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Conformation and Dynamics of Poly(olefin sulfones) in Solution. 1. High-Frequency Dielectric Relaxation and Carbon-13 NMR Relaxation

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ABSTRACT: Dielectric permittivity as obtained by a time-domain reflectometry method is reported for dilute solutions of a number of poly(olefin sulfone) fractions in benzene and dioxane at frequencies between 1 MHz and 10^3 MHz. All the polymers display in this region a dielectric loss mechanism independent of molecular weight that is attributable to segmental rearrangements of the chain backbone in random-coil portions of the chain. Spin–lattice ^{13}C relaxation times give correlation times in reasonable agreement with the dielectric results. The process is faster in dioxane than in benzene, although the former solvent is more viscous.

Introduction

Many years ago Bates, Ivin, and Williams[1] (hereafter BIW) studied the dielectric behavior in dilute solution of alternating copolymers of sulfur dioxide with 1-hexene and 2-methyl-1-pentene. Both of these poly(olefin sulfones) showed a large dielectric loss peak in the radio-frequency range, the frequency of maximum loss varying strongly with molecular weight. The corresponding dipole orientational correlation times τ were rather well predicted by the formula

$$\tau \cong M[\eta]\eta_0/RT \tag{1}$$

in which M is polymer molecular weight, $[\eta]$ is intrinsic viscosity, and η_0 is solvent viscosity. The strength of this loss peak accounts for most of the total dielectric increment above pure solvent, and it was at first supposed that the success of eq 1, which corresponds to diffusional tumbling of the entire macromolecule, implies very high kinetic rigidity of the more or less randomly kinked chains. The fact that SO_2 copolymers with 2-olefins or cyclic olefins were found not to have such a low-frequency relaxation could be rationalized[2] in terms of a predominantly trans conformation at the backbone C–C bonds; and the remaining dielectric increment could probably be attributed to especially large atomic polarization associated with the vibrations of the highly polar sulfone group.

A few years later the postulate of kinetic rigidity was rendered tenuous by the observation[3-5] that for all sulfone polymers the longitudinal ^{13}C nuclear spin relaxation times T_1 indicated quite normal chain flexibility; i.e., the orientational correlation times were of the order of nanoseconds, some 4 or 5 decades shorter than the dielectric values. Attempts to reconcile these observations were unconvincing, and it was decided to reinvestigate the dielectric behavior at higher frequencies. Our first observations on dilute dioxane solutions of three different fractions of poly(1-hexene sulfone) are depicted in Figure 1, where two different and distinct loss peaks are visible for each fraction. The lower peak shifts with increasing molecular weight toward lower frequency, and indeed our data are in good accord with those of BIW. The other peak, which was missed by BIW, is seen to be independent of molecular weight, and this clearly identifies some local process, presumably a backbone segmental motion, as responsible for the dielectric response. Systematic investigation of a number of polysulfones was then undertaken, with the aid of the then very recent improvements[6,7] in the technique of time-domain reflectometry (TDR). In this paper we report the results of these measurements[8] and also of a few further NMR observations amplifying those published earlier.

A wealth of evidence now points to the existence of helical conformations in those polysulfones that exhibit the low-frequency chain-length-dependent dielectric loss mechanism.[9-11] Our own experimental work on the low-frequency dielectric behavior of SO_2 copolymers with various 1-alkenes and with allylbenzene will be described in later papers of this series.

Experimental Section

The various olefin/SO_2 alternating copolymers were prepared by standard free radical recipes.[12] Their preparation, fractionation, and characterization by light scattering and viscosity are described in another paper of this series. Viscosity-average or weight-average molecular weights of all samples used in the present work exceed 2×10^5 and are not further stated except where relevant. The 1-butene/SO_2 polymer was a gift from R. E. Caís and F. A. Bovey of AT&T Bell Laboratories.

Analytical grade benzene and dioxane were dried and distilled over sodium immediately before preparation of solutions for dielectric measurements. The NMR solvents chloroform-*d*, benzene-d_6, and dioxane-d_8 were purchased from Aldrich Chemicals and used as received.

