Two-Parameter Scaling for Polymers in Θ Solvents

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ABSTRACT: We revive an old conjecture that a fixed number of binary contacts between chains collectively make up the topological constraint commonly referred to as an entanglement. This leads us to a general scaling theory for semidilute polymer solutions which involves two length scales, the screening length ξ and the tube diameter a. In good solvents these two lengths have the same concentration dependence and we recover the de Gennes results. In Θ solvents the two length scales depend on concentration differently. Combining the concentration dependences of these two length scales with concepts from theories of rubber elasticity and reptation leads to new predictions for the plateau modulus $G \sim kT/(a^2\xi) \sim c^{7/3}$ and viscosity $\eta \sim M^{2/3}(c/c^*)^{14/3}$ in Θ solvents, where M is the polymer molecular weight and c^* is the overlap concentration. These predictions are found to compare favorably with available experimental data.

Introduction

A simple scaling form for the concentration dependence of viscosity in semidilute solutions has been a goal in polymer science for many years.[1] For solutions of polymers in a good (athermal) solvent, de Gennes[2,3] has derived a scaling law for viscosity as a function of c/c^*, where c is the concentration (monomers per unit volume) and c^* is the concentration where the individual polymer coils start to overlap. This form has been confirmed for good solvents experimentally[4-7] in that it reduces data on the concentration dependence of viscosity for different polymer molecular weights to a common curve. However, this simple scaling has been found to break down for solutions in a Θ solvent,[8,9] where experimental data clearly show that there is a molecular weight dependence of viscosity not accounted for by the c/c^* scaling. The main purpose of this paper is to derive the correct scaling form for the concentration dependence of viscosity in Θ solvents. In so doing, we will also derive the concentration dependences of the plateau modulus and longest relaxation time.

Background Theory

The root mean square end-to-end distance R of a flexible polymer in dilute solution is known to scale[3,10] with degree of polymerization N.

$$R \approx bN^{\nu} \tag{1}$$

The effective monomer size is b, and the Flory exponent ν is $^1/_2$ in Θ solvents (we neglect logarithmic corrections throughout the paper) and roughly $^3/_5$ in good solvents. The overlap concentration (c^*) is determined as the concentration where the density of chain in the pervaded volume of the coil is equal to the overall chain density in the solution.

$$c^* \approx N/R^3 \sim N^{1-3\nu} \tag{2}$$

For $c > c^*$ the solution is termed semidilute. Semidilute solutions are characterized by a screening length[3] (or blob size) ξ.

$$\xi \approx R(c/c^*)^{-\nu/(3\nu-1)} \tag{3}$$

The exponent in eq 3 was evaluated by requiring ξ to be independent of molecular weight. On length scales less than ξ most monomers belong to the same chain. On length scales larger than ξ a monomer predominantly interacts with monomers from neighboring chains, and thus single-chain properties such as excluded-volume interactions and hydrodynamic interactions are screened on distances larger than ξ. The physical picture[3] of the coil is therefore a random walk of blobs of size ξ. Blobs of volume ξ^3 are the only volume elements assigned to a single chain which are space-filling in semidilute solution (i.e. ξ is the length scale where the single-chain density is equal to the overall chain density). This space-filling nature of blobs plays a crucial role in both thermodynamics and rheological properties.

The osmotic pressure is simply kT per blob,[3] where k is Boltzmann's constant and T is the absolute temperature.

$$\pi \approx kT/\xi^3 \sim (c/c^*)^{3\nu/(3\nu-1)} \tag{4}$$

Experimental results for osmotic pressure in both good solvent[11] and Θ solvent[12] seem to confirm eq 4. The osmotic bulk modulus $c(d\pi/dc)$ clearly scales the same way as the osmotic pressure. This led Daoud et al.[13] to propose that the plateau modulus also scales like the osmotic pressure and thus has the concentration dependence of eq 4. This concentration dependence is correct for the good solvent case but turns out to be valid only for impractically high molecular weight polymers at low concentrations for Θ solvents. The Θ solvent modulus has been discussed by Brochard and de Gennes,[14] where they conclude that $G \sim c^2$ in a Θ solvent because the binary interactions which cancel for osmotic pressure must still lead to entanglements and therefore control mechanical measurements. As we shall see, this result is also not quite correct.

