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(57) We have already noted that the fraction $M_\eta = 4 \times 10^6$ is anamolous in this group and displays morphological behavior of a slightly lower molecular weight.
(58) For theoretical reasons Hoffman et al.[10] calculated the undercooling at which the change from one morphological form to the other occurred and found it to be 17.5 ± 0.5 °C for all the molecular weights that are involved. Unfortunately they used a variant[45] of the theory of Flory and Vrij[46] for the melting of molecular crystals. The theory requires that all chains be of exactly the same length and hence cannot be applied to any real polymer system.[46,47] However, for very high molecular weights, such as 2.49×10^6, the melting temperatures for the different models are virtually indistinguishable from one another. For this molecular weight the transition from spherulites to (g) type rods occurs at 128 °C corresponding to an undercooling of 17.5–18 °C in agreement with the erroneous calculation. However, the correct results for the lower molecular weights needs to be recalculated using the theory for the equilibrium melting temperature of finite chains.[47,48] When this is done essentially a constant undercooling, within the limits of the calculation, is still found.

Spin-Label Study of the Poly(methacrylamide)-Type Copolymers in Solution

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ABSTRACT: A series of soluble copolymers of *N*-(2-hydroxypropyl)methacrylamide with 4-nitrophenyl esters of ω-methacryloylamino acids were prepared. By a polymeranalogous reaction with 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl a spin-label was bonded to the copolymers at the ends of side chains of varying length. The mobility of spin-labels thus bonded was studied by the EPR method in methanol solution over the temperature range 213–313 K. The correlation time τ, characterizing the mobility of the spin-label, depends monotonically on the length of the side chain; at 293 K, τ of the copolymers under investigation varies from 1×10^{-10} to 1×10^{-9} s as the number of methylene groups in the amino acid rises from 0 to 11. The activation energy of these motions, $E_{\mathrm{act}} = 3$ kcal/mol, remains the same for all copolymers.

(I) Introduction

The design of water-soluble synthetic polymers as carriers of biologically active groups[1] and enzymatically cleavable bonds[2] needs information about the behavior of various side chains in solution. Therefore effective experimental approaches to conformation and mobility studies of side chains of soluble polymers are needed, one of which is EPR spin labeling. It is well known that the shape of the EPR spectra of nitroxides in solutions depends on the rotational motion (characterized by the correlation time) of the nitroxide group relative to the applied magnetic field, owing to the anisotropy of the hyperfine interaction tensor of the unpaired electron with the nucleus of the nitrogen atom and to the anisotropy of their *g* factor.[3] The rotational motion of the nitroxide group is influenced by the medium, which motivates the use of the above properties in an investigation of the properties of the medium. Nitroxide can be either only physically dispersed in the medium as a spin probe or be chemically bonded as a spin label. An example of the use of spin labels in the study of the motions of polymer segments is a paper by Bullock, Cameron, and Smith.[4] Here we report a study of the mobility of spin labels bonded at the ends of variously long side chains of copolymers of the poly(methycrylamide) type in methanolic solutions.

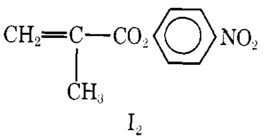
(II) Experimental Section

Preparation of Copolymers. A series of copolymers of *N*-(2-hydroxypropyl)methacrylamide (HPMA) with 4-nitrophenyl esters of methacryloylated ω-amino acids was prepared. The monomers used are described in Table I. A general procedure for the preparation of these monomers and the preparation of copolymers with HPMA by precipitation copolymerization in acetone has been described earlier.[2,5,6] The copolymers were prepared so as to contain 3 mol % of the 4-nitrophenyl ester. Spectroscopic measurements[2] confirm that the concentration of the active ester in the copolymers does not differ from this value by more than 10%. The molecular weight of the copolymers was ca. 40 000. The numbers 2–15 used as subscripts in denoting the monomers indicate the lengths of their side chains.