Low-frequency (10^2–10^5 Hz) dielectric measurements were performed at Dartmouth with a General Radio 1615-A capacitance bridge, 1311-A audio oscillator, and 1232 tuned amplifier and null detector and at Brown with a transformer ratio arm bridge.[13] Preliminary high-frequency data (10^5–10^9 Hz; cf. Figure 1) were obtained at the M.I.T. Insulation Laboratory with resonance-circuit and transmission-line methods.[14] More extensive high-frequency results were later obtained at Brown by the time-domain reflectometry (TDR) difference method and translated to the frequency domain as described elsewhere.[6,7,15] Mean-square dipole moments (esu) per repeat unit, corresponding to the *high-frequency peak only*, were calculated from the expression

$$\langle\mu^2\rangle/x = 27K_bTM_0(\epsilon_0 - \epsilon_\infty)/4\pi N_A d_1(\epsilon_\infty + 2)^2 w \tag{2}$$

where M_0 is the molecular weight of a repeat unit, ϵ_0 and ϵ_∞ are low- and high-frequency permittivity limits of the high-frequency dispersion region, N_A is Avogadro's number, d_1 is solvent density, and w is weight fraction of polymer in the solution. For nonpolar solvents and dilute solutions, this expression is negligibly different from either Onsager or Guggenheim–Smith forms.

For ^{13}C relaxation measurements, the polymer solutions, typically 8% (w/w), were prepared by weight in 10-mm NMR tubes,

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Table I
High-Frequency Dielectric Properties of Poly(olefin sulfones) in Solution

solvent (and concn)	olefin unit of polymer	temp, °C	ϵ_0[a]	ϵ_∞[a]	ϵ''_{max}	$\langle\mu^2/x\rangle^{1/2}$,[b] D	log f_m, Hz
benzene (4.00% (w/w))	1-pentene	23	2.375	2.300	0.0304	1.52 D	7.33
	1-hexene (F1)	6.6	2.433	2.357	0.0305		7.05
	1-hexene (F1)	23	2.369	2.296	0.0286	1.57	7.31
	1-hexene (F1)	40	2.338	2.270	0.0265		7.52
	1-hexene (F1)	50	2.319	2.253	0.0248		7.66
	1-hexene (F2)	23	2.364	2.290	0.0285	1.58	7.31
	1-decene	23	2.336	2.285	0.0208	1.54	7.20
	1-dodecene	23	2.326	2.283	0.0164	1.51	7.13
	1-hexadecene	23	2.315	2.286	0.0116	1.38	7.02
	1-eicosene	23	2.307	2.281	0.0107	1.43	7.00
	cyclohexene	23	2.338	2.299	0.0145	1.14	7.66
dioxane (3.87% (w/w))	1-hexene (F1)	12.5	2.397	2.249	0.0460		7.33
		23	2.362	2.220	0.0440	2.07	7.51
		50	2.305	2.188	0.0364		7.86

[a] Extrapolated on Cole–Cole plots. [b] See eq 2.

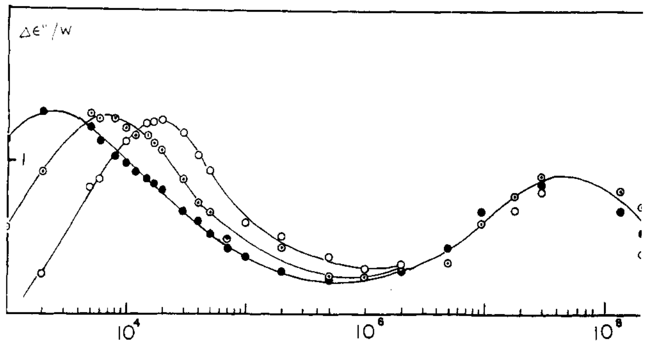

Figure 1. Dielectric loss factor increments over solvent per unit weight fraction of polymer, $\Delta\epsilon''/w$, for three samples of poly(1-hexene sulfone) in dioxane at 25 °C. Concentrations about 3% (w/w). Filled circles, $M_w = 5.1 \times 10^5$; dotted circles, $M_w = 3.3 \times 10^5$; open circles, $M_w = 1.9 \times 10^5$.