The scaling approach was applied to the viscosity of polymer solutions by de Gennes[2] (η_s is the solvent viscosity).

$$\eta \approx \eta_s(c/c^*)^{3/(3\nu-1)} \tag{5}$$

The exponent in eq 5 was evaluated by matching the molecular weight dependence with that of the reptation prediction[3] $\eta \sim N^3$. This result has been confirmed by experiments in good solvents[4-7] but clearly does not work for Θ solvents.[8,9] The underlying physical reason that the simple scaling breaks down for the plateau modulus and viscosity in Θ solvents is that there are two length scales in semidilute Θ solvents.

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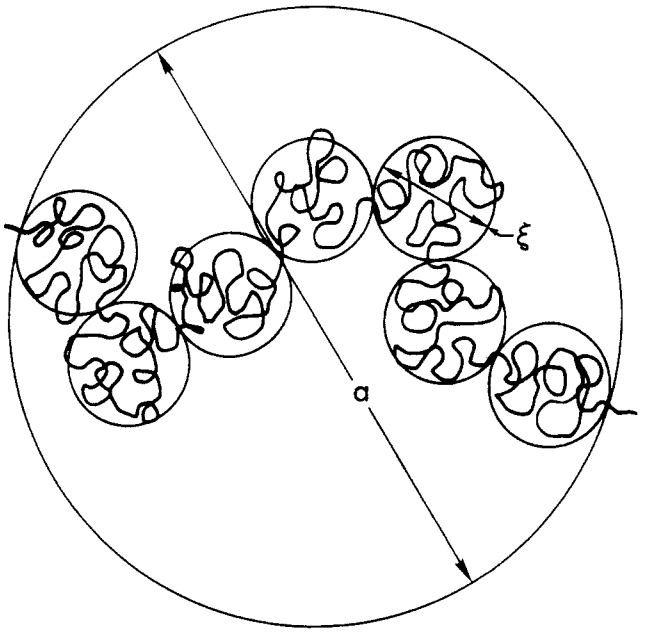

Figure 1. Schematic of an entanglement strand (a random walk of N_e/g blobs of size ξ).

Two Length Scales for the Θ Solvent

In Θ solvents, the coil dimensions are independent of concentration. Thus eq 1 applies for all concentrations with $\nu = {}^1/_2$. The screening length then only screens hydrodynamic interactions (since the excluded-volume interaction cancels at the Θ point).[3,10] The screening length is given by eq 3 with $\nu = {}^1/_2$.

$$\xi \sim c^{-1} \tag{6}$$

The tube diameter, a, is the length scale describing the mesh size of the temporary entanglement network that governs the long time dynamics of polymer solutions.[15] As discussed by Brochard and de Gennes,[14] the tube diameter is controlled by binary contacts. They count intramolecular binary contacts, which occur on a length scale smaller than ξ. The distance between such binary contacts, and thus the distance between self-knots, scales with concentration[14] as $c^{-1/2}$. However, intermolecular binary contacts are required for formation of the temporary entanglement network in polymer solutions. The density of intermolecular binary contacts in a good solvent[3,13] scales as $c^{9/4}$ and the physical distance between such contacts therefore scales as $c^{-3/4}$. The density of binary contacts in a Θ solvent[14,16] scales as c^2, and thus the distance between binary contacts scales as $c^{-2/3}$. Our conjecture about entanglements[14] is that some fixed (but as of yet unspecified) number of binary contacts collectively give rise to the topological constraint which we call an entanglement. Using this conjecture, in good solvent the tube diameter $a \sim \xi \sim c^{-3/4}$, but in Θ solvent the tube diameter has a different concentration dependence than the screening length.

