been given to those factors which exert an important influence on the degree of miscibility achieved: (i) the method of mixing used, (ii) the effects of tacticity, molecular weight, and polydispersity on polymer–polymer miscibility, and (iii) the difference in solubilization power of PVC for PMMA and PMMA for PVC, at least for the homopolymers selected thus far.

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On the Dynamics of Photostimulated Conformational Changes of Polystyrene with Pendant Azobenzene Groups in Solution

Masahiro Irie[‡] and Wolfram Schnabel*[†]

Hahn-Meitner-Institut für Kernforschung Berlin, Bereich Strahlenchemie, D-1000 Berlin 39, Federal Republic of Germany, and Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan. *Received April 23, 1984*

ABSTRACT: Copolymers of polystyrene and 4-(methacryloylamino)azobenzene containing between 2.2 to 6.5 mol % of the latter were irradiated with 15-ns flashes of 347-nm light in cyclohexane solution at 25 °C. It is inferred from optical absorption measurements that the trans → cis isomerization of pendant azo groups occurred during the flash, i.e., with $k \geq 10^8$ s^{-1}. Time-resolved light scattering intensity (LSI) measurement in the microsecond time range yielded evidence for polymer chain contraction (indicated by an increase of the LSI) with a rate constant of 10^3–10^4 s^{-1} as a consequence of the isomerization. At a later stage (several hundred milliseconds after the flash), another very strong light scattering intensity increase was observed, reflecting polymer aggregation and precipitation. The mechanism of conformational change and precipitation was discussed in terms of alterations of the balance of polymer–solvent and polymer–polymer interactions as a consequence of isomerization.

Introduction

Laser flash photolysis in conjunction with the light scattering (LS) detection method is an appropriate tool for investigating the dynamics of macromolecules in solution. Some years ago, the dynamics of disentanglement diffusion were studied by measuring the rate of the change of the light scattering intensity (LSI) after very fast main-chain scission. In this case, the diminution of the average molecular weight gave rise to a decrease of the LSI after irradiation of the polymer solution with a 20-ns flash.[1]

Flash photolysis in conjunction with the LS detection method is also applicable to measure the rate of confor-

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[†] Hahn-Meitner-Institut für Kernforschung Berlin.
[‡] Osaka University.

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mational changes of macromolecules at constant chain length. As can be seen from the Debye equation (1)[2]

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} + \frac{16\pi^2\langle s^2\rangle}{3\lambda_0^2 M_w}\sin^2(\theta/2) + 2A_2 \qquad (1)$$

the light scattering intensity R_θ (Rayleigh ratio) is correlated to the weight-average molecular weight M_w, the mean square radius of gyration $\langle s^2\rangle$, and the second virial coefficient A_2. Here, $K = (2\pi^2 n_0^2/N_A\lambda_0^4)(dn/dc)^2$, c is the polymer concentration, n_0 is the refractive index of the solvent, dn/dc is the specific refractive index increment, λ_0 is the wavelength of the incident light, and N_A is Avogadro's number.

Expansion of the polymer chain leads to an increase in $\langle s^2\rangle$, which causes a decrease of the LSI, whereas upon shrinkage of the chain, which leads to a decrease of $\langle s^2\rangle$, the LSI increases. Advantage was taken of this behavior by measuring the rate of the photostimulated conformational change of polyamides with backbone azobenzene groups.[3]

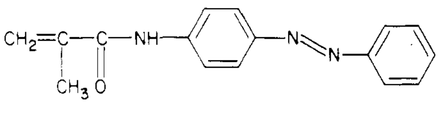
The purpose of the present work was to study the dynamics of the photostimulated conformational change of polystyrene with pendant azobenzene groups. It has been shown previously by Irie and Tanaka[4] that this polymer precipitated in cyclohexane solution at temperatures above the critical miscibility temperature upon irradiation by ultraviolet light. Resolubilization was achieved by irradiation with visible light. Obviously, the insolubilization is correlated to the trans → cis isomerization of the pendant azobenzene groups, as is, vice versa, the resolubilization correlated to the cis → trans isomerization.