which were sealed with a minimum of vapor space (to minimize bumping) after five deoxygenating cycles of freezing, pumping, flushing with dry N_2, and thawing. Spin–lattice relaxation times T_1 were obtained by the standard inversion–recovery pulse sequence method at a frequency of 15.04 MHz in a JEOL 60Q spectrometer, with complete noise decoupling of the protons. The magnetic field was locked on the deuterium resonance. Reproducibility of T_1 was about ±10%. Nuclear Overhauser enhancements, accurate to perhaps ±15%, were evaluated from the ratios of peak areas under complete proton decoupling and under gated decoupling only during data acquisition following each pulse.

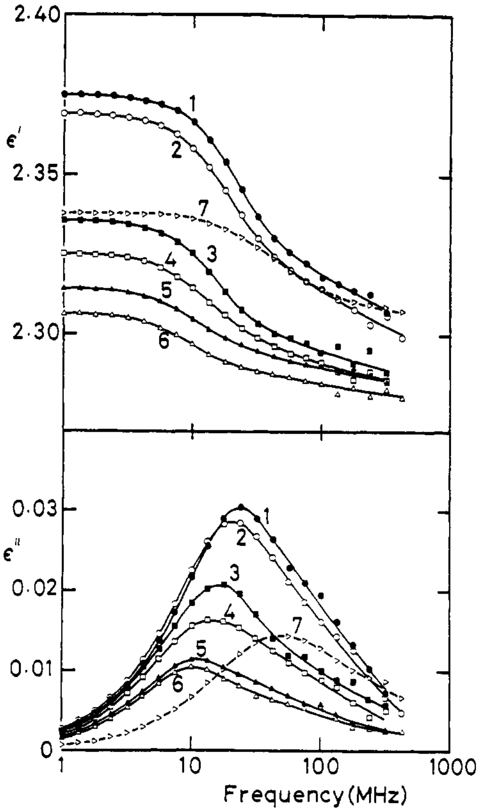

Figure 2. High-frequency dielectric permittivity ϵ' and loss factor ϵ'' in benzene (4% (w/w)) at 23 °C for various poly(olefin sulfones): filled circles, 1-pentene; open circles, 1-hexene (fraction F1); filled squares, 1-decene; open squares, 1-dodecene; filled triangles, 1-hexadecene; open triangles and smooth curve, 1-eicosene; open triangles and dashed curve, cyclohexene. The curves are numbered in the order given above.

Results and Discussion

The preliminary observations of high-frequency dielectric behavior of 1-hexene/SO_2 copolymers have already been mentioned in the Introduction and displayed in Figure 1. The main results of the subsequent more extensive TDR studies of various poly(olefin sulfones) are summarized in Table I. The data for all the polymers in 4% (w/w) benzene solution at 23 °C are shown in Figure 2 as plots of real permittivity ϵ' and loss factor ϵ'' against the logarithms of the frequency. Here it is seen that the frequency f_m of maximum loss in the 1-olefin series decreases systematically with increasing length of the alkyl side group. However, f_m drops by a factor of only 2.2 as the side-chain length mounts from 3 to 18 carbon atoms; and so we conclude that the most important motions along the "reaction coordinate" in the chain space[16] must be those of the backbone atoms, with the resistance in the side group playing a secondary role. The two fractions of 1-hexene/SO_2 polymer, with weight-average molecular weights of 5.1×10^5 (F1) and 7.2×10^5 (F2), give identical relaxation strengths and relaxation times. These data, together with those of Figure 1, show that the high-frequency relaxation is due to a local process independent of chain length.

The limiting high-frequency permittivities ϵ_∞ given in Table I were obtained by extrapolation on Cole–Cole plots. The values at 23 °C are all seen to be very slightly higher than the dielectric constant of pure benzene (2.278 at 23 °C),[17] and they (almost) systematically decrease with increasing side-chain length. Because of the latter observation, we suggest that the small difference can be ascribed to vibrational polarization within the sulfone group. The effects of temperature on the observed values of ϵ_∞ are fully accounted for by thermal expansion.