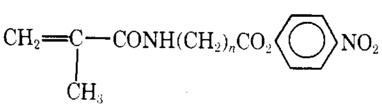
Table I
Characteristics of Monomers

Compd	Mp, °C	Yield, %	$\epsilon \times 10^{-4}$, L mol^{-1}/cm^{-1} [a]	Calcd/found, % C	H	N	Ref
I_2	94–95	80	0.89				2, 5
II_5	101	42	0.92				15, 5
II_6	63–65	40	0.97				5
III_7	116–116.5	35	1.02				7
II_8	115–117	35	1.05	58.81	5.92	9.14	
				58.91	6.03	8.89	
II_9	75–77	40	0.93				2, 5
II_{10}	64–65	35	0.94	61.06	6.63	8.38	
				61.17	6.73	8.31	
II_{11}	78–79	30	1.01	62.05	6.94	8.08	
				62.21	7.15	7.92	
II_{15}	88–91	53	0.94	65.32	7.98	6.92	
				65.28	8.11	6.94	

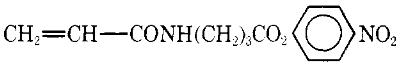
[a] Measured in methanol at λ_{max} 274 nm.



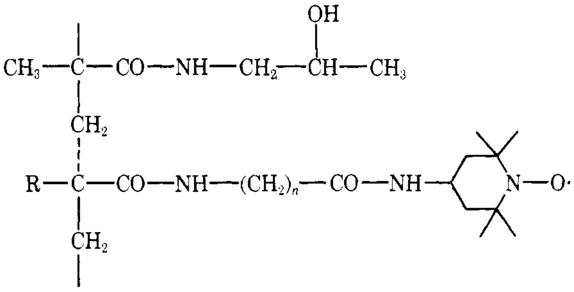
I_2



II_5, $n = 1$
II_6, $n = 2$
II_8, $n = 4$
II_9, $n = 5$
II_{10}, $n = 6$
II_{11}, $n = 7$
II_{15}, $n = 11$



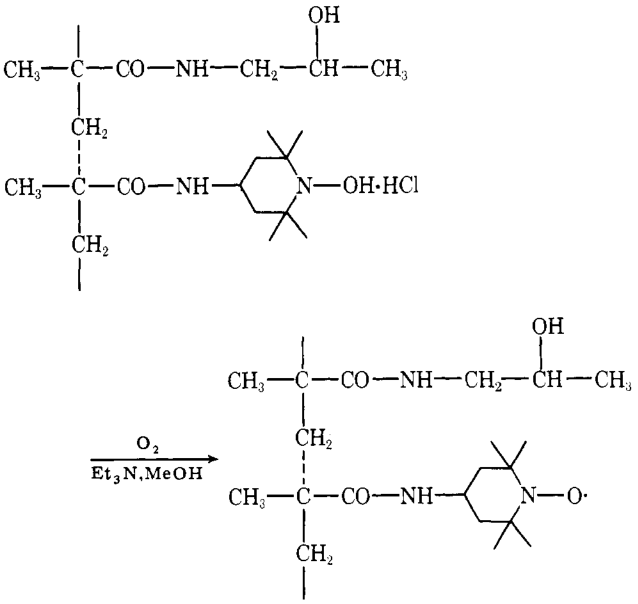
III_7



Copolymers

HPMA–II_5, $n = 1$; R = CH_3
HPMA–II_6, $n = 2$; R = CH_3
HPMA–III_7, $n = 3$; R = H
HPMA–II_8, $n = 4$; R = CH_3
HPMA–II_9, $n = 5$; R = CH_3
HPMA–II_{10}, $n = 6$; R = CH_3
HPMA–II_{11}, $n = 7$; R = CH_3
HPMA–II_{15}, $n = 11$; R = CH_3

