monomer units for this purpose is an appealing and useful one as described earlier;[1-3] however, there may be even greater utility by selecting smaller subunits like CH_2, COO, etc., as done recently.[12] In its present form, the model represents a mean-field approach and does not include sequence order or steric placement of groups and, therefore, cannot account for the importance of spatially specific issues on mixture phase behavior.

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Kinetics of the Conformational Transition of Poly(methacrylic acid) after Changes of Its Degree of Ionization

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ABSTRACT: The kinetics of the conformational transition of poly(methacrylic acid) after a pH jump was followed in a stopped-flow apparatus by monitoring changes in the emission intensity of a dansyl label attached to the polymer chain. Part of the process was too fast to be followed, but the subsequent approach to equilibrium exhibited to a first approximation biphasic kinetics. The rate constants for chain expansion increased sharply with increasing pH. In the contraction of the chain, the final approach to equilibrium took place almost at a constant rate in the pH range 4.11–5.11. A drift in pH, monitored by the absorbance of methyl red, took place over a similar time as the change in the fluorescence of the dansyl label.

Introduction

Phenomena accompanying the ionization of poly(methacrylic acid) (PMA) have features suggesting cohesive forces that oppose the expansion of the chain molecule due to the repulsion between the ionized carboxyls. Katchalsky[2] was first to draw attention to the fact that the viscosity of PMA solutions remains almost constant before a critical degree of ionization, α, is reached; at this point the viscosity increases dramatically, indicating a sudden expansion of the chain molecule. Significantly, the pK of the carboxyl groups, which rises steeply with an increasing polymer charge in the initial stages of the ionization, enters a plateau region at the point at which the viscometric data indicate rapid chain expansion, as would be expected from the dispersion of the electrostatic charge over a much larger volume. Katchalsky believed that the resistance to the chain expansion was due to hydrogen bonding between carboxyl groups, but this interpretation ceased to be plausible when Arnold[3] showed that both the solution viscosity and the pK of poly(acrylic acid) (PAA) increase smoothly with an increasing α. Arnold wrote that the reason for the difference in behavior of the two poly(carboxylic acids) "remains obscure although it could be connected to the greater flexibility of the poly(acrylic acid) molecule".

Leyte and Mandel[4a] suggested that the behavior of PMA may be understood as reflecting an equilibrium between a contracted and an expanded form so that the plateau in the plot of pK against α is analogous to a phase transition. They formulated a procedure for deriving the free energy change for the transition between the two forms and Leyte[4b] concluded from such data that the cooperative chain length contains 30 monomer residues. Various arguments were advanced for and against hydrogen bonding as the origin of the resistance to chain expansion. Anufrieva et al.[5] found that addition of methanol to aqueous PMA solutions produces a smooth increase of viscosity with increasing α, so that the resistance to the chain expansion is eliminated. They concluded that this resistance observed in water solution must be due to hydrophobic bonding. Crescenzi et al.[6] studied the ionization of PMA and PAA by calorimetry and found that while the enthalpy of ionization was a smooth function of α for PAA, the plot for PMA exhibited a striking endothermic peak in the region in which viscosimetry and titration data indicated a rapid transition from a contracted to an expanded form. They noted that the dissociation of hydrophobic bonds would have been expected to be exothermic. Nevertheless, since the enthalpy of the transition from the contracted to the expanded form was found to have a positive tem-

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perature coefficient (a behavior characteristic of the breakup of hydrophobic bonds) hydrophobic bonding was still invoked as responsible for the stabilization of the contracted PMA form.[7] On the other hand, two arguments were advanced against this interpretation: The initial stage of the ionization of PMA in 40% aqueous methanol (a medium in which hydrophobic bonding should be absent) produced a rapid change in the UV absorption beyond that expected from carboxyl dissociation, but no similar effect was observed with PAA.[8] Also, in partialy esterified PMA the transition from the contracted to the expanded form occurred at the same charge density along the polymer chain as in unmodified PMA, although the ester groups should have enhanced hydrophobic bonding.[9]

Another feature of the PMA transition whose interpretation has not been clearly established concerns the cooperativity of the process. Most workers seem to accept the suggestion[5] that the conformational change is highly cooperative, analogous to the helix–coil transition of polypeptides, but Koenig et al.[10] interpreted their Raman spectra as indicating a multiplicity of structures, suggesting a progressive rather than cooperative change.

