On the Disentanglement of Coiled Macromolecules in Solution. Influence of Solvent Quality

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ABSTRACT: Poly(phenyl vinyl ketone) was irradiated in solutions of mixtures of dioxane and 1-propanol with 25-ns flashes of 347.1-nm light at various incident intensities. The rate of fragment separation following the very rapid rupture of chemical bonds in the main chain was measured. For this purpose, the decrease of the intensity of light scattered by the polymer solution (LSI) was monitored as a function of time after the flash at a scattering angle of 90°. It was found that the half-lifetime $\tau_{1/2}$(LSI) is independent of the number of scissions per initial macromolecule Z_s if the fragment size exceeds a critical value (DP)$_{\text{crit}}$, 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)$_{\text{crit}}$ was shifted to lower values: 2×10^3 (100 and 50% dioxane), 150 (47% dioxane), and 60 (45% dioxane). The results are explained by the concept of intramolecular contact pair formation. As the solvent quality is worsened, the number of contact pairs is increased. Therefore, the motions of segments are impeded as indicated by a diminution of the rate of disentanglement.

During recent studies[1,2] of the kinetics of disentanglement diffusion of linear flexible macromolecules, it became obvious that a distinct behavior exists between relatively long and short chains. Evidence could be obtained for the fact that there is a critical chain length above which intramolecular interaction between segments significantly influences the disentanglement diffusion and below which such an interaction becomes negligible as the chain length decreases.

These conclusions were arrived at during the following investigations: Poly(phenyl vinyl ketone) (PPVK) was irradiated in dioxane solutions with 25-ns flashes of 347.1-nm light at various incident intensities. The rate of fragment separation following the very rapid (<100 ns) rupture of chemical bonds in the main chains was measured. For this purpose, the decrease of the intensity of light scattered by the polymer solution was monitored as a function of time after the flash at various scattering angles.

Dioxane is a "good solvent" for PPVK at room temperature (second virial coefficient $A_2 = (2.5 \pm 0.25) \times 10^{-4}$ mol cm^3 g^{-2} for $\bar{M}_w = 5.9 \times 10^5$).[12] Therefore, the coils are expanded appreciably. Furthermore, at rather low polymer concentrations the average distance between individual macromolecules is large, and intermolecular interactions are negligible.

This paper describes experiments which have been carried out in order to investigate the influence of solvent quality on disentanglement diffusion. For this purpose, again PPVK was irradiated with UV flashes in solutions of mixtures of dioxane and 1-propanol and the rate of fragment separation was measured as a function of the number of scissions per initial macromolecule (Z_s).

General Considerations

In principle, disentanglement processes as studied in the present work and entanglement processes might be treated as analogous cases. Entanglement (or interpenetration) of coiled macromolecules plays an important role during diffusion-controlled polymer–polymer reactions, e.g., the combination of macroradicals during the termination of free-radical polymerization. Upon investigating the influence of coil density, it was found that the rate constant of the combination of lateral macroradicals decreased with increasing coil density.[3] On the other hand, it was assumed by several authors[4–6] that the rate constant of diffusion-controlled polymer–polymer reactions should decrease upon an improvement of the solvent quality. Such an effect was expected to occur as a consequence of the thermodynamic excluded volume effect. In other words, as the solvent quality is improved, the interpenetration of coils should become more difficult due to the increasing repulsive potential. Recently Horie and Mita[7] delivered an interesting contribution concerning this problem. The phosphorescence quenching of poly(styrylbenzil) by poly(styrylanthracene) was investigated. A significant chain length effect on the diffusion-controlled quenching rate constant was discovered.

As the solvent quality was improved, the rate constant decreased for DP < 10^3 (DP is the degree of polymerization). At DP > 10^3, the inverse behavior was found: the rate constant increased as the solvent quality became better. Those authors,[7] therefore, concluded that for polystyrene at DP < 10^3 the influence of the thermodynamic (equilibrium) excluded volume effect is prevailing while at DP > 10^3 the solvent dependence of diffusion-controlled rate constants is determined by the kinetic (nonequilibrium) excluded volume effect. The latter effect is described by those authors[7] as a "topological hindrance" imposed on the interpenetrating coils by themselves during the approach of the reactive sites. Indications for an analogous phenomenon becoming important during the disentanglement of macromolecules were obtained in our laboratory recently.[1,2] The existence of a critical chain length was evidenced above which intramolecular interactions determine the rate of disentanglement and below which these interactions become negligible. This finding can be explained in general terms as follows:

The motions of fragments generated by very rapidly occurring main chain ruptures are rather free if the initial coils are highly expanded, unless the molecular weight is rather high. In the latter case, segmental motions might occasionally be hindered which results in a diminution of the rate of fragment separation.