The dynamics of conformational changes can be appropriately studied with a system undergoing conformational changes as a consequence of photoisomerizations such as trans → cis isomerizations of azobenzene, because the latter reaction proceeds very fast under the influence of UV light. In the case of polymers possessing backbone azo groups, a rate constant of about 10^8 s^{-1} was estimated for the trans → cis isomerization.[3] It might be pointed out that aromatic azo compounds, in contrast to aliphatic azo compounds, are rather stable with respect to photochemical decomposition.[5] The quantum yield for decomposition of azobenzene is estimated to be less than 10^{-3}.

In the following, results concerning the dynamics of the contraction of the polymer chains and the subsequent precipitation are reported. The rates of these processes were expected to be reflected by the rates of change in the light scattering intensity of the polymer solution after irradiation by a flash of ultraviolet light.

Experimental Section

A. Materials. Polystyrene samples with pendant azobenzene groups were synthesized by free radical copolymerization of styrene and 4-(methacryloylamino)azobenzene in benzene solution at 60



°C using AIBN as initiator. The polymers possessed unimodal molecular weight distributions ($M_w/M_n = 1.5 \pm 0.1$) as was seen from gel permeation chromatograms (Toyo-Soda H-801). Weight-average molecular weights were estimated from the chromatograms on the basis of a calibration curve obtained with polystyrene. The composition of the copolymers was determined by elemental analysis. The copolymers used in this work are listed in Table I.

Cyclohexane, methylene chloride, and benzene (Uvasol, E. Merck) were used without further purification. Decahydronaphthalene (E. Merck) was distilled under reduced pressure. The polymer solutions were passed four times through a 0.2-μm Millipore filter prior to light scattering measurements.

Table I
Characterization of Polymers

sample	mol % of azobenzene groups	$M_w \times 10^{-4}$ [a]
PS-A-2.2	2.2	3.1
PS-A-4.3	4.3	2.7
PS-A-5.6	5.6	2.0
PS-A-6.5	6.5	1.8

[a] Estimated from GPC using a calibration curve for polystyrene.

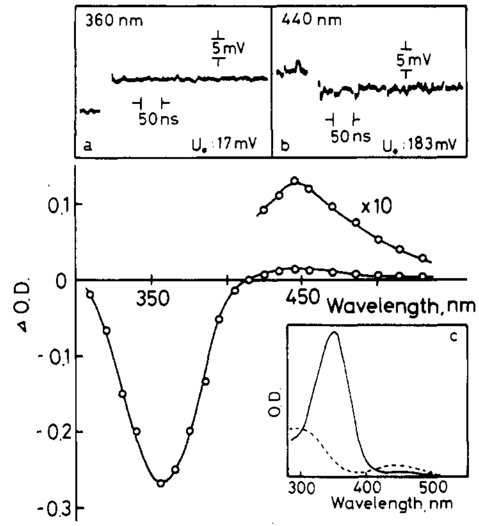


Figure 1. Difference spectra recorded 100 ns after irradiation of a solution of copolymer PS-A-4.3 in cyclohexane solution with a 15-ns flash of 347-nm light. Inserts a and b: oscilloscope traces depicting the change of the optical density at 360 nm (a) and at 440 nm (b). Insert c: optical absorption spectra of the polymer with *trans*-azobenzene groups before (—) and after (---) irradiation with ultraviolet light (410 > λ > 350 nm).

B. Irradiations. The copolymers were irradiated in dilute solutions with single 15-ns flashes of 347-nm light, which were produced by a ruby laser (J. K. Lasers Ltd.) in conjunction with a frequency doubler. The concentration of the copolymer solutions was adjusted to OD = 0.7–0.9 at λ = 347 nm. For light scattering measurements an argon ion laser (Spectra-Physics Model 165) was used as the analytical light source. Details were described before.[1a,6]

Results and Discussion

A. Optical Absorption Measurements on the Trans → Cis Isomerization. Figure 1 shows the difference optical absorption spectrum observed with the copolymer PS-A-4.3 in cyclohexane solution. This spectrum was recorded 100 ns after irradiation of the solution by a 15-ns flash of 347-nm light. As can been seen from the oscilloscope traces in the inserts a and b in Figure 1, the change of the optical absorption occurs during the flash, i.e., with a rate constant greater than 10^8 s^{-1}. The change of the absorption is ascribed to trans → cis isomerizations of azo groups. The absorption spectra of the two isomers differ appreciably, as is shown in the insert c. The trans form has an absorption maximum at 353 nm due to a π–π* transition, whereas the cis form absorbs relatively weakly in this wavelength range. An absorption maximum due to an n–π* transition of the cis form is located at 440 nm.

