions of electronically excited molecules

Physical Reactions
Emission and Absorption:
$^1P^* \longrightarrow {}^1P + h\nu$ (a) Fluorescence
$^3P^* \longrightarrow {}^1P + h\nu$ (b) Phosphorescence
$^3P^* + h\nu \longrightarrow {}^3P^{**}$ (c) T-T Absorption
Energy Transfer:
$S^* + P \longrightarrow S + P^*$ (d) Sensitization
$Q + P^* \longrightarrow Q^* + P$ (e) Quenching
Chemical Reactions
$P^* + RH \longrightarrow \cdot PH + R\cdot$ (f) Hydrogen Abstraction
$P^* + X \longrightarrow [P^* \cdot \cdot X] \longrightarrow P^{\bar{\cdot}} + X^{\overset{+}{\cdot}}$ (g) Electron Transfer
$P^* \longrightarrow R_1^{\cdot} + R_2^{\cdot}$ (h) Homolytic Bond Rupture

$^1P^*$ and $^3P^*$: singlet and triplet excited macromolecules; S, Q, RH and X: low molecular weight compounds

TABLE 2. Aims of studies concerning rapid physical or chemical photo-reactions in polymers

Primary Aims	Elucidation of Reaction Mechanisms	a) Identification of Transient Species
		b) Detection and Measurement of Rates of Elementary Reactions
Secondary Aims	Investigation of Polymer Specific Problems (e.g. intramolecular reactions, interpenetration and disentanglement of coiled macromolecules)	

photochemical tools now available permit the investigation of various polymer specific problems which concern e.g. intramolecular reactions, interpenetration of macromolecules and in connection with disentanglement diffusion preferential solvation and intramolecular contact pair formation. The material dealt with in the following sections concerns typical results which have been arranged according to the detection method applied during the experiments.

A. Luminescence Studies

Energy migration down the chain and intramolecular excimer formation as depicted in Fig.1 are polymer specific processes which have been investigated recently by luminescence studies at various laboratories (1-10).

Fig.2(a) shows time-resolved emission spectra obtained with de-aerated CH_2Cl_2 solutions of poly(styrene) at room temperature (4). With very early time gates a spectrum was obtained which is essentially composed of the monomer emission while the spectrum taken at a later time shows the excimer fluorescence. The decay of the fluorescence is depicted in (Fig.2(b)). The decay lifetimes are 1 ns (monomer) and 19 ns (excimer). Analogous experiments with poly(1-vinylnaphthalene) yielded 7 ns (monomer) and 43 ns (excimer) (4).
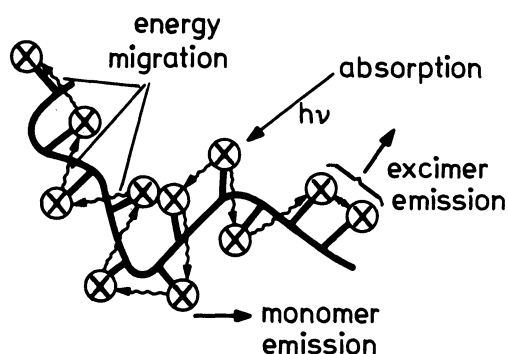
Fig.1. Schematic depiction of
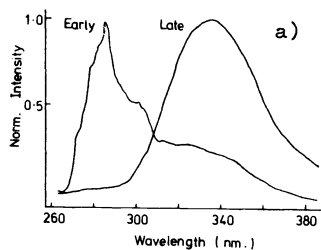energy migration down to chain
and excimer and monomer exmis-
sion

Fig.2.
(a) Time-resolved fluorescence spectra obtained with a
CH_2Cl_2 solution of poly(styrene) (1g/1) in the absence of
O_2 at room temperature. λ_{exc} = 257 nm; early gate: Δt = 0,
late gate Δt = 45 ns.
(b) Decay of fluorescence of poly(styrene) in CH_2Cl_2 solut-
ion; short wave length emission corresponding to monomer
and long wave length emission to excimer fluorescence
(after Phillips et al. (4))
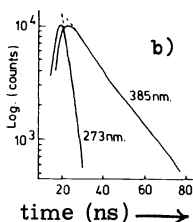
A strong solvent effect on the absorption and the fluorescence spectra of poly(1-vinylnaph-
thalene) indicates the formation of ground state dimers and simultaneously demonstrates
that emission studies are capable of yielding information about the conformation of macro-
molecules in certain cases. Fig.3 shows emission spectra of poly(1-vinylnaphthalene) dis-
solved in methylene chloride and cyclohexane (7). Cyclohexane is a poor solvent for this
polymer. Thus dimer formation is favored.