$$a \sim c^{-2/3} \tag{7}$$

In the melt of pure polymer ($c = 1/b^3$) we know that the tube diameter is considerably larger than the screening length. In semidilute Θ solutions, $\xi < a$ as depicted in Figure 1. As we lower the concentration, the screening length increases faster than the tube diameter, and below some very low concentration c_x the tube diameter follows the concentration dependence of the screening length. In order to have some idea of the crossover concentration c_x, we assume the prefactor for eq 6 is $1/b^2$ and the prefactor in eq 7 is a_1/b^2 where a_1 is the tube diameter in the melt. We can therefore crudely estimate $c_x = (1/a_1)^3$. Typical polymers have $a_1 = 10b$ and thus the volume fraction of polymer corresponding to c_x is of order 10^{-3}. We obtain additional evidence that c_x is very low from Figure 2, where we plot values of ξ and a from experiments on polystyrene in cyclohexane. The experimental values of the static screening length ξ were obtained from neutron scattering by Cotton et al.[17] The line going through those data is $\xi = 5.43/c$ (with ξ in Å and c in g/cm^3), which is consistent with the scaling relation (eq 6). Values of the tube diameter were calculated from the modulus data of Adam and Delsanti[8] using eq 10 with the screening length ξ calculated from the fit of the data for ξ from ref 17. The line drawn through the calculated values of a has a slope of $-{}^2/_3$, so as to be consistent with the scaling relation (eq 7). This line extrapolates to a melt value of $a_1 \approx 100$ Å, which is in good agreement with the accepted value[15] of 82 Å, for polystyrene. The intersection of the two lines in Figure 2 gives an estimate of $c_x \approx 3 \times 10^{-4}$ g/cm^3.

$$a \sim \begin{cases} c^{-1} & c^* < c < c_x \\ c^{-2/3} & c > c_x \end{cases} \tag{8}$$

For ordinary polymers (i.e., all experimental studies which we are aware of) c^* is always larger than c_x and eq 7 describes the full concentration dependence of the tube diameter. Only for extremely high molecular weight polymers (with M of order 10^8) will c^* be less than c_x and eq 8 be needed. Since the case where $c < c_x$ corresponds to $a \sim \xi$, the single parameter scaling results are valid in this regime. We therefore focus on the regime $c > c_x$ in what follows.

Calculation of Plateau Modulus

Plateau modulus in rubber elasticity[18] is determined as $\nu_e kT$, where ν_e is the number of entanglement strands per unit volume. Therefore, the temporary network stores kT per entanglement strand. The entire volume of a sphere of diameter a in Figure 1 is filled with blobs of diameter ξ. However, the relevant volume for plateau modulus is not a^3 but is instead $(N_e/g)\,\xi^3$, where N_e/g is the number of blobs in an entanglement strand (N_e monomers/strand and g monomers/blob). In other words, the blobs making up the entanglement strand (i.e., those actually shown in Figure 1) are jointly storing kT of elastic energy. There are, of course, other blobs within the a^3 volume which are parts of other strands.

We calculate the number of blobs per entanglement strand, N_e/g, from a simple random walk of blobs.

$$N_e/g \approx (a/\xi)^2 \tag{9}$$

We therefore have a general equation for the concentration dependence of the plateau modulus.

$$G \approx kT/(a^2\xi) \tag{10}$$

Equation 10 leads to the de Gennes prediction for the plateau modulus in good solvents $G \sim c^{9/4}$, since a and ξ have the same concentration dependence in good solvents. However, the prediction in a Θ solvent is a new result.

$$G \sim c^{7/3} \tag{11}$$

Not surprisingly, eq 10 is identical with the conventional equation for plateau modulus of polymers from rubber elasticity theory[18] (the entanglement molecular