It was inferred from the very fast trans → cis isomerization of pendant azo groups that neighboring phenyl groups did not impede the isomerization; i.e., phenyl groups do not interact strongly with *trans*-azobenzene groups. Concerning the spectral changes described above it should be pointed out that quite similar results were

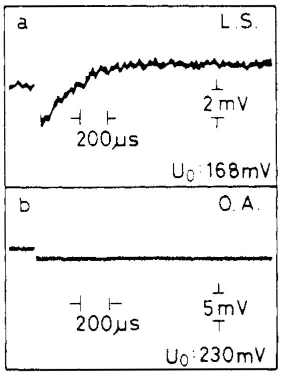


Figure 2. Oscillograms illustrating the increase of the LSI (a) and of the optical absorption (b), both at 514 nm, after irradiation of copolymer PS-A-4.3 in cyclohexane solution (0.13 g/L) with a 15-ns flash of 347-nm light at 25 °C.

Table II
Conformational Relaxation of Polystyrene with Pendant Azobenzene Groups

sample	$M_w \times 10^{-4}$	$\tau_{1/2}$,[a] s
PS-A-2.2	3.1	
PS-A-4.3	2.7	2.1×10^{-4}
PS-A-5.6	2.0	4.0×10^{-4}
PS-A-6.5	1.8	8.5×10^{-4}

[a] Half-lives of the increase of the light scattering intensity at 514 nm and 25 °C.

obtained with all copolymers, including PS-A-2.2, the sample with the lowest content of azobenzene groups.

With respect to the results described below, which are connected with coil contraction and precipitation of the copolymers, it is important to note that the shape of the spectra of *cis*-azobenzene was independent of the content of the azobenzene groups, and no detectable change of the spectra after the flash was observed. This finding suggests that there is no specific interaction between cis azo groups.

B. Light Scattering Measurements on Conformational Changes. With all copolymers except PS-A-2.2, an increase of the LSI after the flash with half-lives of several hundred microseconds was observed. A typical oscillogram demonstrating the LSI change is shown in Figure 2, trace a. It can be seen that the LSI decreased initially. This decrease is due to the concurrent increase of the optical absorption at 514 nm (see oscillogram b) and of the decrease of dn/dc as a consequence of trans → cis isomerization. The refractive index increment was measured with copolymer PS-A-2.2 in cyclohexane solution at 28 °C and 546 nm: dn/dc = 0.125 mL/g before and dn/dc = 0.100 mL/g after trans → cis isomerization.[11]

The relatively slow increase of the LSI is considered to reflect the conformational change involving a decrease of both the radius of gyration of the coils and the second virial coefficient.[8,10] The half-lives of the LSI increase for the various copolymers are compiled in Table II. The fact that no increase of the LSI after the laser flash was observed with copolymer PS-A-2.2 is consistent with the result obtained by stationary irradiations that precipitation did not occur when the content of azobenzene units was less than 3 mol %.[4]

At first glance it appears surprising that a small photochemical effect such as the isomerization of only a few azobenzene groups per chain can induce significant conformational changes in the macromolecules. It can be shown, however, that the balance of polymer–solvent and polymer–polymer interactions can be severely perturbed by trans → cis isomerization of pendant azo groups. It was pointed out in the former paper[4] that the dipole moment increases from 0.5 to 3.1 D upon trans → cis isomerization of the azo groups. It is feasible, therefore, that *cis*-azobenzene groups are more prone to interact with styrene base units than *trans*-azobenzene groups because of dipole-induced interactions. The phenomena observed with the copolymers dissolved in cyclohexane can be, then, interpreted as follows: *trans*-azobenzene groups interact more favorably with solvent molecules than with styrene base units, whereas the reverse situation is true for *cis*-azobenzene groups, which interact less strongly with solvent molecules than with styrene base units. The enhanced capability of *cis*-azobenzene groups of interacting with other segments of the chain is considered to give rise to a shrinkage of the polymer chain in the initial stage after the trans → cis isomerization, i.e., at a time when this interaction is purely intramolecular (in very dilute solution). When different macromolecules collide at a later stage, intermolecular interaction will also become operative. As a consequence, the polymer chains will aggregate and precipitation will be observed (see section C). These processes are schematically illustrated in Figure 3. This model is substantiated by the fact that the increase of the LSI after the flash was not inhibited by low molecular weight azobenzene compounds that were added to the polymer solution. The idea that interaction between cis-azo groups causes coil contraction can be therefore discarded.