Time resolved phosphorescence measurements have been utilized to obtain insight into the
mechanism of diffusion-controlled macromolecular reactions (9). Kinetic investigations
concerning the reaction between macromolecules possessing lateral reactive sites or ana-
logous reactions of macromolecules with small molecules were initiated several years ago
by pulse radiolysis studies (11). Recently it was possible to continue this line of research
in a more refined way by using polymers especially synthesized for this purpose. These
polymers consist of almost monodispers poly(styrene) containing chromophoric or quench-
ing groups attached at definite sites to the chains. Thus, poly(styrylbenzil) (PS-B) was ex-
cited and the benzil phosphorescence was quenched by poly(styrylanthracene) (PS-A). Dona-
tor and acceptor groups were located at the end of the chains:

PS-B   PS-A
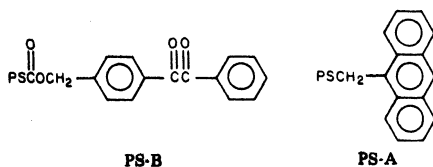
The dependence of the quenching rate constant k_q on the degree of polymerization n is shown
in Fig.4. It is seen that k_q is decreasing with increasing degree of polymerization and that

there is a significant solvent effect at higher chain length. The important result is: the re-
duced rate constant is in poor solvents larger than in good solvents, if $n < 10^3$; on the
other hand, it is in poor solvents lower than in good solvents, if $n > 10^3$. The behavior
found at low degree of polymerization seems to be in accordance with the thermodynamic
(equilibrium) excluded volume effect; the results at high values of n were explained by the
authors (9) by the concept of the so-called kinetic (nonequilibrium) excluded volume effect,
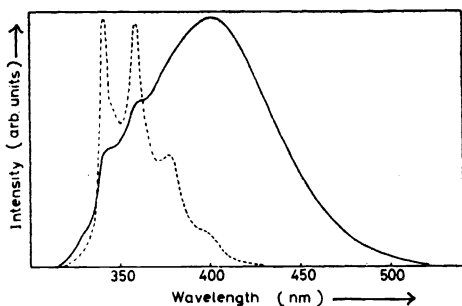the latter is caused by steric hindrance (which retards the rates of encounters of reactive sites).

Fig.3. Uncorrected fluorescence spectra of
poly(1-vinylnaphthalene in CH_2Cl_2 (—) and in
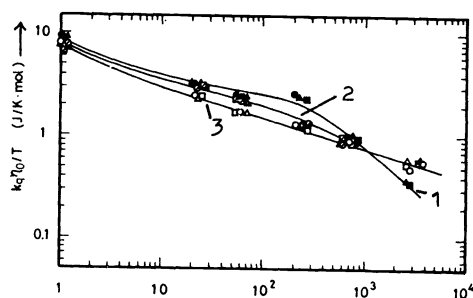cyclohexane (----) at room temperature
(after Irie et al.(7))

Fig.4. Reduced quenching rate constants of
polymer-polymer reactions at 20, 30, and
40°C in various solvents: cyclohexane (1),
butanone (2), and benzene (3) (after Horie and
Mita (9))

B. Optical Absorption Studies

The optical absorption detection method is in many cases appropriate to the identification
of short-lived intermediates such as triplets, free radicals and free ions. It has been
utilized recently in combination with laser flash photolysis (12-16). Excited triplet states
can be evidenced frequently by their absorption (T-T absorption). The extinction coefficient
of the T-T absorption is in certain cases relatively high, thus permitting to follow the fate
of triplets quite easily. Upon irradiation of dilute polymer solutions with high power laser
flashes rather high numbers of triplets per macromolecule can be generated. During an in-
vestigation of copolymers of phenylvinyl ketone and 2-vinylnaphthalene in benzene solution
at room temperature the following results were obtained (13): The photolyzing light (347nm)
was absorbed solely by phenylvinylketone base units.

