On the Kinetics of Polymer Degradation in Solution. 8. Laser Flash Photolysis of Polystyrene

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ABSTRACT: Polystyrene (PSt) was degraded in $CHCl_3$ solution at room temperature by flash photolysis (λ 265 nm) in the presence of oxygen. In the absence of oxygen no degradation was observed. In *p*-dioxane solution polystyrene was not degraded, neither in the presence nor in the absence of O_2. The degradation was detected by time-resolved light-scattering measurements. Precursors of the oxidized species leading to main-chain scission in $CHCl_3$ are macroradicals. Two mechanisms for the formation of macroradicals are assumed: (i) Solvent radicals attack PSt molecules by hydrogen abstraction. The generation of solvent radicals is sensitized by energy transfer from the polymer to the solvent. (ii) Excited PSt molecules form exciplexes with $CHCl_3$, which dissociate into radicals or ions. Measurements of the time dependence of the decrease of the light scattering intensity (LSI) after the flash led to the following conclusions: At low O_2 concentration the observed lifetime τ(LSI) is due to the lifetime of lateral macroradicals P·. The composite rate constant of decay of P· radicals in the absence of oxygen is $2.4 \times 10^2\ s^{-1}$. From the dependence of τ(LSI) on $[O_2]$ it was estimated that $k_{O_2+P\cdot} = (5 \pm 1) \times 10^5\ M^{-1}\ s^{-1}$. At high oxygen concentrations ($[O_2] > 1 \times 10^{-3}$ M) the major portion of the LSI decay corresponds to the decay of the species formed by the reaction P· + O_2, which decays with a rate constant $k = 380\ s^{-1}$.

Polystyrene (PSt) was reported[1] to undergo main-chain scission upon irradiation with 253.7-nm light in oxygen-containing solutions. The highest quantum yields for main-chain rupture were found for PSt solutions in chlorine-containing solvents such as $CHCl_3$ and CCl_4. No evidence was obtained in that work[1] for main-chain scission in the absence of oxygen. Therefore, this polymer was considered appropriate for investigating the kinetics of photooxidative main-chain cleavage using the light-scattering detection method in combination with flash photolysis at λ 265 nm.

The previous paper in this series was devoted to the main-chain degradation of poly-α-methylstyrene (PαMS).[2] In $CHCl_3$ solution PαMS degraded due to an indirect effect. Lateral macroradicals generated by the attack of macromolecules by solvent radicals (presumably chlorine atoms) decomposed via main-chain rupture. Most of the attacking solvent radicals were thought to be formed via energy transfer from the solvent. Oxygen exerted a pronounced inhibition effect on main-chain rupture: It was found to react with lateral macroradicals (rate constant: 5.5×10^5 L/mol s) which otherwise decomposed by main-chain cleavage with a rate constant of $3.5 \times 10^2\ s^{-1}$.

Experimental Section

(a) Materials. Chloroform (Merck, spectroscopy grade) was washed ten times with water, dried over $CaCl_2$, and distilled under argon via a splitting tube column immediately prior to use. *p*-Dioxane (Merck, spectroscopy grade) was also distilled via a splitting tube column. The polystyrene samples used are listed in Table I. They were standard samples with very narrow molecular weight distribution and were used without further purification.

(b) Flash Photolysis Experiments. Quartz cells containing the polymer solutions were irradiated with flashes of 265-nm light from a neodymium glass laser (Korad K-2). The flash duration was 20 ns. The 1060-nm light was twice frequency doubled by means of a KD*P crystal and a ADP crystal in a temperature stabilized oven (45 ± 0.1 °C). The output of the second frequency doubler was typically 0.5 to 1.0 mJ and was monitored by a calibrated photodiode with digital readout.

The analyzing light (λ 514.5 nm) for the light-scattering measurements was provided by an argon–ion laser (Spectra Physics, Model 165-00). Details have been reported in part 1 of this series.[3]

For the evaluation of data the formerly derived[3] eq I and II were used. Equation I describes the dependence of the change of LSI on the degree of degradation α (number of scissions per base unit)

$$\frac{U_\infty - U_L}{U_0 - U_\infty} = \frac{4BcmP_\theta}{\alpha} + \frac{2}{\alpha n_0} \qquad \text{(I)}$$

The designation of the parameters is the same as in part 1: U_0 and U_∞ denote the signal voltages corresponding to the light-scattering intensity before and a long time after the flash, U_L is the signal voltage pertaining to the LSI of the solvent, B is the second virial coefficient, c is the polymer concentration, m is the molecular weight of the base unit, P_θ is the scattering factor, and n_0 is the weight average degree of polymerization before irradiation.