Experiments carried out with PS-A-4.3 at three *different polymer concentrations* (0.11, 0.076, and 0.055 g/L) yielded the same half-life of the LSI change. This result is clear evidence that the process observed in the range of several hundred microseconds is an intramolecular reaction.

In connection with coil contraction observed in this work it appears interesting to draw attention to the fact that upon temperature alteration polymers in solution quite generally undergo conformational changes. With polystyrene ($M_w = 2.6 \times 10^7$) it was found,[7] e.g., that the radius of gyration dropped from about 260 to 40 nm when the temperature was lowered from 50 to 25 °C. This phenomenon is interpreted in terms of the predominance of polymer–polymer interactions (segment–segment contacts) over polymer–solvent interactions developing with decreasing temperature.[8,9]

Experiments with solutions of copolymer PS-A-4.3 in *different solvents* yielded results that are in accordance with the model developed above. With decahydronaphthalene solutions similar effects were observed as with cyclohexane solutions. With benzene and methylene chloride solutions, on the other hand, no slow change of the LSI (in the microsecond range) was observed, although the trans → cis isomerization proceeded to the same extent and at the same rate as in cyclohexane solution and caused a very rapid decrease of the LSI during the flash. This result correlates very well with the findings that photostimulated precipitation occurred in cyclohexane and decahydronaphthalene but not in benzene and methylene chloride solutions.[4] Actually, these results were expected because benzene and methylene chloride are envisaged to interact with polar *cis*-azobenzene groups. Therefore, this kind of interaction will predominate over the interaction of styrene base units with *cis*-azobenzene groups in this case. On the other hand, decahydronaphthalene cannot be polarized and will not interfere with the interaction between styrene base units and cis-azo groups.

Figure 4 shows oscillograms demonstrating a more rapid contraction of the chains at a higher temperature: $\tau_{1/2} = 4 \times 10^{-4}$ s at 25 °C and $\tau_{1/2} = 3 \times 10^{-4}$ s at 35 °C. Since

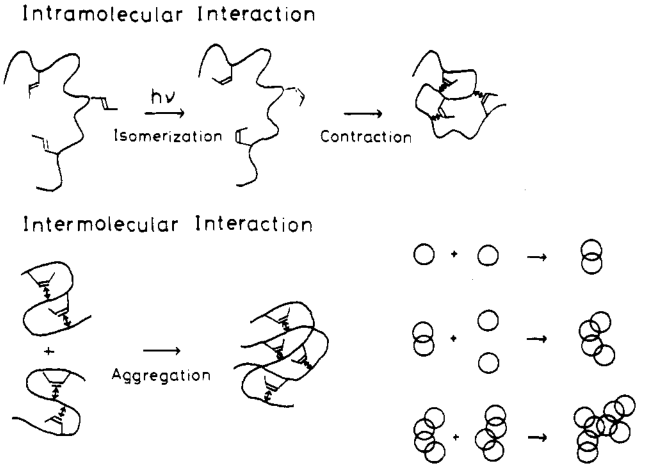


Figure 3. Schematic illustration of chain contraction and precipitation of polystyrene with pendant azobenzene groups.

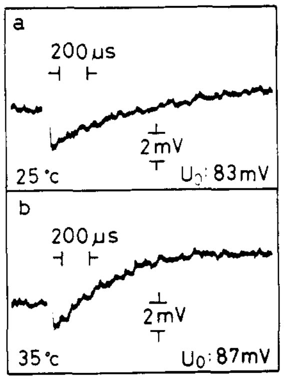


Figure 4. Oscillograms depicting the increase of the LSI after irradiation of copolymer PS-A-5.6 in cyclohexane solution (0.12 g/L) with a 15-ns flash of 347-nm light at 25 (a) and 35 °C (b).