Even at very low polymer concentrations the T-T absorption of naphthalene base units was
detected at the end of a 25 ns flash (see Fig.5), which indicates a very rapidly and effec-
tively occurring energy migration process. The decay kinetics of the T-T absorption after
the flash depended strongly on the incident intensity of the photolyzing light as is shown in
Fig.6. The very rapid decay of the absorption at high absorbed dose rates was correlated
to intramolecular triplet-triplet deactivation processes. The various modes of intramole-
cular reactions of triplet excited moieties are depicted in Fig.7. Selfquenching might be an
important process. Experiments with poly(vinylbenzophenone (PVBP) in benzene solution
at room temperature yielded the following results (16):

At the end of a 25 ns flash identical absorption spectra were obtained with the model com-
pound (p-isopropylbenzophenone) and the polymer as is shown in Fig.8. PVBP triplets de-
cay faster than the triplets of the model compound, as shown in Fig.9. Since this behavior
is not very significantly changed upon decreasing the incident intensity of the laser beam,
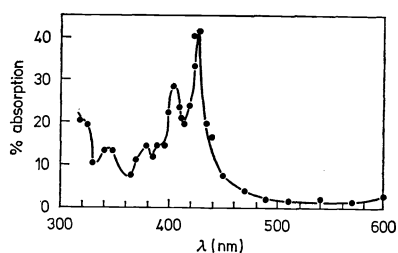it was concluded that selfquenching plays an important role. Actually, an important fract-

Fig.5. Absorption spectrum observed at room temperature at the end of a 347 nm flash in benzene solution containing poly(phenylvinylketone-co-2-vinylnaphthalene. 2-VN fraction: 2.8 mol%. Polymer concentration 2.1×10^{-3} base mol/l. Duration of flash: 25 ns, (13).
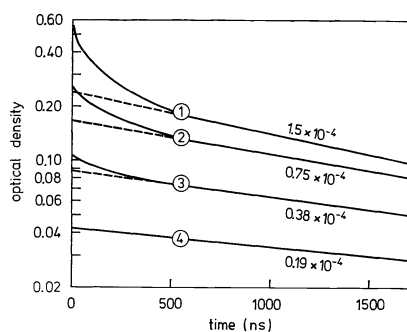

Fig.6. Semilogarithmic plot of the optical density at λ = 430 nm vs. time. Poly(phenylvinylketone-co-2-vinylnaphthalene) containing 19.7 mol% 2-VN. Polymer concentration 2.25×10^{-3} base mol/l. The numbers at the curves designate the absorbed dose per flash in einstein/l. (13).

MODES OF INTRAMOLECULAR
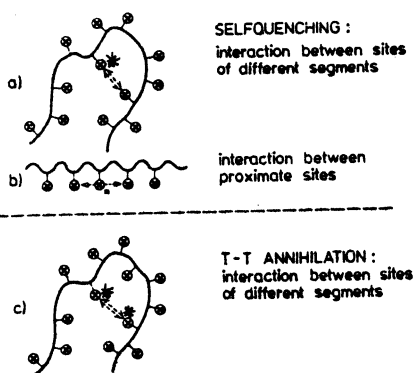REACTIONS OF TRIPLET EXCITED MOIETIES

Fig.7. Schematic depiction of modes of intramolecular reactions of triplet excited moieties.