Although the equilibrium in the transition of PMA from the contracted to the expanded form has been investigated by a variety of techniques, no study of the kinetics of this process *in water solution* seems to have been published. A recent report by Irie and Schnabel[11] deals with the kinetics of the expansion of PMA in methanol, a medium in which the chain molecule expands smoothly with increasing charge density, so that no cooperative transition is involved. A cooperative transition in alternating maleic acid–styrene copolymers has been studied kinetically by Ohno et al.,[12] who took advantage of the difference in the extinction coefficient of phenyl residues when the polymer is in the contracted and the expanded state.

In the present study we used changes in the fluorescence intensity of dansyl-labeled PMA to monitor the rate of conformational transitions after a sudden change in the degree of ionization of the polymer. The dansyl group has been widely used as a "reporter" group, characterizing the extent of contact with water molecules. When this group is transferred from water to a less polar medium, the emission intensity increases sharply and the emission maximum shifts to shorter wavelengths. Dansyl-labeled polymers have been utilized[13,14] to follow the equilibrium in the conformational transitions of maleic acid copolymers with vinyl ethers from the contracted state, in which the dansyl label is shielded from water, to the expanded form. Similarly, the association of dansyl-labeled PAA with polymers acting as hydrogen bond acceptors leads to changes in the emission spectrum reflecting the displacement of water molecules in contact with the dansyl group, and this has been used for the study of both the association equilibrium and the kinetics of complex formation and dissociation[15,16]

Experimental Section

The dansyl-labeled PMA (Dan-PMA) used in this study was prepared as previously described.[13] It had $[\eta] = 44$ mL/g in methanol at 26 °C ($\bar{M}_n = 27000^{20}$). Spectroscopic analysis showed that it contained 0.9 mol % of monomer residues carrying the dansyl label. The labeled poly(acrylic acid) (Dan-PAA) had $[\eta] = 192$ mL/g at full neutralization in 0.5 M NaBr solution at 25 °C ($\bar{M}_n = 350000^{21}$); its dansyl label content was 1.8 mol %.

Static fluorescence measurements were carried out on a Perkin-Elmer spectrofluorimeter at 25 °C. Kinetic data of the change in fluorescence intensity of Dan-PMA after a pH jump were obtained by mixing in a stopped-flow apparatus ionized or unionized 5.6×10^{-3} N Dan-PMA solutions containing 0.4 M NaCl with an equal volume of buffer solutions with an ionic strength of 0.4. These experiments used first the same apparatus as in our previous study,[14] and this apparatus was also used in the experiments in which the drift of pH was followed by the spectral change of methyl red. The final data were obtained with a stopped-flow apparatus built by Kinetic Instruments Inc. of Ann Arbor, MI equipped with an Olis 3820 data acquisition instrument control and operating system supplied by On-Line Instrument Systems, Inc., Jefferson, GA. The emission was passed through a Corning Glass Cut Filter C-73 to eliminate scattered excitation radiation. In all experiments an excitation wavelength of 340 nm was employed. The results of at least five runs were averaged by the computer to minimize noise before the rate constants giving the best fit to the data were computed.

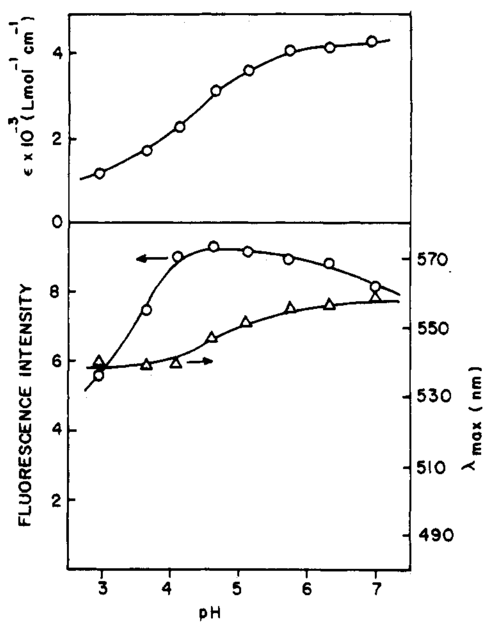

Figure 1. Spectroscopic changes of Dan-PAA (3.2×10^{-3} N) as a function of pH. Ionic strength 0.4.