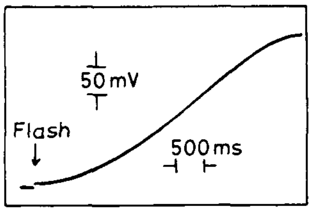


Figure 5. Growth of precipitating particles. Increase of the LSI at 514 nm after irradiation of copolymer PS-A-4.3 in cyclohexane solution (0.21 g/L) with a 15-ns flash of 347-nm and light.

coil contraction depends on the mobility of both the segments and the solvent molecules, it is expected to occur faster at higher temperature.

C. Light Scattering Measurements on Polymer Precipitation. The LSI increase in the 100-μs range observed with the copolymer solution in cyclohexane was followed by another very strong increase several hundred milliseconds later. A typical oscillogram is presented in Figure 5. It shows that the LSI increase is sigmoidal as is expected for the aggregation of particles initiated by a nucleation process. The mechanism is illustrated schematically in Figure 3. After the contraction of single macromolecules, multimerization will occur upon collision of contracted macromolecules. Because contact pair formation is governed by a dynamic equilibrium, intramolecular contacts can be exchanged against intermolecular contacts. During a collision the continuation of these processes yields larger, growing aggregates which finally precipitate.

This mechanism was supported by measuring the rate of LSI increase at various polymer concentrations. The results are shown in Figure 6, where it is seen that upon increasing the polymer concentration, both the rate and the extent of the LSI increase were augmented. This is clear evidence for the fact that the strong LSI increase reflects polymer precipitation.

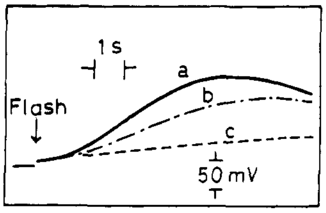


Figure 6. Growth of precipitating particles at different polymer concentrations in cyclohexane: (a) 0.21, (b) 0.14, and (c) 0.085 g/L.

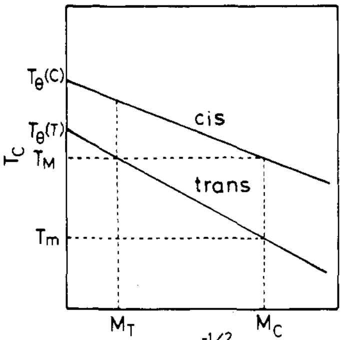


Figure 7. Thermodynamic model of precipitation. Plot of the critical miscibility temperature as a function of the reciprocal square root of the molecular weight. Upper line: all azobenzene groups in cis configuration; lower line: all azobenzene groups in trans configuration.

Principally the photostimulated precipitation of the copolymers can be interpreted in terms of the critical miscibility temperature T_c. In the case of polystyrene dissolved in cyclohexane, T_c is the temperature below which the polymer precipitates. According to Fox and Flory,[9] T_c depends on the molecular weight M as described by

$$T_c = T_\theta(1 - b/M^{1/2}) \qquad (2)$$

where T_θ is the value of T_c at $M = \infty$ and b is an empirical constant. It is assumed that T_θ and b are subject to changes upon conversion of *trans*-azobenzene groups contained in the copolymers to *cis*-azobenzene groups. This is schematically illustrated in Figure 7, where T_c is plotted as a function of $M^{-1/2}$. With all azo groups in the trans configuration, all macromolecules of $M < M_T$ are soluble in cyclohexane at T_M, but after photoisomerization the macromolecules of $M_c < M < M_T$ are insoluble; i.e., they precipitate from the solution. Actually, irradiation results here in the same effect as lowering the temperature of the polymer solution from T_M to T_m.

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(11) Due to the low content of azobenzene groups, copolymer PS-A-2.2 did not precipitate after irradiation.

Polydispersity and Conformation of Diluted Branched Molecules Prepared by Cross-Linking of Polystyrene Solutions

François Schosseler and Ludwik Leibler*

Centre de Recherches sur les Macromolécules, CNRS, 67083 Strasbourg Cedex, France.