Fig.8. Absorption spectra obtained with Ar saturated benzene solutions immediately at the end of a 25 ns flash of 347 nm light. Absorbed dose per flash: 6×10^{-5} einstein/l (a) p-isopropylbenzophenone 7.4×10^{-4} mol/l (b) PVBP, 5.4×10^{-4} base mol/l, $\overline{M}_w$: 2×10^5. (16).
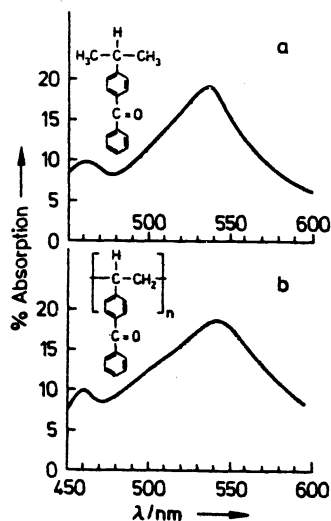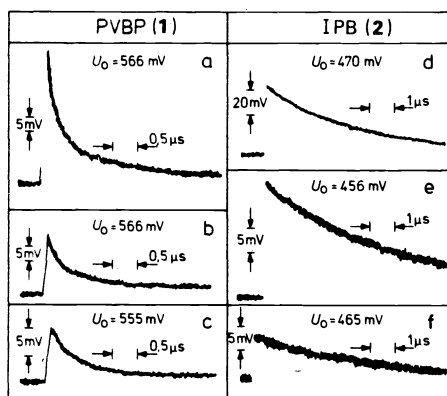
Fig.9. Typical oscilloscope traces demonstrating the decay of the transient absorption after irradiation with a 25 ns flash of 347 nm light. Ar-saturated benzene solutions of poly(vinylbenzophenone) $(7.4 \times 10^{-4}$ base mol/l) and p-isopropylbenzophenone $(7.4 \times 10^{-4}$ mol/l). Absorbed dose per flash (in einstein/l): 2.6×10^{-5} (a), 8.5×10^{-6} (b), 2.9×10^{-6} (c), 3.5×10^{-5} (d), 1.2×10^{-5} (e), 4.3×10^{-6} (f)

$(U_0$: signal voltage before the flash) (14)

ion of selfquenching processes must be due to strong ground state interaction of proximate base units (dimers). Thus it becomes comprehensible why PVBP can be photoreduced by 2-propanol less effectively than benzophenone or the model compound as found at stationary irradiations (17, 18).

Mechanistic photolytic aspects were studied in the case of poly(phenylisopropenyl ketone) (PPIK) and phenyl-t-butyl ketone (pivalophenone) (14):

$$\begin{bmatrix} \overset{\displaystyle CH_3}{\underset{\displaystyle |}{\,}} \\ -C-CH_2- \\ \overset{\displaystyle |}{C=O} \\ \overset{\displaystyle |}{Ph} \end{bmatrix}_n \qquad\qquad \begin{array}{c} CH_3 \\ | \\ H_3C-C-CH_3 \\ | \\ C=O \\ | \\ Ph \end{array}$$

In these two compounds the dominant chemical route of triplet deactivation is α-cleavage. In copolymers of styrene and PIK with a high content of isolated PIK units α-cleavage becomes less probable and Norrish type II processes dominate, although the rate of the latter process is lower than that of the type I process in homo PPIK. This is demonstrated by the spectra of free radicals observed 150 μs after the flash shown in Fig.10. In the case of
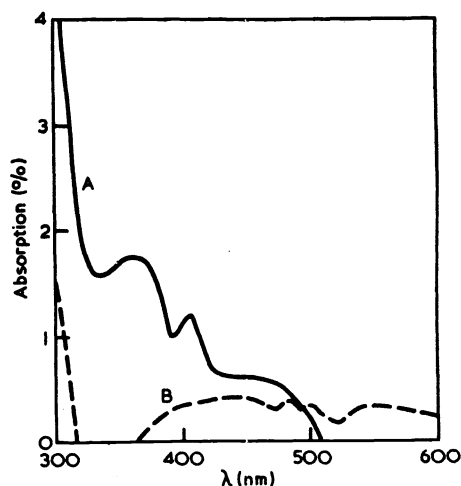

Fig.10. Transient spectra recorded 150 μs after the flash, obtained with benzene solutions of (A) PPIK $(1.5 \times 10^{-3}$ base mol/l) and (B) CP-St-PIK-1 $(1.5 \times 10^{-1}$ base mol/l) at room temperature. Absorbed dose per flash: 1×10^{-5} einstein/l. (14)

homo PPIK the absorption spectrum is essentially showing the absorption of benzoyl radicals, while in the case of the copolymer the spectrum is composed of the spectra of several components, the most important being the ketyl radical.