Figure 2 also shows that at a given weight concentration the strength of the high-frequency relaxation decreases

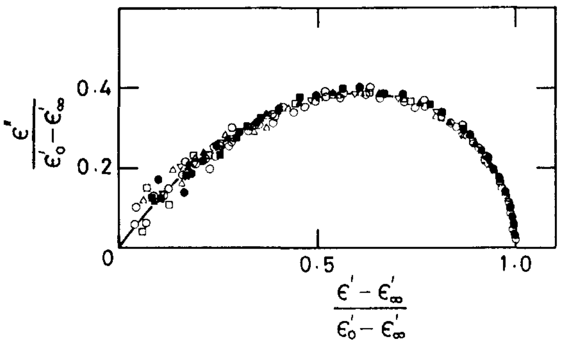

Figure 3. Reduced Cole–Cole diagram for poly(olefin sulfones) in benzene (4% (w/w)) at 23 °C. Same data as in Figure 2.

monotonically with increasing side-chain length, but this is due almost entirely to dilution of the polar groups, as can be seen from the apparent root-mean-square dipole moments per repeat unit given in the table. A quantitative interpretation of these figures requires the addoption of some structural model for the polymers. If we pursue the simple helix–coil picture mentioned in the Introduction, and if we further postulate that the high-frequency motion is typical local segmental rearrangement, such as those observed in many random-coil polymers with transverse dipoles,[18] the strength of the high-frequency loss peak may be used to estimate the fraction of the repeat units residing in random-coil sections of the chain. We thus write

$$(\langle\mu^2\rangle/x) = (1-\theta)D_{\mathrm{rc}}\mu_1^2 \qquad \text{(high-frequency peak only)} \tag{3}$$

where θ is the fractional helix content, μ_1 is the dipole moment of a single sulfone group (~4.5 D, based on model compounds; e.g., dialkyl sulfones), and D_{rc} is the dipole-moment ratio[19] within a random-coil sequence. Strictly, D_{rc} must be a function of sequence length until a limiting value is reached, but here it will suffice to pick a typical figure of $D_{\mathrm{rc}} \cong 0.5$ or 0.6, which then leads to $(1-\theta) \cong 0.2$–0.3; i.e., the higher poly(olefin sulfones) are thus crudely estimated to be about 75% in helical form.

The above interpretation of the high-frequency loss process is not unique, and at least two other alternative local processes might be envisaged as making contributions to the observed relaxation. Once such process could be helix-to-coil (and reverse) conversion of repeat units at the termini of helical sections. Another possibility, recently proposed and discussed by Chambers and Fawcett,[20] is rotation of the more or less rigid helical sections about their long axes. However, poly(cyclohexene sulfone), which has no observable low-frequency peak and therefore negligible helix content, has a quite similar relaxation time (cf. Table I and Figure 2) to those of the poly(1-olefin sulfones), which suggests that the high-frequency process is independent of the possible existence of helices.

The data of Figure 2, minus those for the cyclohexene polymer, are again shown in Figure 3 in the form of a reduced Cole–Cole diagram. The data are well described by a Cole–Davidson function with $\beta = 0.55 \pm 0.03$, a typical magnitude for backbone segmental rearrangements.

The effects of temperature on the high-frequency process are also reported in Table I for one of the poly(1-hexene sulfone) fractions. The measurements in benzene at four temperatures are shown in Figure 4. From the temperature variation of f_{m}, the Arrhenius activation energy is found to be 24 ± 2 kJ mol^{-1}. If we assume the diffusion limit of the Kramers expression for the relaxation rate, we may subtract a viscous-flow activation energy of 9 kJ mol^{-1} for benzene and obtain an apparent barrier height of about 15 kJ mol^{-1}, well within the range to be expected for a single backbone internal rotation. Thus these results appear to conform to the behavior of other polymers with transverse dipoles[18] and to the general theoretical view of local segmental rearrangements developed by Helfand and his co-workers.[21]