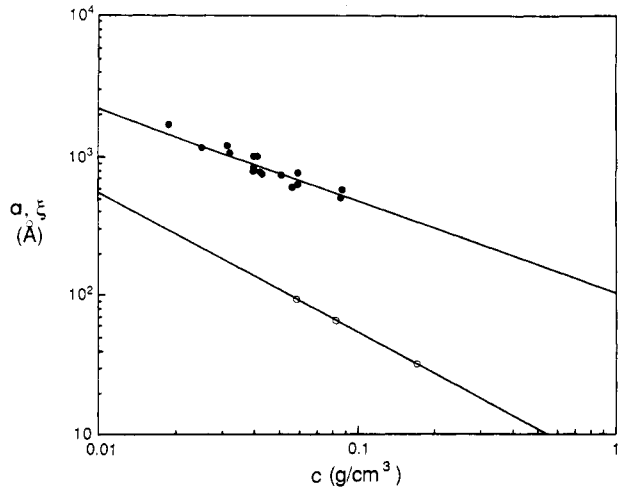

Figure 2. Concentration dependence of the two length scales in a Θ solvent (polystyrene in cyclohexane at 35 °C). Open circles are data for the screening length ξ from neutron scattering (ref 17). Filled circles are values of the tube diameter a calculated from the data of refs 8 and 17 using eq 10. The lines have slopes of −1 and −2/3.

weight in a Θ solvent is $M_e \sim a^2$ and $\xi \sim c^{-1}$).

$$G \approx kT/(a^2\xi) \approx cRT/M_e \tag{12}$$

Calculation of Relaxation Time and Viscosity

We calculate the longest relaxation time from reptation theory,[15] assuming relaxation is Zimm-like inside blobs and relaxation of strands of blobs between entanglements is Rouse-like. (This essentially assumes that excluded volume and hydrodynamics are screened at the same length scale ξ).

$$\tau \sim \eta_s\xi^3(N_e/g)^2(N/N_e)^3 \sim \eta_s a^4/\xi(N/N_e)^3 \tag{13}$$

The second result is obtained by using eq 9. The viscosity is determined from the product of plateau modulus and longest relaxation time since all other relaxation times in the terminal zone are determined by τ.

$$\eta \approx G\tau \approx \eta_s(a/\xi)^2(N/N_e)^3 \tag{14}$$

For semidilute solutions in a good solvent (and Θ solutions of extremely high molecular weight polymers with $c^* < c < c_x$), $a \sim \xi$, $N_e \sim a^{1/\nu} \sim c^{1/(1-3\nu)}$, and we get de Gennes' result for viscosity.

$$\eta \sim \eta_s M^3 c^{3/(3\nu-1)} \sim \eta_s(c/c^*)^{3/(3\nu-1)} \tag{15}$$

For solutions in a Θ solvent with $c > c_x$, $\xi \sim c^{-1}$, $a \sim c^{-2/3}$ (see eq 8), and $N_e \sim a^2 \sim c^{-4/3}$.

$$\eta \sim \eta_s M^3 c^{14/3} \sim \eta_s M^{2/3}(c/c^*)^{14/3} \tag{16}$$

We therefore predict that the simpler c/c^* scaling for viscosity should be replaced by $\eta/(\eta_s M^{2/3})$ scaling as a power of c/c^* for Θ solutions.

Comparison with Experiments

Experimental results[6,8,19-22] for the concentration dependence of plateau modulus are consistent with a power law in concentration, with an exponent α between 2 and 2.5 (see Table III of ref 20).

$$G \sim c^\alpha \tag{17}$$

Therefore, all results are roughly consistent with the scaling predictions of $\alpha = {}^9/_4$ in good solvent and $\alpha = {}^7/_3$ in Θ solvent. Relatively few studies compare plateau moduli in good solvents and Θ solvents (or near Θ solvents), and their results are summarized in Table I. While the experimental errors on α are too large for comparison of theory and experiment in an absolute sense, there is a tendency for α in a Θ solvent to be between 0% and 10% larger than in a good solvent. The ratio of α in a Θ solvent to that in a good solvent predicted by our scaling theory is 28/27 = 1.04, in excellent agreement with experiments.