C. Light Scattering Studies

Photo**induced** processes usually proceed according to a series of consecutive reactions comprising several photophysical and photochemical steps up to the formation of stable endproducts. The total rate of such a process is determined by the slowest elementary reactions in the series. Sometimes the rate of a single step is much lower than the rates of all other steps.

If a change of a physical property related to the chemical change is measured, the rate of change of the physical property is identical to the rate of the slowest step. Furthermore, if one considers a photo-process involving macromolecules and leading to a change of the molecular size, this change will become detectable by monitoring the intensity of the light which is scattered by the macromolecules. The rate of the change of light scattering intensity (LSI) can be correlated to a physical or a chemical process as will be explained by considering a photo-process leading to main chain rupture. According to the simplified scheme depicted in Fig.11, two extreme cases can be discriminated:

(i) $v_b \gg v_c$

The lifetime of an intermediate formed during or after the light absorption is much shorter than the time for separation of the fragments of the macromolecules, i.e. the rate of step (b) is much faster than the rate of step (c). The observed rate of LSI decrease is due to the rate of separation of the fragments, i.e. in the case of macromolecules with coil conformation due to the disentanglement diffusion.
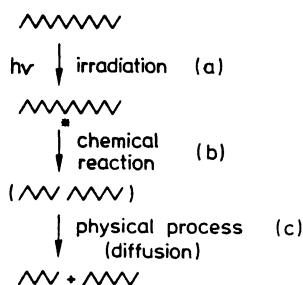

Fig.11. Schematic depiction of photochemical main chain scission of a coiled macromolecule in solution.

(ii) $v_b \ll v_c$

The lifetime of the intermediate causing main chain rupture is much longer than the time of separation of the fragments, i.e. the rate of step (b) is much lower than the rate of step (c). In this case the observed rate of LSI decrease is correlated to the lifetime of the intermediate, i.e. to a chemical reaction. Thus, time resolved light scattering measurements may serve under these conditions to measure rate constants of reactions of lateral macroradicals, undergoing main chain scission, with radical scavengers etc..

The straightforward correlation of the rate of LSI decrease with either of the two cases will, of course, be restricted to those systems, where the interval between the two steps is sufficiently large. In the following sections typical examples for both cases will be presented.

A-1) LSI Studies Concerning Chemical Reactions

At present investigations in the author's laboratory are concentrating around two topics: photocrosslinking and photo-oxidative main chain degradation. As an example for the latter case results obtained with polystyrene are presented (22). This polymer was irradiated in solutions of chloroform, carbontetrachloride, dichloromethane and p-dioxane with 20 ns flashes of 265 nm light. Main chain degradation was found to occur only in $CHCl_3$ and CCl_4 solutions in the presence of oxygen. With O_2-free solutions no degradation was observed. Typical oscilloscope traces demonstrating the change of LSI after the flash are shown in Fig.12. The degree of degradation increased with increasing O_2-concentration and approached a limiting value at $[O_2] > 1 \times 10^{-3}$ mol/l. It is therefore assumed that an oxygenated intermediate is formed which causes main chain rupture. By a given absorbed dose a defi-
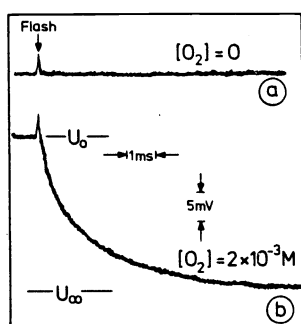
Fig.12. Oscilloscope traces demonstrating the time depend-
ence of the light scattering intensity at $\Theta = 90°$ after a 20 ns
flash of 265 nm light at r.t., Polystyrene in $CHCl_3$: 9.3 x 10^{-4}
base mol/l in the absence of oxygen (a) and at $[O_2]$: 2 x 10^{-3}
mol/l. Dose absorbed by the solution per flash: 3.2 x 10^{-6}
einstein/l. (22).