Equation II describes the time dependence of the LSI according to a first-order process:

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

U_t denotes the signal voltage at time t after the flash. The rate constant k is equal to the reciprocal lifetime of the LSI decay.

(c) Preparation of Samples. In order to carry out irradiations in the absence of oxygen polymer solutions were either bubbled with argon containing 1 ppm oxygen or treated by several freeze–pump–thaw cycles on a vacuum line. In order to establish well-defined O_2 concentrations, samples were bubbled with argon–oxygen mixtures which were obtained by combining the two gases in a mixing device with an "endOmess" instrument (Friedrichsfeld) in front of the exit for continuous O_2 analysis. O_2 concentrations in $CHCl_3$ solutions were calculated on the basis of 9.2×10^{-3} M O_2 being equivalent to a pressure of 1 atm at 16 °C.[9]

(d) Actinometry. The number of photons absorbed by the solution was determined with the potassium ferrioxalate actinometer[7,8] ($\phi[Fe^{2+}] = 1.25$). Under normal laser operations the incident intensity varied between 1.0 and 1.5×10^{15} photons per flash. The extinction coefficients of the substances used are at λ 265 nm: 210 $M^{-1}\ cm^{-1}$ (PSt), $8.1 \times 10^{-4}\ M^{-1}\ cm^{-1}$ ($CHCl_3$), and $1.25 \times 10^{-2}\ M^{-1}\ cm^{-1}$ (*p*-dioxane). Under typical reaction conditions with $[PSt] = 9 \times 10^{-4}$ base mol/L about 0.3 to 0.5×10^{15} photons per flash were absorbed in a volume of about 0.28 cm^3 (diameter of neodymium laser beam: 0.6 cm) which surrounded the scattering volume of about 0.02 cm^3 (diameter of argon ion laser beam: 0.16 cm). During all experiments the major portion of the light was absorbed by the polymer. In the case of a $CHCl_3$ solution containing 9×10^{-4} base mol/L about 30% of the incident light was absorbed by the PSt and only 3% by the solvent.

Results

(a) Influence of Oxygen. With oxygen-free chloroform solutions of PSt no change of the light-scattering intensity (LSI) after the flash indicating main-chain scission or cross-linking could be observed. Upon the addition of O_2, however, main-chain scission could be detected. Figure 1 shows typical oscilloscope traces demonstrating the time dependence of LSI after the flash. A pronounced decrease of LSI in the MS range becomes obvious in the case of the oxygen containing solution.

According to eq I the ratio $(U_0 - U_\infty)/(U_\infty - U_L)$ is a measure for the degree of degradation α. Figure 2 shows that this ratio is increasing steadily with increasing O_2 concentration and is approaching a limiting value.

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Table I
Polystyrene Samples Used During This Work

Sample	Origin	Mol wt	Degree of polymerization n_0
A	Knauer/Berlin	2×10^6	1.92×10^4
B	Mann Research Lab., New York, N.Y.	8.6×10^5	8.3×10^3
C	Mann Research Lab., New York, N.Y.	4.98×10^5	4.8×10^3
D	Mann Research Lab., New York, N.Y.	4.11×10^5	3.95×10^3
E	Mann Research Lab., New York, N.Y.	1.6×10^5	1.54×10^3

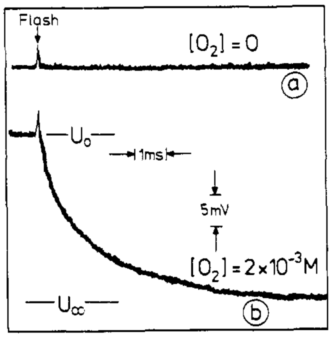


Figure 1. Oscilloscope traces demonstrating the time dependence of the light-scattering intensity ($\theta = 90°$) after a 20 ns flash of 265 nm light at room temperature. Sample A in $CHCl_3$ (9.3×10^{-4} base mol/L) in the absence of O_2 (a) and at $[O_2] = 2 \times 10^{-3}$ M (b). Dose absorbed by the solution per flash: 3.2×10^{-6} einstein/L.