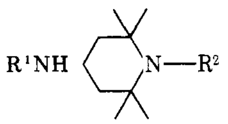
4-Amino-2,2,6,6-tetramethylpiperidine-1-oxyl was used as the spin label; data on the derivatives used in this work including the preparative methods are given in Table II. The spin label was bonded to the ends of the amino acid side chains by aminolysis of the copolymers prepared so that 0.2 g of the copolymer with the 4-nitrophenyl ester was heated in dimethyl sulfoxide (2 mL) with 0.1 g of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl in a sealed ampule to 333 K for 8 h. The copolymers were purified by dialysis, carried out after diluting the solution to 10 mL with water in a dialyzation tube (Firm Serva, pores 15–20 Å, diameter 20 mm), in 1000 mL of distilled water for 3 × 5 h; the length of the immersed part of the tube was 50 mm. The dialysis was then continued for 10 h after 1 mL of 2% HCl had been added and for another 10 h after the addition of 1 mL of 5% $NaHCO_3$. The copolymer solution was then evaporated to dryness, dissolved in 2 mL of ethanol, precipitated into 20 mL of acetone, and dried. The spin-label concentration in the samples was approximately 1×10^{10} g^{-1}, which corresponds to a yield of aminolysis of ca. 80%. In the case of the copolymer HPMA–I_2 the yield of aminolysis was very low, probably owing to the steric inaccessibility of the 4-nitorphenol ester of methacrylic acid in the copolymer. The copolymer HPMA–I_2 was therefore prepared by the copolymerization of HPMA with 2,2,6,6-tetramethyl-4-methacryloylamino-1-hydroxypiperidine hydrochloride.[10] The polymer thus formed (0.2 g) was oxidized with oxygen in a 10% methanolic solution in the presence of 1 mL of triethylamine for 8 h with vigourous shaking; the copolymer obtained was reprecipitated into acetone. The molecular weight and spin-label concentration of HPMA–I_2 prepared by the procedure corresponded to the other copolymers of the series.



copolymer HPMA–I_2

Measurements of the EPR Spectra. The EPR spectra were recorded with a JEOL JES-PE-3X spectrometer provided with an EC-100 computer allowing simulation and on-line integration of the EPR spectra, and with a JES-VT-3A temperature controller, stabilizing the temperature in the cavity to ±0.5 K. A platinum resistance thermometer was used for exact temperature measurements in the cavity. The line widths were determined by means of an NMR marker JES-FC3. The absolute values of the spin-label concentration in the samples were determined by comparing the second integrals of the spectra with the second integral of the spectrum of a standard (DPPH solution in benzene). The concentrations were calculated taking into account changes in the quality factor of the cavity determined from the intensity of the line of an internal standard (Mn^{2+} in MgO), placed

Table II
Characteristics of the Derivatives of 4-Amino-2,2,6,6-tetramethylpiperidine



No.	R^1	R^2	Mp/Bp, °C/Pa	Calcd/found, % C	H	N	Ref
1	H	H	61–65/133 125–130/2130				8, 9
2	CH_3CO	H	123–125				8
3	$CH_2{=}C(CH_3){-}CO$	H	115–116 (ref 126–127)	69.58 69.83	10.78 11.06	12.45 12.51	10
4	CH_3CO	O·	144–145	61.93 62.01	9.92 10.14	13.13 13.09	9
5	$CH_2{=}C(CH_3){-}CO$	O·	148–150[a] 146–148[b]				10
6	$(CH_3)_3C{-}CO$	O·	171–173	65.85 65.77	10.65 10.82	10.97 10.96	11
7	$CH_2{=}C(CH_3){-}CO$	OH·HCl	Does not melt up to 250 °C				10
8	H	O·	35–36 97–98/533				9

[a] Prepared by methacryloylation of **8**. [b] Prepared by oxidation of **3**.