nite number of activated species is formed, all of which end up in main chain scissions if
they can react with oxygen before becoming deactivated otherwise, i.e. at sufficiently high
O_2 concentrations. Fig.13 shows first order plots of the LSI decrease vs. time. These re-
sults were obtained with $CHCl_3$ solutions of different O_2 concentrations. The rate of LSI
decrease becomes higher as the oxygen concentration increases. At $[O_2] > 10^{-4}$ mol/l first
order kinetics cannot be applied anymore. At significantly higher O_2-concentration the LSI

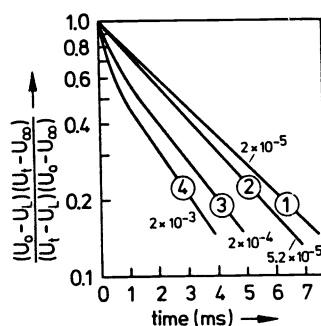Fig.13. Time dependence of the decrease of LSI. Polysty-
rene in $CHCl_3$ (9.3 x 10^{-4} base mol/l). Dose absorbed by
the solution per flash: 3.2 x 10^{-6} einstein/l. First-order
plots obtained at various oxygen concentrations as indicat-
ed at the curves in mol/l. U_o, U_∞, U_t designate sig-
nal voltages being proportional to the light scattering in-
tensities before the flash (o), at time t and a very long time
after the flash. The subscript L designates "solvent". (22)

decrease was found to follow a second order law. The latter finding was revealed during re-
cent reinvestigations which led to a somewhat modified understanding of the kinetics of the
LSI decrease in this case. The results obtained so far appear to be in accordance with the
reaction mechanism shown in Table 3.

Macroradicals are presumably formed via exciplexes of CT character according to react-
ions (f) and (g) or (h) in Table 3. Solvent radicals generated by the photolysis of the solvent
are considered to contribute only insignificantly to the mechanism due to the low value of
the extinction coefficient of $CHCl_3$ at 265 nm ($\varepsilon = 8.1$ x 10^{-4} l/mol cm). The overwhelming
portion of the light is absorbed by the polymer ($\varepsilon = 210$ l/(base mol)cm).

It is assumed that at low O_2 concentrations the rate of LSI decrease is correlated with re-
action (i), and it was estimated that $k_{(i)} = 5$ x 10^5 l/mol s. At higher O_2 concentrations,
probably the rate of reaction (m) becomes determining for the rate of LSI decrease.

A-2) LSI Studies Concerning the Dynamics of Polymer Chains in Solution

Poly(phenylvinylketone) (PPVK) and copolymers of PVK and styrene were found being ap-
propriate for the investigation of disentanglement diffusion (19,20). Main chain scissions
are generated in these polymers via a Norrish type II mechanism involving triplet excited
moieties. The triplet lifetime is one or two orders of magnitude shorter than the observed
first order lifetimes τ(LSI) of the LSI decrease. From the dependence of the lifetime
τ(LSI) on the microviscosity of the solutions it was inferred that τ(LSI) is correlated to
the disentanglement motion of the fragment molecules generated by main chain scission.
Recent studies in this field concerned the influence of solvent quality on disentanglement
diffusion (23). PPVK was irradiated in solutions of mixtures of dioxane and 1-propanol
with 25 ns flashes of 347 nm light at various incident intensities. The decrease of the LSI
was monitored as a function of time after the flash at a scattering angle of $90°$. Results
are presented in Fig.14. $\tau_{1/2}$(LSI) is independent of the number of scissions per initial

TABLE 3. Photolytic main chain degradation of polystyrene in chloro-
form solution (P and S designate polymer and solvent mole-
cules, respectively)