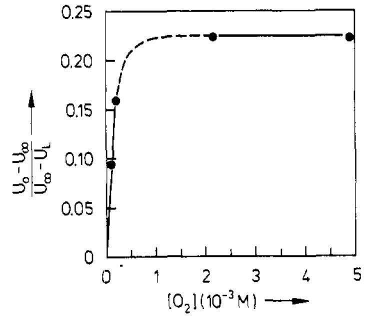


Figure 2. The extent of light-scattering intensity decrease as a function of oxygen concentration. Sample A in $CHCl_3$ (9.3×10^{-4} base mol/L) at room temperature. Dose absorbed by the solution per flash: 3.2×10^{-6} einstein/L.

In Figure 3a plots according to eq II obtained with solutions of different oxygen concentrations are shown. It is seen that the rate of LSI decay becomes greater as the oxygen concentration is increased. At higher O_2 concentrations the plots become curved indicating that the LSI decay is correlated to at least two different mechanisms. The lifetime of the longer living mode of LSI decay decreases with increasing O_2 concentration but becomes constant at $[O_2] > 1 \times 10^{-3}$ M, as is shown in Figure 3b.

From the relatively long lifetimes of the LSI decay (τ(LSI)) it can be inferred that chemical processes determine the rate of LSI decay. Diffusion processes are expected to proceed with lifetimes smaller by one or two orders of magnitude.[4-6] The fact that at low oxygen concentrations ($<10^{-3}$ M) τ(LSI) is becoming shorter with increasing O_2 concentration is considered as evidence for τ(LSI) as corresponding to the lifetime of the precursor of the oxidized product which decays via main-chain rupture.

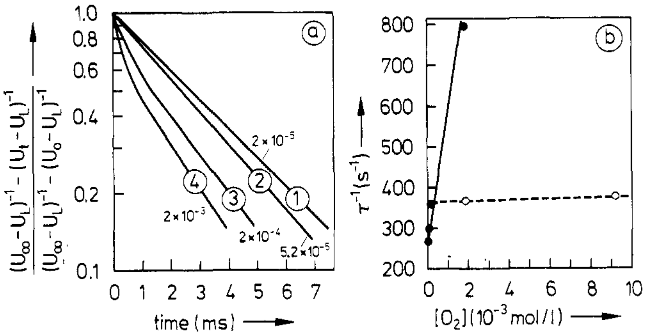


Figure 3. Time dependence of the decrease of the light-scattering intensity. Sample A in $CHCl_3$. Polymer concentration: 9.3×10^{-4} base mol/L; dose absorbed by the solution per flash: 3.2×10^{-6} einstein/L. (a) First-order plots according to eq II for various oxygen concentrations (indicated at the curves in mol/L). (b) Reciprocal lifetime of LSI decay as a function of oxygen concentration: (○) long-lived component; (●) short-lived component.

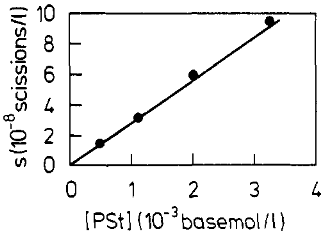


Figure 4. Number of main-chain scissions per liter vs. the polymer concentration at constant incident intensity of 2.7×10^{-9} einstein/flash. $[O_2]$: 1.8×10^{-3} M.

(b) Influence of Polymer Concentration and Molecular Weight. At constant incident intensity of the 265-nm light the yield of main-chain scissions S increased almost linearly with polymer concentration up to about 3×10^{-3} base mol/L when PSt was irradiated in $CHCl_3$ solution. Typical results are shown in Figure 4. This behavior would be expected, if main-chain scissions were due to a direct effect (i.e., due to photons absorbed by the polymer). In this case eq III should hold. With

$$S = \phi(S)D \tag{III}$$

and

$$D = \frac{I_0(1 - e^{-c'd\epsilon})10^3}{V} \tag{IV}$$

eq V is obtained:

$$S = \frac{\phi(S)I_0(1 - e^{-c'd\epsilon})10^3}{V} \tag{V}$$

which converts to eq VI if $c'd\epsilon \ll 1$:

$$S = \frac{\phi(S)I_0c'd\epsilon 10^3}{V} \tag{VI}$$

S = number of scissions/l flash; $\phi(S)$ = quantum yield of main-chain scission; I_0 = incident intensity (photons/flash); D = absorbed dose (photons/l flash); V = irradiated volume (mL); c' = polymer concentration (base mol/L); d = optical path length (cm); and ϵ = extinction coefficient (L/mol cm).