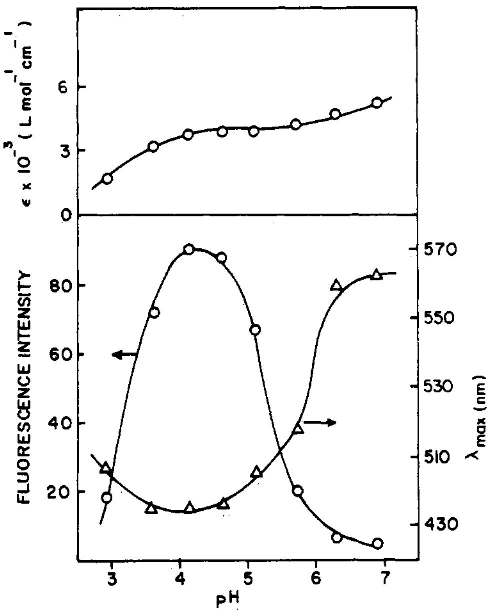

Figure 2. Spectroscopic changes of Dan-PMA (2.3×10^{-3} N) as a function of pH. Ionic strength 0.4.

Results

Equilibrium Measurements. Before studying the kinetics of conformational transitions by changes in the emission spectra of Dan-PMA, we found it instructive to compare the equilibrium behavior of the dansyl label in Dan-PAA and Dan-PMA as a function of pH. The results

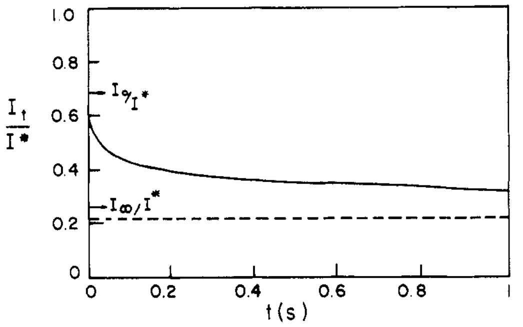

Figure 3. Changes of Dan-PMA fluorescence intensity after mixing with a buffer to a final pH 5.52 at 20 °C.

are shown in Figures 1 and 2. The ionization equilibrium of the free dansyl group is characterized by $pK_a \sim 4$,[11] and the increase in the absorbance of Dan-PAA with a rise in pH is the expected result of the gradual deprotonation of the label. In the case of Dan-PMA a plateau is observed between pH 4.5 and 5.5, the region in which the chain expands from the contracted to the expanded state, and at pH 6.9 the extinction coefficient is similar to that for Dan-PAA. The appearance of the plateau suggests that a less polar environment depresses the extinction coefficient of the label at 340 nm.

The differences between the emission characteristics of the dansyl label when attached to the two poly(carboxylic acids) is much more dramatic. For both Dan-PAA and Dan-PMA the emission intensity first increases with a rising pH and then decreases after reaching a maximum. However, the magnitude of these emission intensities is entirely different in the two polymers. Although the label concentration in the Dan-PAA solution was 2.8 times as high, the emission intensity at pH 3 was only a third of that observed in Dan-PMA solution. For Dan-PAA the emission intensity increased by a factor of 1.7 to a maximum at pH 4.6 and decreased slightly with a further increase of pH to pH 6.9. The emission intensity for Dan-PMA rose by a factor of 4.5 to a maximum at pH 4.2 and dropped precipitously by a factor of 18 on passing to pH 6.9. These differences reflect the tightly coiled state of Dan-PMA in acid solution and the drastic change in the environment of the label as the molecules change from the contracted to the expanded state. Changes in the location of the emission maximum can be interpreted with an even greater assurance, since previous work in this laboratory[17] has shown that the wavelength of the emission maximum, λ_{max}, is affected only to a negligible degree by the ionization of the dansyl label and is, therefore, a reliable indicator of the microenvironment of the dansyl group. The gradual rise of λ_{max} in Dan-PAA from 540 nm at pH 3 to 565 nm at pH 6.9 reflects, therefore, the slowly increasing exposure of the label to water; for Dan-PMA λ_{max} lies at pH 3 at the much lower value of 507 nm, *decreases* to a minimum of 495 nm at pH 4.2, and rises steeply to 562 nm at pH 6.9. This behavior suggests that PMA becomes even more compact in the initial stages of ionization—possibly due to hydrogen bonding between ionized and un-ionized carboxyls—before the tight coiling is disrupted by the mutual repulsion of the ionized groups.