As the solvent quality is becoming worse, the coil expansion is reduced, i.e., the segment density is increased. Thus, the hindrance of segmental motions becomes more pronounced, an effect which certainly should depend

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significantly on the chain length.

The influence of solvent quality might be elucidated more clearly by applying the concept of contact pair formation to the case of disentanglement diffusion.

For a given polymer/solvent system, the probability w_{CP} for contact pair formation is determined by a thermodynamic interaction parameter and is considered as being a physical constant under definite conditions (temperature, pressure, etc.).

w_{CP} is defined as the probability that a single base unit of a chain approaches another base unit of the same chain so closely that physical interaction (dipole–dipole, van der Waals, etc.) becomes possible. A simple model might be based on the assumption that w_{CP} is independent of the degree of polymerization. The number of contact pairs per macromolecule is then given by

$$n_{CP} = \tfrac{1}{2} w_{CP} (\mathrm{DP})^2 \qquad (1)$$

An influence of contact pairs on disentanglement diffusion is expected only if DP exceeds a critical chain length $(\mathrm{DP})_{crit}$, i.e., if n_{CP} is significantly greater than unity. In other words, if the fragment chain length is rather small ($(\mathrm{DP}) < (\mathrm{DP})_{crit}$), the separation of fragments is not influenced by intramolecular interaction. w_{CP} is increasing if the solvent quality is becoming worse. Therefore, it follows that $(\mathrm{DP})_{crit}$ should become smaller if the solvent quality becomes worse.

The dependence of n_{CP} on DP and solvent quality has been dealt with recently by other authors who were considering the number of knots a polymer coil forms. Vologodski et al.[8] estimated from random walk computer experiments that the number of knots is rather high if the excluded volume equals zero and that in a "good solvent" only a few knots are formed per macromolecule. Brochard and de Gennes[9] derived from scaling laws that at Θ conditions

$$n_{CP} \propto (\mathrm{DP})^{0.5} \qquad (2)$$

and for a good solvent ($T \gg \Theta$)

$$n_{CP} \propto \ln(\mathrm{DP}) \qquad (3)$$

From eq 2 and 3, it follows that by increasing DP from 10^2 to 10^4 n_{CP} increases by a factor of 2 in a good solvent whereas the respective factor is 10 for a Θ solvent. At constant DP, n_{CP} should be significantly higher in a Θ solvent than in a good solvent.

To conclude, it is expected that in our case disentanglement diffusion should be strongly influenced by the solvent quality. The critical fragment size above which disentanglement diffusion is determined by intramolecular interaction should be shifted to lower values upon a diminution of the solvent quality.

Experimental Section

(a) Apparatus. Dilute solutions of poly(phenyl vinyl ketone) (PPVK) were irradiated in the presence of air in rectangular quartz cells with 25-ns flashes of 347.1-nm light from a ruby laser (Korad Model K1QS2) with the aid of a frequency doubler. An argon-ion laser was used as the analytical light source (λ 514 nm, Spectra Physics Model 165-00). The photomultiplier signal was fed into a 7A22 plug-in (Tektronix) and displayed on a 7633 storage oscilloscope (Tektronix). The change of the light scattering intensity was monitored at a scattering angle of $\vartheta = 90°$. Further details have been described.[11]

(b) Materials. The PPVK sample used was identical with one of the samples used during the previous work[2] ($\bar{M}_w = 5.9 \times 10^5$, $\bar{M}_n = 3.7 \times 10^5$), obtained by γ irradiation of bulk phenyl vinyl ketone at room temperature.[11] Dioxane and 1-propanol (p.a., Merck) were carefully dried and fractionally distilled via a splitting tube column (Fischer, Bonn).