If an indirect effect would prevail (photons absorbed by the solvent create reactive species which attack the polymer and generate main-chain scissions) S should be independent of the polymer concentration except at very low values of the latter. The conclusion arrived at so far seems, however, fictitious since PSt was not degraded at all in CH_2Cl_2 and p-di-

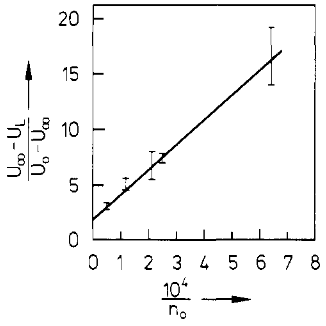


Figure 5. Influence of the initial molecular weight on the extent of main-chain degradation. $(U_\infty - U_L)/(U_0 - U_\infty)$ vs. the reciprocal degree of polymerization. [PSt]: 1.2×10^{-3} base mol/L. $[O_2]$: 2.1×10^{-3} M. Dose absorbed by the solution per flash: 3.9×10^{-6} einstein/L.

oxane solution, neither in the presence nor in the absence of O_2. If the scission process would be due to a direct effect, degradation would also be expected to occur in these solvents, since it is not feasible that they should impede main-chain scission (e.g., by acting as a quencher for excited PSt molecules or as a radical scavenger for macroradicals). Thus, it is assumed that PSt transfers excitation energy to chloroform which subsequently decomposes, thus forming radicals which attack the polymer and cause its degradation. Alternatively, the results demonstrated in Figure 4 could indicate that charge-transfer interactions between PSt and $CHCl_3$ are involved in the generation of a species, which reacts with O_2 thus forming a product which decomposes by main-chain scission (see Discussion).

Values of the quantum yield $\phi(S)$ were obtained from the results shown in Figure 4 or from experiments with PSt samples of different average molecular weight. The values agreed within the error limit. Figure 5 shows a plot of $(U_\infty - U_L)/(U_0 - U_\infty)$ vs. the reciprocal degree of polymerization n_0. From the slope of the straight line $\phi(S)$ was estimated as being equal to 0.4 if only the energy absorbed by the chloroform was accounted for. Based on the energy absorbed by the polymer $\phi(S)_p \approx 0.03$ is obtained. Subject to the inaccuracy of our method for quantum yield determinations, the latter value is considered to agree fairly well with $\phi(S)_p = 0.044$ reported by Price and Fox.[1]

Discussion

The results suggest that the main-chain degradation of PSt in chloroform solution is caused by solvent radicals $R_s\cdot$ attacking the macromolecules P. The reactive solvent molecules are essentially formed by energy transfer from the polymer to the solvent.

As indicated by the low quantum yield $\phi(S)_P \approx 0.03$ (based on the energy absorbed directly by the polymer) this energy transfer is, if it occurs, not very effective.

From the fact that main-chain cleavage is only observed when oxygen is present in the solution, it is inferred that the intermediate causing main-chain cleavage is an oxidized species which is formed by the reaction of lateral macroradicals with O_2.

The sequence of elementary reactions leading to main-chain scission and competing processes are depicted in the following reaction scheme, where S denotes chloroform and P polystyrene:

$$P + h\nu \rightarrow P^* \qquad (a_1)$$

$$S + h\nu \rightarrow S^* \qquad (a_2)$$

$$P^* + S \rightarrow P + S^* \qquad (b)$$

$$S^* \rightarrow 2R_s\cdot \qquad (c)$$

$$R_s\cdot + P \rightarrow R_sH + P\cdot \qquad (d)$$

$$R_s\cdot + O_2 \rightarrow X\cdot \qquad (e)$$

$$X\cdot + P \rightarrow XH + P\cdot \qquad (f)$$

$$P\cdot + O_2 \rightarrow PO_2\cdot \qquad (g)$$

$$PO_2\cdot \rightarrow P_{ox}\cdot \qquad (h)$$

$$PO_2\cdot \rightarrow P_1 + P_2\cdot \qquad (i)$$

$$P_{ox}\cdot \rightarrow P_1 + P_2\cdot \qquad (j)$$

$$P\cdot + P\cdot \rightarrow \text{products} \qquad (k)$$

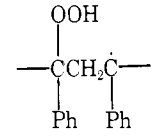
$$P\cdot + R_s\cdot \rightarrow \text{products} \qquad (l)$$

