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Poly(tetrafluoroethylene): Molecular Weight Distributions and Chain Stiffness[†]

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ABSTRACT: Low molecular weight poly(tetrafluoroethylenes) have been prepared that, as characterized by DSC, have lower melting points but similar virgin morphologies when compared to high molecular weight polymer. Dynamic rheometry and creep measurements are used to characterize the molecular weight distributions of these polymers. The molecular weight distributions are shown to be bimodal, which is consistent with a heterogeneous polymerization medium where the surfactant plays an important role in determining the morphology of the virgin polymer. Additionally, these results illustrate that the inherent chain stiffness of poly(tetrafluoroethylene) is very similar to that of polyethylene at least in terms of the number of chain atoms between entanglements.

Introduction

Virtually from the discovery of poly(tetrafluoroethylene)[1] (PTFE) there has been considerable interest[2] as to the chemical/physical origins of its unusual properties as compared to polyethylene. These differences have been attributed[3] to either a difference in the repeat unit chemical structure and/or the chain architecture. A major impediment to further development of this understanding has been the apparent intractability of this polymer. Although the dissolution characteristics of PTFE are now well understood[4] and some solution characterization methods appear to be potentially applicable,[5,6] there exist no estimates of molecular weights or distributions of undegraded polymer based upon solution methods. Melt rheology has been previously used to characterize molecular weight distributions of copolymers of hexafluoropropylene with tetrafluoroethylene (FEP).[7] We report here the use of melt rheology, using a slight modification of previously established methods,[8] to characterize the molecular weight distributions and number of chain atoms between entanglements for PTFE. These results yield further insight into the relationship of the unique properties of this polymer to its chemical structure and the morphology produced in the polymerization process.

Experimental Section

Low molecular weight homopolymers of tetrafluoroethylene were prepared by free radical dispersion polymerization in an aqueous medium containing ammonium perfluorooctonate as the surfactant. Molecular weights and distributions were manipulated by variation of the relative concentrations of disuccinic acid peroxide initiator and hydrocarbon chain transfer agent to the monomer concentration. From the molar ratio of monomer to initiator, assuming radical coupling as the only termination mechanism, we anticipated $M_n \leq 3 \times 10^5$. Differential scanning calorimetry measurements were performed on samples of about 5-mg weight with heating rates of 10 °C/min from −70 to 400 °C with a Mettler DSC30 equipped with a data logging station.

Dynamic rheometry measurements were made on a Rheometrics System IV rheometer at 380 °C in a parallel-plate geometry. Low molecular weight PTFE samples that had been initially cold pressed into 2.54-cm-diameter disks of 0.1-cm thickness were loaded under dry nitrogen gas. Measurements of the dynamic shear moduli were made at frequencies from 0.01 to 500 rad/s. Measurements of the dynamic tensile modulus were made on the same instrument over the same temperature and frequency range; the PTFE used in the tensile measurements was a commercial very high molecular weight polymer whose molecular weight is very approximately in the range $M_w = 10^7$–10^8.

Table I

Room Temperature and Melting Enthalpy of Virgin PTFE

polymer	$\Delta H_r{}^a$	$\Delta H_f{}^a$	R^b	T_m,^{d} °C	$\Delta H_c{}^c$	T_c,^{e} °C
PTFE-5	2.55	17.1	14.9	328.4	14.4	313.0
PTFE-6	2.19	16.2	13.5	326.5	15.1	314.1
PTFE-7	2.52	16.1	15.6	327.7	14.7	313.3

[a] Enthalpy at room temperature (ΔH_r) or melting transition (ΔH_f) of virgin polymer (cal/g). [b] $(\Delta H_r/\Delta H_f) \times 100$. [c] Enthalpy of crystallization of once-melted polymer (cal/g). [d] T_m is the peak melting temperature of virgin polymer. [e] T_c is the peak crystallization temperature of once-melted polymer.

Results

Results from the DSC characterization of the three homopolymers are given in Table I. The values of the latent heats of the room temperature transitions (ΔH_r) and the melt transition (ΔH_f) are consistent with those previously identified as being characteristic of virgin high molecular weight polymer.[9,10] Additionally, the ratio of the enthalpy of the room temperature transitions to the enthalpy of fusion is close to the value (13–14%) found[9] for virgin polymer. The melting point of these polymers is significantly lower (326.5–328.5 °C) than has been found for very high molecular weight virgin polymer; however, the depression of the melting point is consistent with previous literature results[10,11] on the dependence of virgin polymer melting point with molecular weight. Furthermore, from the enthalpies of crystallization and the melting points of the virgin polymers listed in Table I, we can estimate[12] an upper bound for M_n of less than 3×10^5. Therefore, the DSC data indicate that these polymers are of much lower molecular weight but possess a similar morphology as compared to virgin very high molecular weight commercial material.

Dynamic rheometry results for the three low molecular weight PTFE samples are shown in Figure 1. The strain was sufficiently small to be in the linear viscoelastic regime.