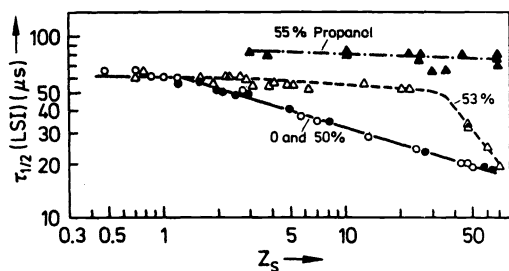|		
Generation of Macroradicals	$P + h\nu \longrightarrow P^*$	(a)
	$S + h\nu \longrightarrow S^*$	(b)
	$S^* \longrightarrow 2R_S\dot{}$	(c)
	$R_S\dot{} + P \longrightarrow R_SH + P\cdot$	(d)
	$P^* + S \longrightarrow P + S^*$	(e)
	$P^* + CHCl_3 \longrightarrow (P^*...CHCl_3)$	(f)
	$(P^*...CHCl_3) \longrightarrow \begin{cases} P\cdot + H\dot{C}Cl_2 + HCl \\ P\overset{+}{\cdot} + (HCCl_3)^{-}\dot{} \\ \downarrow \\ P\cdot + H^+ \end{cases}$	(g) (h)
Reactions of Macroradicals	$P\cdot + O_2 \longrightarrow PO_2\dot{}$	(i)
		(j)
	$PO_2\dot{} \longrightarrow P\dot{}_{ox}$	(k)
	$P\dot{}_{ox} \longrightarrow F_1 + F_2\dot{}$	(l)
	$2PO_2\dot{} \longrightarrow 2PO\cdot + O_2$	(m)
	$PO\cdot \longrightarrow F_1 + F_2\dot{}$	(n)
	$P\cdot + P\cdot \longrightarrow$ products	(o)
	$P\cdot + R_S\dot{} \longrightarrow$ products	(p)

Fig.14. The 1st order halflife time of de-
crease of the light scattering intensity at $\theta =$
90° vs. the number of scissions per initial
macromolecule. Poly(phenylvinylketone)
(5×10^{-3} base mol/l; $\overline{M}_{w,o} = 5.9 \times 10^5$) in
dioxane/1-propanol mixtures of the following
propanol contents: (o 0%, (●) 50%, (Δ) 53%,
and (▲) 55%). (Tagawa and Schnabel (23)).

macromolecule Z_S if the fragment size exceeds a critical value $(DP)_{crit}$, i.e. at low values
of Z_S. $\tau_{1/2}(LSI)$ decreased with increasing Z_S steadily if the average fragment size was
smaller than the critical value. Upon worsening the solvent quality the critical fragment size
$(DP)_{crit}$ was shifted to lower values (i.e. to higher values of Z_S): 2×10^3 (100 and 50% dio-
xane), 150 (47% dioxane) and 60 (45% dioxane). The results are explained by the concept of
intramolecular contact pair formation as indicated in Fig.15.

It is again taken into consideration that the process of main chain rupture is a series of con-
secutive steps. After scissions of chemical bonds in the main chains have been accomplish-
ed (step (a)) disentanglement diffusion follows (steps (b) and (c)). If the fragments of the rup-
tured macromolecule are tight together by contact pairs the latter must detach (step (b)) be-
fore the fragments can move freely (step (c)). It is inferred from the results that the rate of
contact pair detachment (step (b)) is lower than the rate of the successive step (c). Thus,
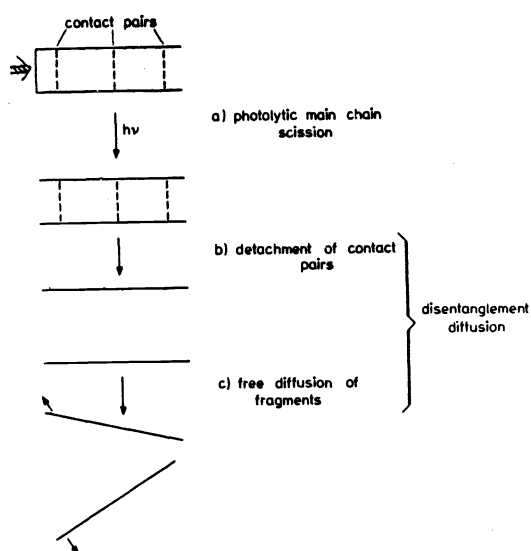
Fig. 15. Schematic depiction of disentanglement diffusion of a coiled macromolecule after photolytic bond rupture in the main chain.