$$P\cdot + S \rightarrow P + R_s\cdot \qquad (m)$$

$$P\cdot + P \rightarrow P + P\cdot \qquad (n)$$

Radicals P· formed by reaction (d) or (f) do not decompose by main-chain scission (no degradation was observed in the absence of oxygen). They undergo nondegradative processes as depicted by reactions (k) to (n).

So far the oxidized species undergoing main-chain cleavage has not yet been identified. Possibly the radical $PO_2\cdot$ undergoes a rearrangement before a scission in the main chain is accomplished. Such a rearrangement could result in the formation of the radical designated as $P_{ox}\cdot$ in the reaction scheme. $P_{ox}\cdot$ could be the radical

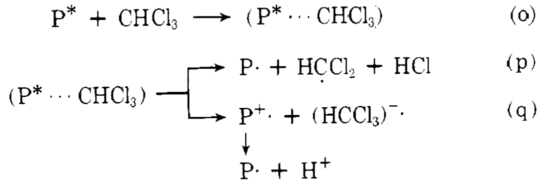


$$-\overset{OOH}{\underset{Ph}{C}}CH_2\overset{\cdot}{\underset{Ph}{C}}-$$

formed by intramolecular hydrogen abstraction.

Concerning the observed rates of LSI decay the results are interpreted as follows: at low oxygen concentration only one mode of LSI decay is observed (see Figure 3a straight lines (1) and (2)). In the series of consecutive reactions leading to main-chain rupture the slowest (i.e., the rate-determining) step is correlated to the observed rate of LSI decay. Since the lifetime τ(LSI) decreased with increasing O_2 concentration only reactions (e) and (g) have to be considered. Reaction (e) can be excluded from consideration for the following reasons: (i) Lifetimes about 10^3 faster than those found would be expected (about 10^{-6} s based on the rate constant $k(O_2 + \cdot Cl) \approx 10^9$ L/mol s). (ii) The decrease of the lifetime with increasing $[O_2]$ would not be related to the increase of the degree of degradation since chlorine atoms should be at least as reactive toward hydrocarbon for H-atom abstraction as the radicals X formed during reaction (e).

An alternative mechanism involving charge-transfer interactions between excited PSt and chloroform appears also feasible for the formation of macroradicals:



$$P^* + CHCl_3 \longrightarrow (P^* \cdots CHCl_3) \qquad (o)$$

$$(P^* \cdots CHCl_3) \longrightarrow P\cdot + H\dot{C}Cl_2 + HCl \qquad (p)$$

$$(P^* \cdots CHCl_3) \longrightarrow P^{+\cdot} + (HCCl_3)^{-\cdot} \qquad (q)$$

$$P^{+\cdot} \longrightarrow P\cdot + H^+$$

Contrary to the other mechanism, in this case reactions of O_2 with solvent radicals are not expected to interfere with the formation of $PO_2\cdot$.

If we assume that at low O_2 concentrations the LSI decay is correlated to reaction (g) the respective rate constant can be determined. By plotting $(\tau(\text{LSI}))^{-1}$ vs. $[O_2]$ according to eq VII (see Figure 3b)

$$(\tau(\mathrm{LSI}))^{-1} = \tau_0^{-1} + k_g[O_2] \qquad \text{(VII)}$$

$k_g = (5 \pm 1)\ 10^5$ L/mol s was found, which compares with $(5.5 \pm 0.5)\ 10^5$ L/mol s for the reaction of lateral poly(α-methylstyryl) radicals with O_2[2]. By extrapolation of τ^{-1} for $[O_2] \rightarrow 0$ the lifetime τ_0 of macroradicals in the absence of oxygen was found as ca. 4×10^{-3} s.