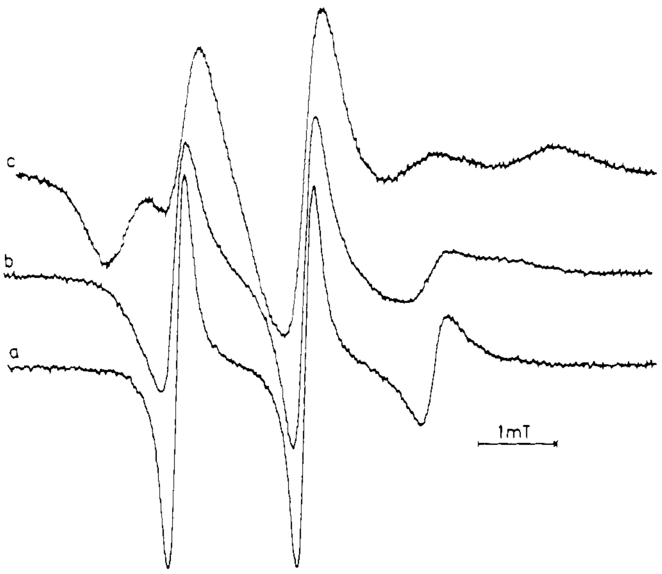


Figure 1. EPR spectrum of a methanolic solution of the spin-labeled copolymer HPMA-I$_2$ recorded in an inert atmosphere at: (a) 313 K, (b) 273 K, (c) 213 K.

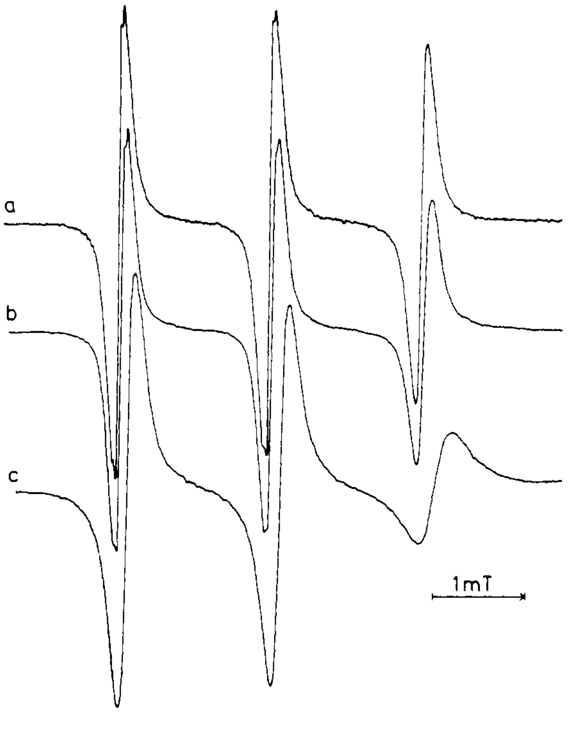


Figure 2. EPR spectrum of a methanolic solution of the spin-labeled copolymer HPMA-II$_{15}$ recorded in an inert atmosphere at: (a) 313 K, (b) 273 K, (c) 213 K.

in the cavity beyond the temperature stabilization system, and the temperature influence on the occupation of the energy levels according to the Boltzmann distribution.

All the copolymers were investigated in methanolic solutions at a concentration of 10 mg of copolymer/mL of solvent. The solutions were measured in a quartz measured measuring cell LC 02, active volumn 0.05 mL, both in the air, when oxygen is present in the solvent, and under an inert nitrogen atmosphere. The spectra were recorded over the temperature range 213–313 K at 20 K intervals.

(III) Results and Discussion

Examples of the EPR spectra are given in Figures 1 and 2, showing spectra of the copolymers HPMA-I$_2$ and HPMA-II$_{15}$, which in the series under investigation represent the extreme cases of the length of the spin-labeled side chains. One can see that the mobility of the spin-label is greatly affected by the chain length. In the case of the above copolymers under the given experimental conditions, the mobility comprises the range of the motional narrowing of the spectral lines and partly overlaps the range of slow motions. Figure 2 also shows that in the spectra of copolymers with a long side chain one can, after removal of oxygen from the sample and at elevated temperature, partly distinguish the hyperfine structure due to interaction of the unpaired electron with the 12 protons of the methyl groups of the spin-label bonded in positions adjacent to N–O·. The correlation times were therefore determined from the EPR spectra by three different methods, all of which presume spatially isotropic motions.