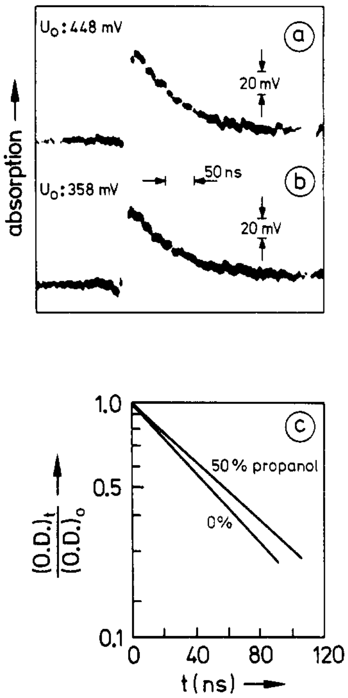


Figure 1. Decay of the precursor for main chain scission. Change of the optical density at 420 nm and [PPVK] = 5×10^{-3} base mol/L. Oscilloscope traces: (a) 100% dioxane, (b) dioxane/1-propanol 50/50 (v/v); and (c) first-order plots of the decay.

(c) Evaluation of Data. Half-lifetimes of the decrease of the light scattering intensity $\tau_{1/2}(\mathrm{LSI}) = 0.69/k$ were obtained from first-order plots according to[11]

$$\ln\left(\frac{(U_\infty - U_L)^{-1} - (U_t - U_L)^{-1}}{(U_\infty - U_L)^{-1} - (U_0 - U_L)^{-1}}\right) = -kt \qquad (4)$$

U denotes the signal voltage. The subscripts 0, t, and ∞ designate the state of the system before the flash, at time t, and a long time after the flash. U_L is the signal voltage measured in the case of the pure solvent.

Results

(a) Cloud-Point Determinations. In a solvent–nonsolvent system, changes of the molecular dimensions of dissolved macromolecules are expected to become most significant at solvent compositions rather close to the critical point. Typical results demonstrating this behavior have been reported by Kunst[10] (system: poly(isobutene)/n-heptane/1-propanol). Therefore, it appeared to be advisable to study polymer solutions in solvent mixtures corresponding to compositions in the neighborhood of the demixing point. The latter was determined by measuring the turbidity of PPVK solutions (5×10^{-3} base mol/L) in mixtures of dioxane and 1-propanol with a SOFICA light scattering instrument. The precipitation point was found at 23 °C as pertaining to 57 vol % 1-propanol.

(b) Flash Photolysis Experiments. (1) Triplet Lifetime Determinations. The experiments described in the following sections are devoted to the measurement of the rate of disentanglement diffusion in various mixtures of dioxane and 1-propanol. A prerequisite for the application of photochemical main chain degradation as a means of generating a nonequilibrium distribution of macromolecules under comparable conditions is, of course, the inertness of the solvent components toward the main chain scission process.

In order to check this, precursor lifetimes were measured by monitoring the transient absorption after the flash.

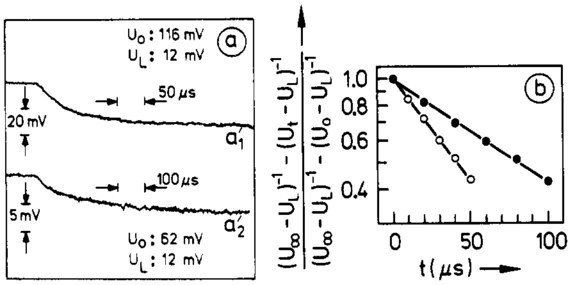


Figure 2. Decrease of the light scattering intensity at $\theta = 90°$ after a 25-ns flash. PPVK (5×10^{-3} base mol/L; $\bar{M}_{w,0} = 5.9 \times 10^5$) in dioxane/1-propanol mixtures: (a) typical oscilloscope traces; (a$_1$) 50 vol % 1-propanol; (a$_2$) 55 vol % 1-propanol; (b) first-order plots according to eq 4; (○) corresponding to trace a$_1$; (●) corresponding to trace a$_2$.

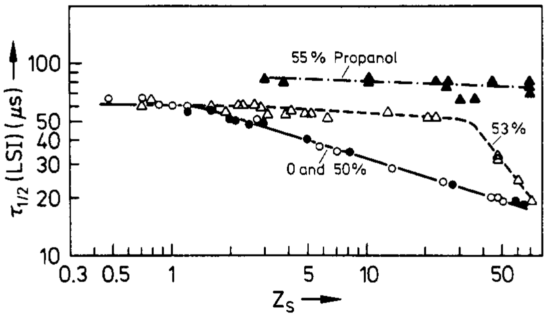


Figure 3. The half-lifetime of the decrease of the light scattering intensity at $\theta = 90°$ vs. the number of scissions per initial macromolecule. PPVK (5×10^{-3} base mol/L, $\bar{M}_{w,0} = 5.9 \times 10^5$) in dioxane/1-propanol mixtures of the following propanol contents: (○) 0%, (●) 50%, (△) 53%, and (▲) 55%.