At oxygen concentrations greater than about 1×10^{-3} mol/L practically all macroradicals have reacted with O_2, as is inferred from the fact that the degree of degradation becomes independent of $[O_2]$ (see Figure 2). The plots demonstrating the decay of the LSI become curved at higher oxygen concentrations (see Figure 3). A possible explanation is that as the oxygen concentration increases the rate of the reaction $P\cdot + O_2$ becomes faster. Therefore, the cleavage reaction becomes rate determining for the LSI decay at relatively high oxygen concentrations. In other words, at $[O_2] \approx 10^{-5}$ mol/L $v_g = k_g[O_2][P\cdot] < v_i = k_i[PO_2\cdot]$ and at $[O_2] \approx 10^{-3}$ mol/L $v_g > v_i$. This conclusion is supported by the fact that an increase of $[O_2]$ by a factor of 100 results in an increase of the degree of degradation by a factor of only 5. That means, as the absorbed dose is kept constant, the initial concentration of $PO_2\cdot$ undergoes only a little change. Thus, the increase of O_2 causes a transition from $v_g < v_i$ to $v_g > v_i$. The curves 3 and 4 in Figure 3 could then be interpreted by correlating the slowly decaying mode of the LSI decay to the decomposition of $PO_2\cdot$ or $P_{ox}\cdot$, as depicted by reactions (i) and (j), respectively. The respective rate constant is 380 s^{-1}. This conclusion is affirmed by the fact that the lifetime of the slowly decaying mode is approaching a limiting value with increasing $[O_2]$, i.e., for a given dose the concentration of the oxidized species leading to main-chain scission has reached its maximum value, when all radicals $P\cdot$ generated by that dose have reacted according to reaction (g). The relatively small portion of LSI decaying rapidly at high $[O_2]$ is thought to be due to reaction (g) which is solely responsible for the LSI decay observable at low $[O_2]$, as is shown in Figure 3b. The straight line correlated to reaction (g) passes the transition range to the $[O_2]$ range where reaction (i) is becoming rate determining.

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Kinetics of the Helix-Coil Transition of Polypeptides

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ABSTRACT: The mean relaxation time of the peptide units in the helix-coil transition of a polypeptide was calculated by means of an extension of Glauber's dynamical theory of the one-dimensional Ising model. The critical slowing down is found near the transition midpoint for all units and is strong for the middle units of the chain. The mean relaxation time of the unit is dependent on the position of the unit in the chain. NMR spectra were simulated by use of the calculated mean relaxation times of the units. From comparison of the simulated NMR spectra with experiment, it is shown that the appearance of separate peaks of α-CH in the NMR spectra is due to the polydispersity in molecular weight of the polypeptide sample.

Recently kinetics of the helix-coil transition of polypeptides has been studied both experimentally and theoretically. Unlike the situation for the equilibrium theory, the kinetics of the helix-coil transition is not well established. Previous theories[1,2] treat the initial rates of relaxation of the helical content by perturbation from equilibrium. The initial rate treatment has been widely and successfully used to interpret experimental data obtained by approach-to-equilibrium measurement, such as temperature jump,[3] ultrasonic absorption,[4] dielectric relaxation,[5] and yields relaxation times of the order of 10^{-5}–10^{-8} s associated with the kinetics of the transition. On the other hand, high resolution nuclear magnetic resonance spectroscopy has been used to study the helix-coil transition under equilibrium conditions.[6] The NMR observation of separate peaks of α-CH in the transition region, separated by chemical shift differences of the order of 10^2 Hz, implies the presence of lifetimes of about 10^{-2} s or greater.[7]

Though several workers[8-12] have investigated this contradiction in relaxation time, two theoretical models have been proposed to investigate this contradiction. Ullman,[9] Bradbury et al.,[10] and Nagayama and Wada[11] have explained the NMR peaks in terms of molecular weight polydispersity. On the other hand, Ferretti et al.[7,11] and Miller[12] have attributed this discrepancy to slow nucleation of helix units from random-coil polypeptide and concluded that the fast times by both experiments and theories are related to the time for adding to or melting one helix unit from an existing helical sequence and the slow time by NMR measurement is related to the formation of helix from random-coil polypeptide. The approach-to-equilibrium measurements investigates the relaxation of approach to new equilibrium of the helical content of the polypeptide chain when the system at equilibrium is perturbed. On the other hand, NMR measurement is concerned with more microscopic temporal states of individual peptide units under equilibrium conditions.

In this paper, we are concerned with the mean relaxation

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