Kinetics of Coil Expansion. A typical trace of the change in emission intensity after an unneutralized Dan-PMA solution is mixed with a buffer is shown in Figure 3, where the final pH was 5.52. On this plot the fluorescence intensity I_∞ observed when equilibrium was attained (after 90 s) is shown as a dashed line, I_t is the fluorescence intensity at time t, and I^* is the fluorescence observed after dilution of the Dan-PMA solution with an equal volume of 0.4 M NaCl (i.e., the fluorescence that would have been observed after mixing if the buffer had not increased the ionization of the polymeric acid).

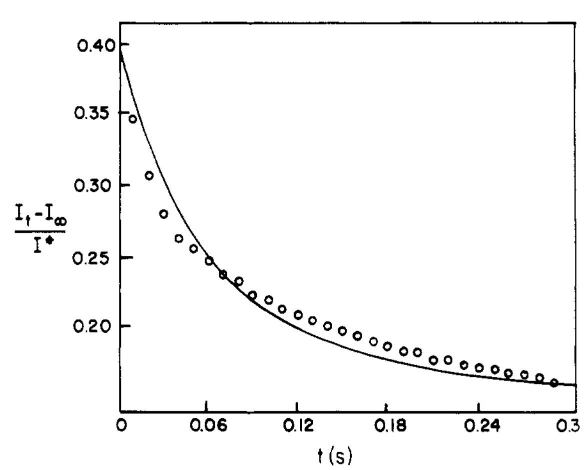

Figure 4. Comparison of computed curve with experimental points for the initial stage of experiment in Figure 3.

Table I
Kinetics of Fluorescence Change of Dan-PMA after Partial Ionization

final pH	temp, °C	$(I^* - I)/I^*$	f	k, s^{-1}	k', s^{-1}	q
4.95	25	0.19	0.70	7.9	0.26	0.74
5.52	15	0.77	0.60	18.2	0.60	0.47
5.53	20	0.80	0.56	19.9	0.71	0.51
5.52	25	0.77	0.60	21.6	0.98	0.52
5.52	30	0.79	0.44	29.8	1.27	0.51
5.52	35	0.80	0.51	32.6	1.50	0.53
5.91	25	0.91	0.38	68.8	2.22	0.73
6.83	15	0.91	0.16	367[a]	29.0	0.29
6.83	20	0.91	0.11	367[a]	32.5	0.23
6.83	25	0.91	0.11	400[a]	36.7	0.31
6.83	30	0.91	0.08	456[a]	39.3	0.72

[a] Because of the large relative change in f with a change of temperature, the temperature dependence of k is not interpretable for the final pH 6.83.

As can be sure, a good portion of the fluorescence change after the pH jump was too fast to be followed by our technique. In this particular case only about 60% of the fluorescence decay could be followed with the first reading, I_0, corresponding to $t \sim 1$ ms. The observable portion was fitted by the computer to eq 1:

$$(I_t - I_\infty)/(I_0 - I_\infty) = q \exp(-kt) + (1 - q) \exp(-k't) \qquad k > k' \quad (1)$$

It was found in this and all the other experiments reported that the final approach to equilibrium was well characterized by k', while the initial stage of the observable fluorescence change was only approximated by biphasic kinetics. This is illustrated in Figure 4, where the curve obtained by computer fitting of the data to eq 1 is compared with the experimental points.