Table I
Experimental Values of α in Good and Θ Solvents

α		
good solvent	Θ solvent	ref
2.36 ± 0.2	2.5 ± 0.2	6, 8
2.11 ± 0.1	2.32 ± 0.1	21
2.3 ± 0.1	2.3 ± 0.1	22

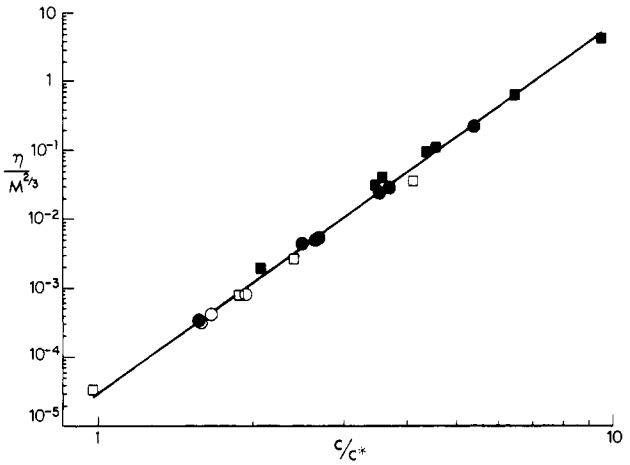

Figure 3. Viscosity data of Adam and Delsanti[8] in a Θ solvent (polystyrene in cyclohexane at 35 °C) plotted in the scaling form of eq 16: open circles, $M = 2.89 \times 10^6$; open squares, $M = 3.84 \times 10^6$; filled circles, $M = 6.77 \times 10^6$; filled squares, $M = 2.06 \times 10^7$.

Viscosity data for different molecular weight polymers in good solvents can be reduced to a common curve by plotting viscosity as a function of c/c^*.[4-7] However, when applied to Θ solvents, this scaling does not work.[8,9] Our scaling theory predicts that $\eta/M^{2/3}$ should scale as a power law in c/c^* in a Θ solvent (see eq 16). We therefore replot the data of Adam and Delsanti[8] on four different molecular weights of polystyrene in cyclohexane (a Θ solvent) in this form in Figure 3. Clearly, this scaling is of the proper form, as all data are reduced to a common power law, with an exponent of 5.4.

Roy-Chowdhury and Deuskar[9] have data on viscosity of polybutadiene solutions in two different Θ solvents (isobutyl acetate and dioxane) for three different polymer molecular weights. We plot their data as $\eta/(\eta_s M^{2/3})$ as a function of $c[\eta]$ in Figure 4 (intrinsic viscosity $[\eta] \sim 1/c^*$). Clearly, our scaling theory works for these data as well, since all data are reduced to a single curve which is a power law with exponent 4.8 for $c[\eta] > 2$.

There is evidence in the literature that viscosity has a stronger concentration dependence in poor solvents than in good solvents.[5-9,20] This observation is predicted by our scaling theory which predicts $\eta \sim c^{3.75}$ in good solvent and $\eta \sim c^{4.67}$ in Θ solvent. Experimental values of those exponents are typically slightly larger than the predicted values in both solvents (see Table III of ref 20). Mechanisms of relaxation other than reptation (such as contour length fluctuations) may account for this discrepancy.[20] If we include the effect of fluctuations in a very crude manner in eq 14 by using $(N/N_e)^{3.4}$ instead

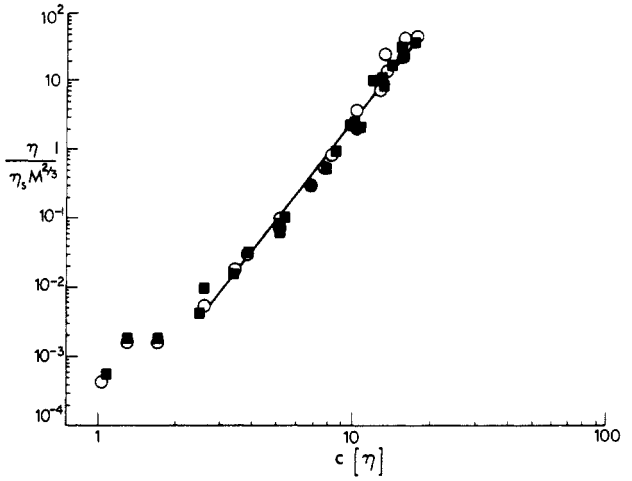

Figure 4. Viscosity data of Roy-Chowdhury and Deuskar[9] in two Θ solvents plotted in the scaling form of eq 16 ($[\eta] \sim 1/c^*$): open circles, polybutadiene in isobutyl acetate at 20.5 °C; filled squares, polybutadiene in dioxane at 20.2 °C.

of $(N/N_e)^3$, we increase the exponents for the concentration dependence of viscosity in both good and Θ solvents by roughly 0.5.