Method A. In the region of motional narrowing we start from the known expression

$$\tau = 6.27 \times 10^{-9}\,\Delta H(0)\left[\left(\frac{Y(0)}{Y(-1)}\right)^{1/2} - \left(\frac{Y(0)}{Y(+1)}\right)^{1/2}\right] \quad (1)$$

in which $Y(M^{\infty})$ is the amplitude of the first derivation of a spectral line with the spectral number[3] M^{∞}, and $\Delta H(0)$ is the peak-to-peak line width of the derivative of the central absorption line corresponding to $M^{\infty} = 0$ (expressed in mTorr). The numerical constant was obtained from experimentally determined values of the **A** tensor, $A_{\parallel} = 3.58$ mTorr = 100.3 MHz, $A_{\perp} = 0.79$ mTorr = 22.15 MHz, and the **g** tensor values taken from the literature (e.g. ref 12), $g_x = 2.0089$, $g_y = 2.0061$, and $g_z = 2.0027$. One must bear in mind that the observed spectral lines form an envelope of the hyperfine structure of the methyl protons. We therefore used a procedure similar to that employed by Bullock and co-workers.[4] We calculated the shapes of the spectral lines formed by superposition of 13 Lorentzian components with the splitting constant $a_{\mathrm{Me}}{}^{\mathrm{H}} = 0.041$ mTorr and with the respective intensities, for various line widths of these components from the interval $\Delta H^{\mathrm{k}} = 0.05$ to 0.40 mTorr. From the simulated lines thus obtained we constructed calibration curves which allowed $\Delta H(0)$ and $(Y(0)/Y(+1))^{1/2}$ obtained directly from the spectra to be transformed into values corresponding to the components of the hyperfine structure, $\Delta H^{k}(0)$ and $\Delta H^{\mathrm{k}}(\pm 1)/\Delta H^{\mathrm{k}}(0) = (Y^{\mathrm{k}}(0)/Y^{\mathrm{k}}(\pm 1))^{1/2}$. These values were then substituted into eq 1.

Method B. Kuznetsov and co-workers[13] showed that in the region of motional narrowing, eq 1 and directly $\Delta H(0)$ and $Y(M^{\infty})$ taken from the spectra might be used also in the case when the observed spectral lines were an envelope of the hyperfine structure, assuming that the spectral lines were broadened. A natural source of such broadening is oxygen broadening which in measurements performed in air assumes sufficiently high values.[13]

Method C. In the region of slower motion ($\tau \geq 5 \times 10^{-9}$), in which eq 1 can no longer be used and equations suggested by Goldman and co-workers[14] cannot yet be used, the correlation times were determined by means of a dependence between the correlation time τ and the parameter $\varkappa$ defined by eq 2, determined by Kuznetsov and co-workers.[12]

$$\varkappa = \frac{H(\tau) - H(\tau \rightarrow 0)}{H(\tau \rightarrow \infty) - H(\tau \rightarrow 0)} 100 \quad (2)$$

Here, $H(\tau)$ is the position of the maximum on a line lying in the lower field ($M^{\infty} = -1$) in the derivation record of the analyzed spectrum, and $H(\tau \rightarrow 0)$ and $H(\tau \rightarrow \infty)$ are the positions of the same maximum for limiting values of τ.