the rate of step (b) is determining the total rate of the disentanglement process. If the average distance between scissions is significantly smaller than that between sites of contact pairs (at $Z_s > Z_s(crit)$) $\tau_{1/2}(LSI)$ is correlated to step (c). In this case the disentanglement process cannot be influenced by contact pairs. On the other hand, if the average distance between scissions is much larger than that between sites of contact pairs the influence of contact pairs on disentanglement is becoming important. For $Z_s < Z_s(crit)$ the rate of contact pair detachment is only very slightly influenced by Z_s as is inferred from Fig. 14. The rate of step (b) should, however, be influenced by the contact pair density which is expected to increase as the solvent quality is worsened. This assumption is substantiated by the finding that at $Z_s < Z_s(crit)$ $\tau_{1/2}(LSI)$ is increasing as the 1-propanol content approaches the cloud point (see Fig. 14). It appears that the concept of contact pair formation proves as useful in order to understand phenomena referring to the influence of solvent quality on disentanglement diffusion. The experimental technique applied provides, on the other hand, a powerful tool for the detection of intramolecular contact pairs in macromolecules.

In connection with disentanglement diffusion following main chain degradation another aspect shall be briefly discussed. It concerns preferential solvation (20). When certain binary solvent mixtures were used it turned out that the rate of LSI decrease was diminishing upon augmenting the concentration of one of the solvent components. $\tau_{1/2}(LSI)$ approached eventually a limiting value at relatively low concentrations of this component. Typical results obtained with chloroform solutions of poly (N-vinylpyrrolidone-co-phenylvinylketone) containing 10 mol% phenylvinylketone are presented in Fig. 16(b)). It can be seen that $\tau_{1/2}(LSI)$
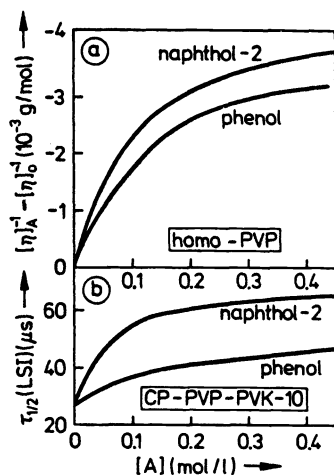

Fig. 16. Preferential solvation of Poly(N-vinylpyrrolidone-co-phenylvinylketone) containing 10 mol% PVK. $\overline{M}_{n,o}$: 4.4×10^5; $c_{Polymer}$: 4×10^{-2} base mol/l. Solvent: CHCl$_3$.

(a) $[\eta]_A^{-1} - [\eta]_o^{-1}$ and

(b) $\tau_{1/2}(LSI)$ vs. the additive concentration.

(Dobrowolski and Schnabel, unpublished results).

increased and approached a limiting value upon the addition of 2-naphthol or phenol.
The change of $\tau_{1/2}$(LSI) is paralleled by an increase of the intrinsic viscosity $[\eta]$. In Fig.
16(a) the difference $[\eta]_A^{-1} - [\eta]_0^{-1}$ as measured for a homo-PVP sample is plotted vs. the
concentration of the additive. This difference is frequently used to measure the extent of
preferential solvation (sometimes defined as coefficient of preferential solvation (25).The
negative sign of the difference $[\eta]_A^{-1} - [\eta]_0^{-1}$ indicates that the additive is preferentially ad-
sorbed by the polymer.

The results can be understood on the basis of preferential solvation as depicted schemati-
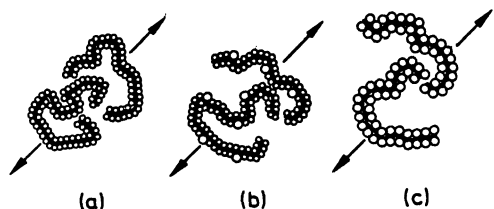cally by Fig. 17.

(a)   (b)   (c)

Fig.17. Schematic depiction of the influence of
preferential solvation on the separation of frag-
ments.
(a) Totally solvated by small molecules,
(b) partially solvated by bulky molecules,
(c) totally solvated by bulky molecules.

In pure chloroform the macromolecules are solvated by chloroform molecules. As the se-
cond component is added successively more and more solvating $CHCl_3$ molecules are re-
placed by bulky molecules of the additive. Thus, the mobility of the macromolecules is de-
creased, i.e. the time of fragment separation increases. The fact that $\tau_{1/2}$(LSI) approaches
a limiting value confirms this assumption.

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