Figure 1a,b shows typical oscilloscope traces, and Figure 1c shows the respective first-order plots of the decay of the transient absorption. The transient absorption is considered being due to triplet excited base units (T–T absorption). As can be seen from Figure 1, the rate of decay of the transient absorption is the same within the error limit for pure dioxane and a 1:1 mixture of dioxane and 1-propanol. Numerous additional experiments yielded that the lifetime of the precursor is independent of the solvent composition up to the demixing point. Therefore, it is concluded that main chain rupture is not influenced by the composition of the solvent in the present case.

(c) Disentanglement Diffusion Measurements. Figure 2a shows typical oscilloscope traces demonstrating the decrease of the light scattering intensity after the photolysis flash. Plots according to eq 4 are shown in Figure 2b. From these and other similar plots, half-lifetimes $\tau_{1/2}$(LSI) of the light scattering intensity decrease were obtained.

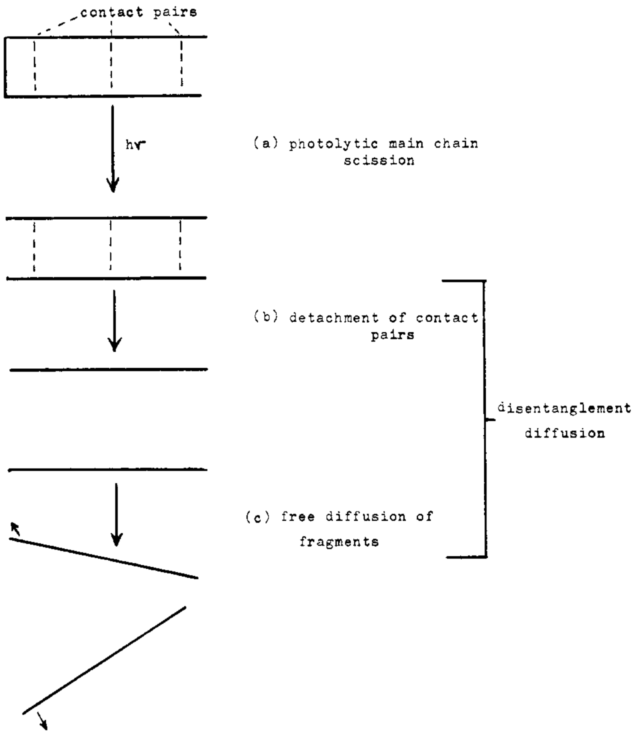
As the absorbed dose per flash is increased, the number Z_s of main chain scissions per initial macromolecule is also increased according to

$$Z_s = \frac{D_{abs}\phi(S)}{c_{polymer}}\left(\frac{\text{scissions}}{\text{molecule flash}}\right) \qquad (5)$$

D_{abs} is the absorbed dose per flash (einstein/L); ϕ(S) is the quantum yield of main chain scission (0.3); and $c_{polymer}$ is the polymer concentration (mol/L).

An increase of Z_s corresponds to an increase of the average number of fragments generated per initial macromolecule during a single flash. As a consequence, the average chain length of the fragments is decreasing with increasing Z_s. Figure 3 shows $\tau_{1/2}$(LSI) as a function of Z_s.

Scheme I
Schematic Depiction of Disentanglement Diffusion of a Coiled Macromolecule after Photolytic Bond Rupture in the Main Chain



Identical results were found for 100% dioxane and a dioxane/1-propanol mixture containing 50% 1-propanol. Here $\tau_{1/2}$(LSI) is almost independent of Z_s up to $Z_s \approx 2$. At higher values of Z_s, $\tau_{1/2}$(LSI) is steadily decreasing. At a 1-propanol content of 53%, $\tau_{1/2}$(LSI) is almost constant up to about $Z_s \approx 20$ and is decreasing above. The critical Z_s value is shifted to higher values, i.e., to lower values of the average fragment length. Figure 3 shows, furthermore, that at a 1-propanol content of 55% the half-lifetime is only slightly changed with increasing Z_s. Actually, the critical range was not reached up to the highest values of the absorbed doses per flash. The 1-propanol content of this solvent mixture corresponds to a state very close to the demixing point. Therefore, it is assumed that the macromolecules are tightly coiled in this case.