The results obtained are summarized in Figure 3. In the spectra of the first two copolymers HPMA-I$_2$ and HPMA-II$_5$ no resolution of the hyperfine interaction with the protons of the methyl groups could be observed even in measurements under an inert atmosphere; in Figure 3, these copolymer results are given obtained by analyzing spectra measured under an inert atmosphere by means of methods A and B and at 213 K also employing method C. The other copolymers were investigated both in an inert atmosphere and in the presence of oxygen; Figure 3 shows the results obtained with these copolymers using the methods A and B. Figure 3 demonstrates that the correlation times determined for the individual copolymers from various measurements and employing various methods coincide surprisingly well, especially bearing in mind the magnitude of the error, which in the determination of relative changes in the series under investigation is estimated as 10%. Such agreement confirms the conclusions of Kuznetsov and co-workers[13] and the correctness of method A, based on simulation of the shape of the spectral line, and justifies the use of method B also for cases in which the hyperfine structure of the methyl protons is not resolved owing to the longer correlation times ($1 \times 10^{-9} > \tau > 5 \times 10^{-10}$).

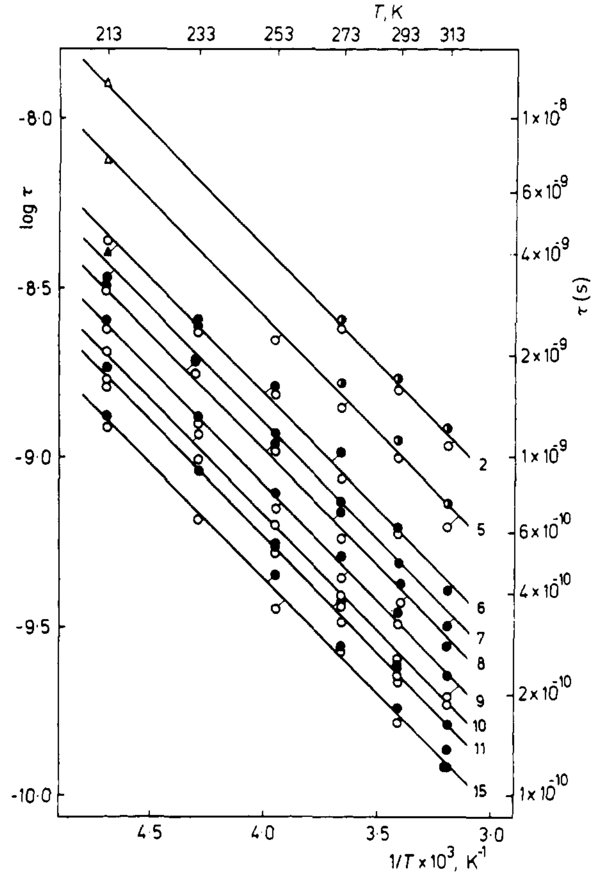


Figure 3. Dependence of log τ on $1/T$. The correlation times τ characterizing the motion of the spin label were determined by analyzing the EPR spectra of methanolic solutions of the spin-labeled copolymers (atmosphere, method of evaluation): (○) inert, A; (●) air oxygen, B; (◑) inert, B; (△) inert, C; (▲) air oxygen, C. The length of the side chain of the copolymer is indicated by a digit at the right margin of the plot.

Figure 3 distinctly shows the monotonic dependence of the correlation time characterizing the motion of the spin-label on the length of the side chain by which the spin-label is attached to the copolymer. This correlation time increases with decreasing length of the side chain from 15 to 2 atoms by roughly one order of magnitude for each given temperature value. Preliminary measurements were also made with free nitroxides 6 and 8 (cf. Table II) in methanol and with nitroxide 6 in a solution containing 10 mg of poly-N-(2-hydroxypropyl)methacrylamide in 1 mL of MeOH, at concentrations identical with those of the spin-label in the copolymers under investigation. A preliminary evaluation of the spectra thus obtained shows that the respective correlation times are lower by approximately one order of magnitude than those for HPMA-II$_{15}$. In our view, the ascertained linear dependence of log τ on $1/T$ with the same slope for all the copolymers under investigation can be interpreted so that the thermal activation of the motion of the spin labels bonded at the ends of variously long side chains is characterized within the limits of experimental error by the same activation energy $E_{\mathrm{act}} = 3$ kcal/mol = 12.5 kJ/mol. Shortening of the side chain is reflected only in hampered motion of the spin label, which increases the correlation time.