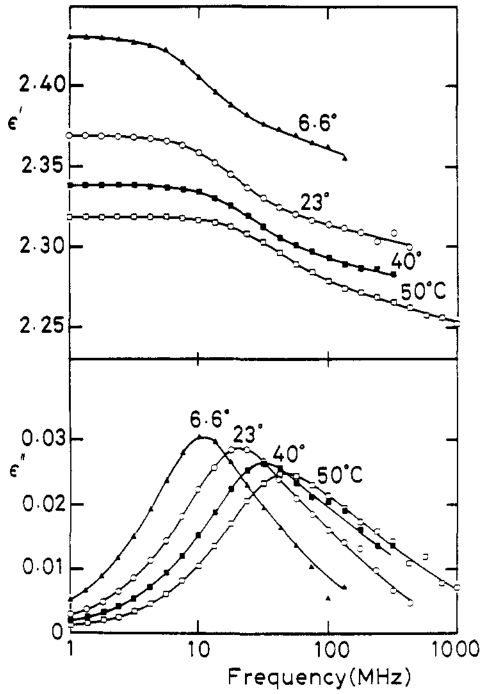

Figure 4. Effect of temperature on dielectric response of poly(1-hexene sulfone), fraction F1, in benzene (4% (w/w)).

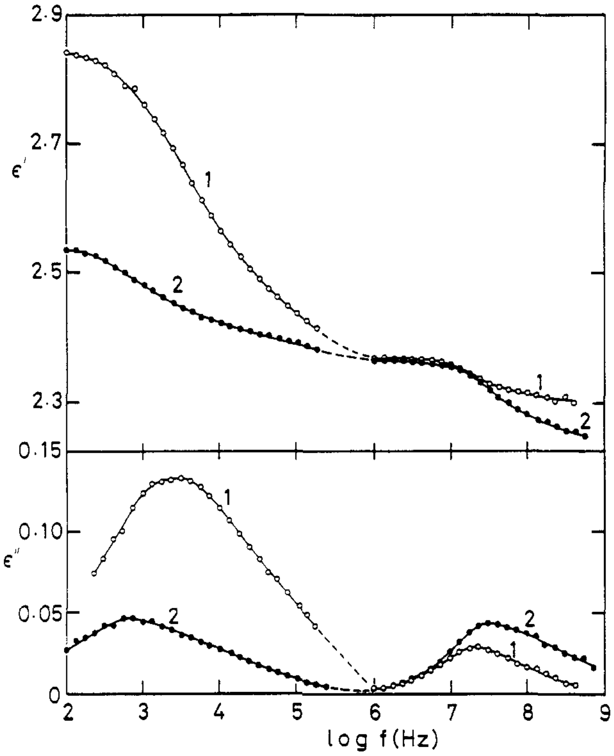

Figure 5. Dielectric dispersion and loss factor of poly(1-hexene sulfone), fraction F1, over a wide frequency range at 23 °C in several solvents: Curves 1, open circles, in benzene at 4.00% (w/w); curves 2, filled circles, in dioxane at 3.87% (w/w).

The *solvent effect* is, however, much more than merely a change in viscosity. To dramatize this, we show in Figure 5 the entire dielectric spectrum for a single fraction of

Table II
^{13}C Spin-Lattice Relaxation Times and Nuclear Overhauser Enhancements for Backbone Carbon Atoms of Several Poly(olefin sulfones) (Concentration 8% (w/w))