Discussion

The results obtained with the high molecular weight sample clearly demonstrate the strong influence of solvent quality on disentanglement diffusion. It was found that at solvent compositions in the neighborhood of the demixing point (a) the fragment separation is strongly retarded and (b) the critical fragment size below which intramolecular interaction is not impeding anymore the disentanglement diffusion is shifted to significantly shorter chain length. The critical chain length amounts to about DP $\approx 2 \times 10^3$ in dioxane and mixtures of dioxane and 1-propanol containing up to about 50 vol % alcohol. At a 1-propanol content of 53%, $(\text{DP})_{crit}$ is about 150, and at a 1-propanol content of 55%, $(\text{DP})_{crit}$ is smaller than 60.

These results can be explained by the concept of contact pair formation described in the introduction section. As the solvent quality is strongly worsened, the number of contact pairs is increased. Therefore, the segment motion is impeded which results in a diminution of the rate of disentanglement.

An interesting phenomenon is, of course, the fact that $\tau_{1/2}$(LSI) is almost independent of Z_s for $Z_s < Z_s$(crit). For the understanding of this effect, it has to be considered that the process under consideration is composed of a series of consecutive steps, as shown in Scheme I. After scissions of chemical bonds in the main chains have been accomplished (step (a)), disentanglement diffusion follows (steps (b) and (c)). If the fragments of the ruptured macromolecule are tight together by contact pairs, the latter must detach (step (b)) before the fragments can move freely (step (c)). It is inferred from our results that the rate of contact pair detachment (step (b)) is slower than the rate of the successive step (c). Thus, 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 Figure 3. 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 Figure 3).

In conclusion, it might be pointed out that the concept of contact pair formation proves useful in order to understand phenomena referring to the influence of solvent quality on disentanglement diffusion.

The experimental technique applied during this work provides, on the other hand, a powerful tool for the detection of intramolecular contact pairs in macromolecules.

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Molecular Motion of Polymer Main Chains in the Solid State as Studied by Photoisomerization

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ABSTRACT: Molecular motion of polymer main chains in the solid state was investigated in an amorphous, single-phase polyurethane matrix, which has small concentrations of azobenzene residues as molecular probes built into the polymer main chain. Photochemical trans → cis isomerization of the azobenzene residue, which involves 2–3 kcal/mol of energy barrier, is found to proceed with equal ease in the rubbery state as in dilute solution, while below T_g the rate is somewhat slowed down. The relative quantum yield in the rubbery state is only 30% lower than that in the dilute solution, while at temperatures 20 °C below T_g, the quantum yield is lowered by a factor of 3. These results exclude a crankshaft motion in the rubbery state, but the hindered rotation in the glassy state may experience some additional restraints, although these restraints are not sufficient to suggest a doubling of the activation energy as would be required in a crackshaft motion. Composition of the photostationary states indicates that in the solid state a portion of the trans isomer is unable to isomerize to the cis form, probably due to the unfavorable environment. The extent of this difficulty increases with decreasing temperature of the solid matrix.

Local motions of polymer main chains in the solid state are extremely important because of their relation to many observable bulk properties such as toughness. Such motions have been studied in the solid state by a variety of techniques, such as dielectric dispersion,[1-3] NMR relaxation[1,4-6] including more recently ^{13}C NMR, fluorescence depolarization,[7-9] sound absorption,[10,11] and ESR of spin-labeled polymers.[12] More recently, excimer fluorescence,[13-16] which occurs due to the emission from a sandwich complex of an excited molecule with a second molecule in the ground state, has been utilized as a sensitive technique for studying hindered rotations with low activation energies.

UV and visible spectroscopy have also been utilized for the study of the hindered rotation, which is usually the mechanism for local motions in polymer chains. The spectroscopic method, by which rotation around a well-defined bond is followed kinetically, provides an additional advantage because one can follow precisely the progress of the isomerization process so as to obtain a dispersion of the rate constants rather than an average relaxation time. The azoaromatic group is such an example. It has been well known that the energy difference between the ground states of the trans and cis isomer is about 10 kcal/mol.[17] The stable trans form of an azoaromatic group may be photoisomerized to the cis form, reaching a photostationary state, and the reverse cis → trans isomerization occurs in the dark. In earlier work of Paik and Morawetz[18] and in more recent work by Eisenbach,[19] this technique was utilized in order to follow a hindered ro-

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