Conclusions

Starting from the conjecture that the topological constraint referred to in the literature as an entanglement is due to the collective effect of a fixed number of binary intermolecular contacts, we derive a scaling theory for semidilute solutions which incorporates the effects of two length scales, the screening length and the tube diameter. The results of this general theory for plateau modulus and viscosity are eqs 10 and 14, respectively. We test the theory in two well-defined limits: good solvent and Θ solvent. In good solvents the two length scales have the same concentration dependence, and thus we recover the simple and elegant single parameter scaling derived by de Gennes.[2,3] For Θ solvents the two length scales have different concentration dependences, and this results in slightly more complicated scaling relations for semidilute Θ solvents. Brochard and de Gennes have already pointed out that these length scales may have different concentration dependences in a Θ solvent. However, they calculate the concentration dependence of the tube diameter from the concentration dependence of intramolecular binary contacts. We contend that intermolecular binary contacts are required for entanglement. The number of contacts which collectively form an entanglement turns out to be rather large (of order 100) resulting in $a > \xi$ (see Figures 1 and 2). The exact number of contacts required for entanglement formation is expected to be purely geometrical, and we plan to explore this via computer simulations. It is important to note that while the binary interchain interactions that make up the tube are quite local, the fact that many contacts are required for a single entanglement implies that *entanglements are not local.* Our model in fact predicts that the entanglement strand volume ($a^2\xi$) does not have the same concentration dependence as the entanglement volume (a^3) in a Θ solvent—a fact which is inconsistent with any local notion about entanglements.

Recently Lin[23] and Kavassalis and Noolandi[24] have suggested that entanglements are controlled by a constant number of strands per volume a^3. Our conjecture for entanglement is consistent with theirs in the melt and in good solvent (where $a \sim \xi$), but we differ in our treatment of the Θ solvent. The entanglement strand volume in our theory is $a^2\xi$. Since a and ξ have different concentration dependences in Θ solvent (see Figure 2), we predict the number of strands per volume a^3 to increase with concentration, as $a/\xi \sim c^{1/3}$.

Rubber elasticity expresses the plateau modulus as kT per entanglement strand which leads to $G \sim kT/(a^2\xi)$. This results in the de Gennes scaling laws for modulus and viscosity in good solvent. When combined with our mean-field conjecture of the concentration dependence of the tube diameter in a Θ solvent $a \sim c^{-2/3}$, we arrive at new predictions for the modulus and viscosity in semidilute Θ solvent (eqs 11 and 16). Clearly, the resulting predictions for plateau modulus and viscosity are in accord with experimental data (see Table I and Figures 3 and 4). The prediction of the plateau modulus exponent $\alpha = {}^7/_3$ is also in good agreement with a recent calculation by Iwata and Edwards[25] of $\alpha = 2.36$ for semidilute Θ solutions.

Obviously, it would be interesting to experiment with polymers of sufficiently high molecular weights that $c^* < c_x$, so that the predicted crossover in the vicinity of c_x for modulus and viscosity in Θ solvents could be tested. Unfortunately, the experimental difficulties associated with these extremely high molecular weights ($\sim 10^8$) may preclude these tests for some time.

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Registry No. Polystyrene, 9003-53-6; polybutadiene, 9003-17-2.