			T_1, ms (NOE)	
olefin	solvent	temp, °C	methine	methylene
1-butene	$CDCl_3$	38	48 (1.7)	24 (1.7)
		47	50 (1.9)	31 (1.8)
		58	55	32
		67	73 (2.0)	36 (1.7)
		82	75 (2.2)	40 (2.1)
1-pentene	$CDCl_3$	47	60	28
		58	69 (2.3)	41 (2.3)
		68	92 (2.3)	51 (2.1)
1-hexene	$CDCl_3$	47	57 (2.0)	30 (2.0)
		57	70 (2.4)	39 (2.3)
		67	87 (2.5)	48 (2.5)
1-hexene	benzene-d_6	36	37 (1.6)	23 (1.7)
		45	44 (1.9)	24 (1.9)
		54	44 (1.8)	25 (1.8)
		60	50 (2.1)	28
1-hexene	dioxane-d_8	26	40 (1.8)	21 (1.7)
		40	43 (2.0)	25 (1.8)
		54	53 (2.1)	30 (2.0)
1-octene	benzene-d_6	41	39 (1.5)	19 (1.5)
		66	44 (1.7)	24 (2.0)
1-octene	dioxane-d_8	40	46	54
		54	60 (2.2)	30 (2.3)
		74	87 (2.7)	50 (2.3)
1-decene	$CDCl_3$	54	50 (2.2)	27 (2.0)
1-dodecene	$CDCl_3$	54	45 (1.9)	25 (1.8)
1-hexadecene	$CDCl_3$	54	43	28

poly(1-hexene sulfone) in benzene (curve 1) and in dioxane (curve 2) at the single temperature of 23 °C. It is seen that the low-frequency loss peak is much stronger in benzene (as already noted by BIW), while the high-frequency peak is higher in dioxane. In terms of our helix-coil model this means that the helix content is depressed in dioxane, and it turns out that the average helical sequence length is also less in this solvent. Detailed numerical discussion is left for another paper. We may recall that (in addition to polypeptides, where the effect can of course be enormous) solvent influence on helix stability has been noted in other polymers, among them the poly(alkyl isocyanates).[22]

More remarkably, the value of f_m for the high-frequency peak is about 60% greater in dioxane than in benzene, although dioxane is about twice as viscous. The temperature coefficients (cf. Table I) are, however, almost identical in the two solvents. This means, according to Kramers-type theory, that the dimensions of the moving unit are somehow greater in benzene than in dioxane, resulting in a greater effective friction coefficient despite the lower solvent viscosity. In fact, benzene is thermodynamically the better of the two solvents for the polysulfones with long aliphatic side chains,[23] and we can thus speculate that the side groups are more extended from the chain backbone in this solvent. Unfortunately we did not obtain data for poly(cyclohexene sulfone) in dioxane, which might have afforded a test of this speculation.

We should also remark that the dipole moment ratio for the poly(cyclohexene sulfone), as calculated from the data in Table I, is only about 0.06. As long ago explained by Fawcett and Ivin,[2] this low value is undoubtedly due to the predominance of trans conformations at the C-C bond in the polymer backbone, and similar low figures are expected in other 1,2-disubstituted olefin/SO_2 polymers.

Spin-lattice relaxation times T_1 for the backbone methine and methylene carbon atoms are reported in Table II, followed in almost all cases by the nuclear Overhauser enhancement factors in parentheses. Relaxation times for side-chain carbon atoms were also observed in many of the solutions but are not reported here; they indicate the expected degree of flexibility in an alkyl chain and are not of primary interest to the present work. Comparison with previously published data,[3,4] where possible, indicates fair agreement.

A glance at Table II reveals that the relaxation times for the methylene carbons are always roughly half of those for the methine carbons, as would be expected if both atoms move more or less in concert in the segmental rearrangement process. Two other more salient features are the following:

(a) For the series in chloroform as solvent, the length of the alkyl side chain has relatively little effect on T_1 for the backbone carbons at a given temperature. This is in agreement with the dielectric data in benzene (Table I).

(b) For both 1-hexene and 1-octene polysulfones, at 54 °C, the value of T_1 for a given carbon is somewhat larger in dioxane than in benzene, indicating slightly shorter correlation times in the former solvent. Thus, as for dielectric relaxation, solvent viscosity does not alone control this relaxation process.

The Overhauser enhancement factors are invariably below the extreme-narrowing limit, so that a single-exponential correlation function is, as usual, inadequate to account for the results. We do not report any calculated correlation times, but these are inevitably of the order of 1 ns, in rough agreement with the dielectric relaxation times, but, as usual, somewhat shorter. We conclude that the nuclear spin and dielectric relaxations are due to the same local chain motions.