Table I lists values of the fraction of the fluorescence change which could be followed kinetically, $f = (I_0 - I_\infty)/(I^* - I_\infty)$, and the kinetic parameters k, k', and q as a function of the final pH and the temperature. The following observations may be made:

Both k and k' increase sharply with an increase of the final pH. We assign less significance to k, since the initial stage of the observable process should probably be represented by a continuous distribution function of rate constants. On the other hand, k' characterizes the final approach to equilibrium and here the rate constant for the change in fluorescence intensity should be closely related to that describing chain expansion. The data illustrate the

Table II
Kinetics of Fluorescence Change after Partial Protonation of Fully Ionized Dan-PMA

final pH	temp, °C	$(I_\infty - I^*)/I_\infty$	f	k, s^{-1}	k', s^{-1}	q
4.11	15	0.80	0.48	4.60	0.20	0.54
4.11	25	0.80	0.43	10.8	0.53	0.66
4.11	30	0.80	0.38	19.1	0.96	0.56
4.11	35	0.80	0.35	33.2	1.63	0.50
4.65	25	0.80	0.30	26.8	0.67	0.51
5.11	25	0.80	0.20	58.3	0.88	0.66

increase in conformational mobility as the polymer chain expands, with k' 140 times larger at pH 6.83 than at pH 4.95. Yet, even with the most expanded chain, the k' values indicate a surprisingly slow approach to the conformational equilibrium. The q values listed in Table I show considerable scatter. Their value is highly sensitive to the point at which the kinetics first become observable by our technique, and we do not believe that they lend themselves to a reliable interpretation.

The temperature dependence of k' leads to $\Delta H^\ddagger$ = 33 kJ mol^{-1} and $\Delta S^\ddagger$ = −130 J K^{-1} mol^{-1} for a final pH 5.52 and to $\Delta H^\ddagger$ = −13 kJ mol^{-1} and $\Delta S^\ddagger$ = −171 J K^{-1} mol^{-1} for a final pH 6.83. The striking increase in the enthalpy of activation for the more contracted state of the polymer chain could be due to a number of causes, such as cohesion of the hydrophobic methyl groups, hydrogen bonding between ionized and un-ionized carboxyls, and chain entanglements. The large negative entropies of activation may be related to the structuring of water molecules in contact with the methyl groups and to electrostriction due to carboxylate charges.

Kinetics of the Transition from the Expanded to the Contracted State. The collapse of Dan-PMA from the fully ionized state (pH 11.3) to final pH values of 4.11, 4.65, and 5.11 could again be followed only for the part of the process that could be fitted by biphasic kinetics. A typical trace is shown in Figure 5, and the kinetic parameters for the various experimental conditions are listed in Table II. The data are striking in that they show that k is quite sensitive to the final pH, whereas k' remains almost constant. This seems to suggest that the final approach to equilibrium takes place in the contracted state over all of this pH range. The temperature dependence of k for a final pH 4.11 yields $\Delta H^\ddagger$ = 84 kJ mol^{-1} and $\Delta S^\ddagger$ = 63 J K^{-1} mol^{-1}, while data for k' lead to $\Delta H^\ddagger$ = 75 kJ mol^{-1} and $\Delta S^\ddagger$ = 79 J K^{-1} mol^{-1}. It would appear that the release of bound water, leading to a large increase of entropy, takes place during the part of the approach to conformational equilibrium which can be followed by our procedure. The high enthalpy of activation illustrates the difficulty with which conformational changes take place in the "supercontracted" state of PMA.

Kinetics of the Response of a pH Indicator after a pH Jump. Any change in the conformation of Dan-PMA would be expected to be accompanied by a change in the ionization equilibrium. Since the course of the conformational transitions could be followed in the stopped-flow apparatus by a change in the fluorescence intensity, there seemed to be a reasonable change that a corresponding change in pH could also be monitored. We carried out, therefore, a series of experiments in which unlabeled PMA was mixed with NaOH or buffer solutions in the presence of methyl red, following the change in the absorbance at 525 nm, the absorption maximum of the acid form of the indicator.

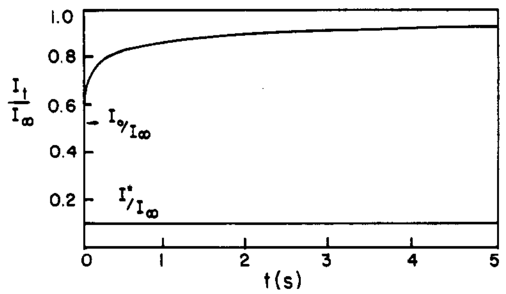

Figure 5. Changes of Dan-PMA fluorescence intensity after mixing the fully neutralized polymeric acid with a buffer to a final pH 4.11 at 15 °C.