Microstructure of Poly(but-2-ene sulfone) and the Role of the SO_2–Olefin Charge-Transfer Complex in the Polymerization Reaction[1]

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ABSTRACT: Two model compounds for the poly(but-2-ene sulfone) chain have been prepared and characterized by IR and NMR spectroscopy, and the crystal structure of one of these, *meso*-2,3-bis(isopropylsulfonyl)butane, has been established. Similarities in the infrared and ^{13}C NMR spectra of the models and of the polymer chains allowed us to identify *meso*-but-2-ene and *rac*-but-2-ene residues within the polymers, and the influence of other microstructural features upon the fine structure of the ^{13}C NMR spectra has been observed. While the polymer derived from *cis*-olefin has racemic residues irrespective of the preparation temperature, the polymer derived from the *trans*-olefin has an increasing proportion of *meso*-alkene structures as the temperature is lowered. This we interpret as proving that the charge-transfer complex is the main reacting species at low temperatures.

Introduction

There has been a long debate over the role of the charge-transfer complexes that form from olefins and sulfur dioxide in the reaction scheme for the formation of the 1:1 alternating copolymers, the poly(olefin sulfone)s.[2-5] A proof that the complex itself is a reacting species in the free-radical chain reaction has not previously been offered. This we attempt to do, by showing a relationship between the structure of the olefinic monomer and the microstructure of the poly(but-2-ene sulfone) chain with the aid of ^{13}C NMR spectroscopy. This chain is extremely simple in structure, as there are only achiral sulfonyl and chiral methylmethylene units present, the latter being found as pairs: $-SO_2-$ alternating with $-CH(CH_3)-CH(CH_3)-$.

The existence of the charge-transfer complexes in mixtures of olefins and SO_2 has been demonstrated by a number of methods; with styrene, they have a straw yellow color,[3] but more often they are detected in the UV spectrum[3,4] or by monitoring the ^1H NMR shifts as a function of the composition.[5,6] The phase diagram of mixtures of SO_2 and 2,3-dimethylbut-2-ene shows a temperature maximum at a 1:1 proportion,[5] as do mixtures of SO_2 and vinyl chloride.[6] By the same measure isobutene forms a 2:1 complex with SO_2[7] and vinyl chloride also forms a 1:2 complex.[6] (In that case the second SO_2 molecule is probably coordinated through the chlorine atom.) Typically, if a 1:1 complex is assumed, for 10:1 mixtures of SO_2 and olefin, at least 40% of the olefin might be in the complexed form,[2,5] so the reaction must be influenced by their presence. It is not possible to argue from the 1:1 copolymer composition that a 1:1 complex is a reacting species; the composition may simply reflect the ability of the radical of one monomer to react only with the free form of the other monomer.[4,8-10] Computer simulations have shown that the formation of the variable composition poly(vinyl chloride sulfone) might involve the complex at a low temperature, but there were other explanations.[11] In terpolymerizations with acrylonitrile or with *n*-butyl acrylate, the increase in polymer content of 1-butene and sulfonyl residues upon UV irradiation has been attributed to the activation for propagation of the olefin–SO_2 charge-transfer complex by a quantum of light.[12,13] Here we develop new arguments, based upon the stereochemistry of the residues derived from *cis*- and *trans*-but-2-enes in the polysulfones, that point to the charge-transfer complex being a reacting species at low temperatures.

According to the infrared spectra, identical polysulfones were obtained from the cis and trans isomers of but-2-ene when these were first examined.[14,15] However ^{13}C NMR spectroscopy later found a new type of residue, that formed from the *trans*-olefin when the preparation temperature was lowered to near −78 °C.[16] Structural assignments were then made on the basis of the γ carbon effect of Grant and Paul[17] coupled with an assumption that the preferred conformation of the C–C bond was trans, but the possible interference of a larger conformationally sensitive γ effect from the two oxygen atoms of the sulfone group[18] was neglected.

To check these assumptions, we have prepared and characterized two model compounds for the polymer chain. They contain *meso*-2,3-bis(alkylsulfonyl)butane and *rac*-2,3-bis(alkylsulfonyl)butane structures, the alkyl groups being isopropyl groups. Thus they represent one alkylene residue of the polymer flanked on each side by a sulfone group and a unit equivalent to half an alkylene residue:

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