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Registry No. (1-Hexene)·(sulfur dioxide (copolymer), 34903-07-6; (1-pentne)·(sulfur dioxide) (copolymer), 42255-65-2; (1-decene)·(sulfur dioxide) (copolymer), 33990-98-6; (1-dodecene)·(sulfur dioxide) (copolymer), 33990-99-7; (1-hexadecene)·(sulfur dioxide) (copolymer), 33991-01-4; (1-eicosene)·(sulfur dioxide) (copolymer), 25104-33-0; (cyclohexene)·(sulfur dioxide) (copolymer), 28206-79-3; (1-butene)·(sulfur dioxide) (copolymer), 25104-10-3; (1-octene)·(sulfur dioxide) (copolymer), 30795-19-8.

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Interactions of Sterically Stabilized Particles Suspended in a Polymer Solution

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ABSTRACT: We present a theory for the destabilization and restabilization of sterically stabilized colloidal particles suspended in a polymer solution. First, we calculate the structure of a layer of chains attached to a surface in equilibrium with a polymer solution. We then determine the concentration profiles of the free polymer chains near the anchored layer via a self-consistent field theory. There is a depletion of mobile chains near the steric layer similar to the depletion layer next to a hard wall. The existence of a depletion layer produces a weak attractive interaction between colloidal particles. We show typical concentration profiles and interaction energies and we discuss how colloidal stability depends on the surface density of anchored chains and the concentration of free chains.

1. Introduction

The weak flocculation of colloidal particles induced by nonadsorbing polymers has been studied experimentally for many aqueous[1-4] and nonaqueous[5,6] suspensions. Several theories attribute this flocculation to a depletion of polymer segments around a hard particle.[7-10] The gradient in polymer concentration near the particles leads to a positive surface energy and hence an attraction between particles. The suspension tends to minimize the volume inaccesible to the polymer by forming weak clusters. Addition of this depletion-layer attractive potential energy to a hard-sphere or electrostatic repulsion allows satisfactory prediction of the weak flocculation of several suspensions.[3,4,6,10,11] Additionally, the existence of the depletion layer for flat plates has been confirmed by optical experiments.[12]

Many suspensions are not made up of hard spheres but comprise particles protected from flocculation by a layer of polymer chains attached to their surfaces. This way of protecting particles is known as steric stabilization and has been studied extensively in experiment and theory.[13] The polymer chains in the dense steric layer repel one another and are stretched from their free coil conformation, thus providing a repulsion between particles whenever two steric layers are forced to overlap. This repulsion may be of a range and magnitude sufficient to prevent flocculation due to London–van der Waals attractions.

When sterically stabilized particles are suspended in a polymer solution, the interactions are complicated by the repulsion between anchored and free chains. Indeed, several experimental studies[1,5,13] show that low concentrations of free polymer can cause a weak flocculation, while at higher concentrations the system remains stable. The goal of this paper is to present a mechanism for this flocculation and restabilization and to relate the mechanism to the structure of the anchored layer and the free polymer concentration profile.

de Gennes[14] has recently studied the interactions between a solution of mobile chains and a layer of chains anchored to a single wall, focusing on the conformations of the attached chains. He found that the structure of the anchored layer can be classified by several regimes depending on its surface density, molecular weight, and the concentration and molecular weight of the free chains. In order to investigate the interactions between sterically stabilized particles suspended in a polymer solution, one must determine the concentration profile of free chains between two steric layers. The regimes defined by de Gennes for the structure of a single steric layer suggest a mechanism for the destabilization and restabilization of polymer-coated colloidal particles suspended in a polymer solution. We have proposed[15] that the destabilization occurs at low free polymer concentrations where a depletion layer forms. We predicted equilibrium restabilization as the free polymer solution concentration aproaches that in the anchored layer and the depletion layer is supressed. In this paper we present detailed self-consistent field calculations of the unattached polymer concentration profiles and the resulting interaction potential between particles, thus determining stable and unstable regimes in polymer concentration and anchored chain surface density.

The paper is organized as follows. We begin in section 2 with a mean-field calculation of the structure of a single steric layer in equilibrium with a free polymer solution. In section 3 we present a self-consistent field calculation