A more thorough description of this phenomenon would require more information provided by measurements within a broader temperature range, in various media and with various types of the spin labels and copolymers. The respective experiments are in progress.

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Dynamical Scaling for Polymers in Theta Solvents

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ABSTRACT: We construct scaling laws for the motions of very long flexible chains, at the Flory compensation temperature theta; they are more complex than for the case of good solvents. For instance, a single chain in a good solvent makes but few knots on itself. But in a theta solvent we expect it to be self-knotted. In the present paper we concentrate on the problem of *semidilute* (entangled) solutions, and we derive a scaling law for the sedimentation coefficient vs. concentration. We then discuss spontaneous fluctuations of concentration, which can be studied by photon beat methods. At long wavelengths the restoring force (due to the osmotic pressure in the solution) is weak and we predict a cooperative diffusion coefficient D_c *linear* in concentration. At shorter wavelengths one might think that, the frequencies being higher, the restoring forces become dominated by the rubber elasticity of the transient network. However, a simple model suggests that this second regime is never realized.

I. Introduction and Remarks on the Single-Chain Problem

The dynamics of polymer solutions in *good solvents* have been studied recently from the point of view of scaling laws.[2a] The crucial assumption underlying this discussion was the notion that monomer–solvent friction is dominant when compared either to friction between different chains or to internal barrier effects inside one chain. With this assumption, a comparatively simple set of dynamical scaling laws could be produced. Since then, two series of inelastic light-scattering experiments have been performed on polystyrene solutions well above the theta point.[2b,3]

The first experiment probed the collective (gellike) fluctuations of concentration at long wavelengths[2b] and led to a cooperative diffusion coefficient D_c increasing with the monomer concentration c like $D_c \sim c^{0.68}$.

From ref 2a, the scaling prediction for D_c is

$$D_c \sim c^{\nu/(3\nu-1)} \qquad \text{(good solvent)} \qquad \text{(I.A)}$$

where ν is the exponent giving the size R_F of one coil in a good solvent as a function of the polymerization index N.

$$R_F \sim aN^\nu \qquad \text{(good solvent)} \qquad \text{(I.B)}$$

With the Flory value $\nu = 3/5$ the theoretical exponent for D_c is 0.75. In fact the agreement is even better if one uses the value of ν which fits best the viscosity and self-diffusion data in the dilute limit, of order of $\nu = 0.55$.

The second experiment,[3] using chains of very high N (molecular masses M up to 10^7 daltons), probed the inner modes of a single coil and showed a non-Lorentzian spectrum with a half-width $\Delta\omega_\mathbf{k}$ increasing like a power of the wave vector $\mathbf{k}$

$$\Delta\omega_k \sim \mathbf{k}^x$$

where $x = 2.8 \pm 0.4$. The theoretical prediction here was $x = 3$.

Thus we say the assumptions and the scaling analysis of ref 2a are not too far from reality. At this stage it appeared natural to extend the analysis toward the case of theta solvents, where the static conformations of the chains become nearly ideal. We decided to do this and found, to our great surprise, that theta solvents are considerably more difficult than good solvents!

This can be qualitatively understood from Figure 1, where we consider a single chain in a good, and in a poor, solvent. In a good solvent, the chain is very much swollen and makes no knots on itself. In a poor solvent, it is more compact and makes *many self-knots.* We have found two justifications for this statement.

(1) Let us assume that the number of entanglement points in a coil (K) is proportional to the number of nearest neighbor contacts (P)

$$K = fP \qquad \text{(I.1)}$$

where f is a numerical coefficient. Comparison with mechanical data on strongly entangled systems (molten polymers) suggests that f might possibly be as small as 10^{-2}. We assume that f is a geometrical constant and is independent of the polymerization index N.