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ABSTRACT: Polystyrene chains in semidilute solutions have been cross-linked through the action of ^{60}C γ-rays. The reaction has been stopped at different stages before the gel point, and the sol phase has been diluted in a good solvent. Light scattering measurements have been analyzed in terms of theories of sol–gel transition and conformation of randomly branched molecules. The measured dependence of the average molecular weight and the average radius of gyration on the irradiation time suggests that the critical exponent τ characterizing the polydispersity of the pregel phase is smaller than the mean field prediction $\tau = {}^5/_2$.

I. Introduction

The gelation of polymer melts through the action of cross-linking agents (vulcanization) or of high-energy radiation is of substantial industrial importance and has been studied experimentally for many years. A statistical theory of such a gelation process was proposed by Flory[1] and Stockmayer[2] some 40 years ago. de Gennes[3] has shown recently that despite the fact that the Flory–Stockmayer theory neglects the effects of cyclizations and steric hindrances it should give an adequate description of a vulcanization process in a melt of long polymer chains. Hence, the theory is able to predict the distribution of the molecular weight of chains in a sol phase, its evolution as a function of the reaction time, and the gelation threshold.

Less is known about the formation of gels through the cross-linking of precursor polymer chains in a solution. The properties of the gelation transition depend both on the molecular weight of precursor chains and on their concentration. In a relatively dilute solution and/or for short chains cyclizations and steric hindrances should play an important role in the critical region near the gel point.[4] Daoud[4] argues that the gelation transition is then analogous to the connectivity transition in the percolation model and is described by the percolation critical exponents. Such an asymptotic behavior in the vicinity of the gelation threshold would be very different from that predicted by the Flory–Stockmayer theory.[5]

The irradiation with γ-rays offers a particularly convenient method of cross-linking the polymer chains in a solution. The cross-linking action of high-energy radiation has been demonstrated for a large number of polymers (e.g., poly(vinyl alcohol)[6], polystyrene[7], and poly(vinyl chloride)[8]) and solvents.[9] In this paper we present new experimental results concerning the gelation of polystyrene solutions in cyclopentane induced by ^{60}Co γ-rays.[10] We study the solutions with concentration close to the overlap concentration c^* for which it may be expected that the critical region is fairly large and that it is possible to make a distinction between the classical and the percolation-type behavior.

The sol–gel transition can be studied by in situ or dilution experiments. In an in situ experiment one studies one particular sample during the gelation process without affecting the reaction bath. Typical examples are the measurements of the viscoelastic properties of the sol or gel phase with the use of a magnetic sphere rheometer[11,12] or of the quasi-elastic light scattering.[13] The principal obstacle in using in situ observation lies in a difficulty of characterizing the polymer molecules in a concentrated solution by standard physicochemical methods. This difficulty does not exist in dilution experiments in which the reaction is stopped at some stage and the system is then diluted. However, the dilution experiments have one major drawback; they require a preparation of many absolutely identical samples in which reaction proceeds under strictly identical conditions. In usual chemical systems this is not really possible and for instance, the fluctuations of a few percent in the gel point for identically prepared samples are not unusual. Such fluctuations do not allow one to determine precisely the distance from the gel point for each particular sample, and it is difficult to determine the critical exponents near the gelation threshold. This problem may be overcome by measuring simultaneously two different types of averages (moments) of the distribution of the molecular weight of polymer molecules in the sol phase. It is possible then to test the validity of different theories without knowing exactly the advancement of the reaction with respect to the gel point for each particular sample.[14]

In the present work we have characterized the diluted sol phase by elastic light scattering. We measured the weight-average molecular weight $M_w(t)$ and the z-average radius of gyration $\langle R_g^2(t)\rangle_z$ of polymer molecules as a function of the irradiation time t for two different molecular weights of precursor chains. An analysis of the variation of the radius of gyration as a function of the average molecular weight gives information about the distribution of the molecular weight of molecules in a pregel phase and the validity of different theories of the gelation process.

II. Experimental Section

We used two different anionically prepared polystyrenes as linear precursors: one of molecular weight 55 000 and polydispersity 1.2 and the other with $M_w = 205\,000$ and $M_w/M_n = 1.07$.

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