Static measurements revealed that PMA reduces the absorbance of methyl red by about 20% in acid solution, suggesting that the indicator forms a complex with the polymer. This effect disappears at pH 4.5. However, if the indicator was in the PMA solution before it was mixed with base, its acid form would be stabilized as long as it is complexed with the polyanion, and a drift in the absorption after mixing could reflect both a drift in pH and a slow desorption of the indicator from the polymer. On the other hand, if the indicator was added only to the NaOH solution (or a buffer at a pH >4.5), this complication should be eliminated.

Table III lists the results obtained, where $A^* - A$ is the total change in the absorbance of the indicator due to the rise in pH (where A^* is the absorbance observed when the unneutralized PMA solution containing the indicator was diluted with an equal volume of 0.4 N NaOH) and ΔA is the part of this change that could be followed kinetically. When methyl red was added to both the PMA and the NaOH solutions before mixing, the decay in the absorbance was biphasic. When the indicator was added only to the NaOH solution, ΔA was much reduced and the absorbance followed simple exponential decay. This observation suggested that with the second procedure the complications due to effects resulting from indicator binding were eliminated, so that ΔA was due only to a drift of pH. This interpretation was confirmed by experiments in which a PMA solution was mixed with a pH buffer, so that the pH was fixed after mixing. In that case a finite ΔA was observed when the methyl red was added to both solutions, but ΔA = 0 when only the buffer had contained the indicator. The rate constant 0.14 s^{-1} observed for the change in the absorbance of methyl red when PMA was

Table III
Behavior of Methyl Red Indicator after Mixing of a PMA Solution with NaOH or a Buffer[a]

placement of methyl red	pH	α	$A^* - A$	ΔA	q	k s^{-1}	k' s^{-1}
in PMA and NaOH soln	5.08	0.2	−0.475	−0.091	0.53	19	0.43
	5.41	0.4	−0.648	−0.103	0.51	91	3.5
	5.90	0.6	−0.858	−0.083		200	
in NaOH soln	5.12		−0.483	−0.036[b]		0.14	
	5.35		−0.641	−0.016[c]		0.17	
in buffer and PMA soln	5.00		−0.398	−0.061	0.40	20	0.33
in buffer only	5.00		0.0	0.0			

[a] [PMA] = 1.16 × 10^{-2} N, [methyl red] = 5.4 × 10^{-3} g/L, ionic strength 0.4. [b] corresponding to a pH change of 0.09. [c] Corresponding to a pH change of 0.05.

neutralized to pH 5.12 (with the indicator added originally to the base) is in reasonable agreement with the rate constant $k' = 0.26\ s^{-1}$ found for the change in emission intensity of Dan-PMA when it was partially neutralized to a final pH 4.95.

Discussion

The cooperative helix–coil transition of synthetic polypeptides has maximum relaxation times in the range 10^{-8}–10^{-6} s,[18] several orders of magnitude shorter than observed by Ohno et al.[12] or in this study. But it is obvious that "cooperativity" means something very different in the case of a polypeptide, involving change from a regular to a disordered structure, and in the case of vinyl polymers, where both the contracted and the expanded forms are disordered. At the midpoint of the polypeptide transition, the chain contains long helical and randomly coiled sequences; no analogous structure is conceivable at the midpoint of the PMA transition. Thus, the kinetic theory of the cooperative helix–coil transition[19] is not applicable to our system. Any cooperativity of a different type that may be involved in the transition between the contracted and the expanded form of PMA would be reflected in the rapid part of the process, which we could not observe by our technique.

One would expect the deprotonation of the dansyl label on addition of base to Dan-PMA to be too rapid to be followed by our techniques, so that any change in emission intensity should only reflect changes in the polarity of the microenvironment of the label. For final pH values corresponding to a low degree of ionization, this may involve only conformational changes of the contracted form, and the slowness of the process may perhaps be understood as a consequence of the various restraints to any change of shape of the tightly coiled chain. It is satisfying that the drift in pH, as monitored by the absorbance of methyl red, should take place over a similar time as the change in the emission of the dansyl label.

On the other hand, the approach to equilibrium of Dan-PMA when the chain was highly expanded was surprisingly slow. The low enthalpy of activation is similar to that expected for a single hindered rotation in a chain consisting of carbon–carbon bonds and it is only due to the very large negative entropy of activation that the process is observable in a procedure which can follow only processes with relaxation times in at least the millisecond range.

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