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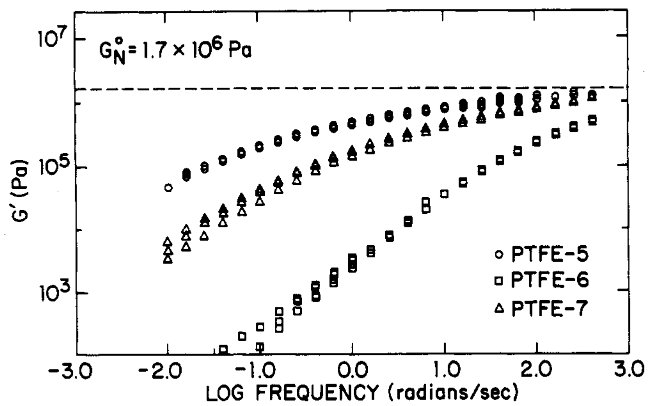

Figure 1. Elastic shear moduli of three PTFE samples at 380 °C versus shear rate. Three data sets for each polymer. Horizontal line is G_N^0 (see text).

Transformation of these curves to molecular weight distribution curves encompasses many assumptions.[8] For this reason, we describe here the procedure, with potential pitfalls, we have used.

As we have previously shown[8] for monodisperse, blended, and polydisperse samples of polystyrene, the dynamic elastic modulus (G') in the terminal zone, as a function of frequency (ω), can be transformed to a cumulative molecular weight distribution. In the high-frequency limit of the terminal zone, G' reaches its plateau value of G_N^0. As the frequency is decreased G' decreases monotonically; this initial decrease reflects the disentangling[13] of the lowest molecular weight chains. As the frequency is further decreased, chains of progressively higher molecular weight are able to disentangle on this time scale until all chains are disentangled when the time scale of the experiment becomes of the order of the terminal relaxation time. If we assume that the unrelaxed chains at any frequency are diluted by, but not entangled with, the relaxed chains, the contribution of the unrelaxed chains to the storage modulus is proportional to the square of the weight fraction of unrelaxed chains (W_u^2)[8]

$$W_u = (G'(\omega_i)/G_N^0)^{0.5} \qquad (1)$$

where ω_i is the frequency at which all chains whose molecular weight is less than M_i have relaxed and $[G'(\omega_i)/G_N^0]^{0.5}$ is defined as the square root of the reduced modulus. This approach is derived from the theoretical and experimental analysis of concentrated polymer solutions[13,14] and has been previously shown to be applicable to polystyrene melts with substantially different molecular weight distributions.[8]

Figure 2 illustrates this transformation for sample PTFE-7. This transformation assumes that each monodisperse component of the molecular weight distribution has a single relaxation frequency. At frequencies smaller than this characteristic frequency we assume that this component makes no contribution to the elastic modulus. This assumption partially ignores the distribution of relaxation times that exist for a monodisperse polymer.[15] Nevertheless, this method has been demonstrated[8] to be quite satisfactory for generating molecular weight distributions that are in good, but not perfect, agreement with results obtained from gel permeation chromatography. The data of Figure 2 are then fitted to an equation of the form

$$(G'(\omega)/G_N^0)^{0.5} = \sum_i A_i[1 + \tanh (B_i(X + C_i))]/2 \quad (2)$$

where the index i has values of 1 and 2. $X = \log \omega$. A_i, B_i, and C_i are adjustable parameters which are determined in a least-squares sense by fitting eq 2 to the data. The values of A_i, B_i, and C_i determined for the three PTFE samples via this procedure are given in Table II. (This fitting function describes the data sets just as well as the function[8,16] used previously but offers the advantage of increased numerical stability in the fitting procedure.) From the values given in Table II the relative magnitude of the two components used to fit the data is given by A_i ($\sum A_i = 1$); B_i defines the width of the curve (a smaller B corresponds to a broader curve), and C_i is the relative position of the curve on the abscissa. Using $i = 1$ in eq 2 yields only a symmetrical sigmoidal curve for the square root of the reduced modulus as a function of frequency. Figure 2 illustrates that a one-term fit does not fit the data as well as a two-term fit for PTFE-7. A two-term fit has been used to fit the data for all three polymers, and this procedure can yield a molecular weight distribution that appears by visual inspection to be monomodal (see the curve for PTFE-6 in Figure 4 and footnote c in Table III).

Next the abscissa is transformed to a relative molecular weight (MW) scale by use of the relationship

$$1/\omega = K_1(\mathrm{MW})^{3.4} \qquad (3)$$

The value of K_1 is determined from polystyrene standards.[8] The cumulative molecular weight (CMW) distribution is given by plotting CMW = 1.0 − W_u from eq 1 vs MW from eq 3. Alternatively, the differential molecular weight

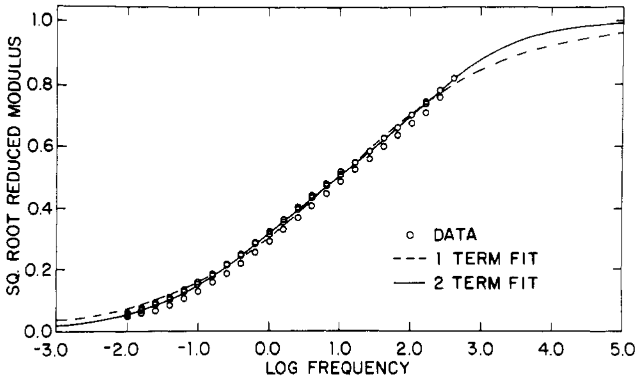

Figure 2. Square root of the reduced modulus, $(G'(\omega)/G_N^0)^{0.5}$, of PTFE-7 versus ω with the curves fitted from eq 2 for one and two terms in the sum; the dashed line is for a one-term fit, and the solid line is for a two-term fit. Three data sets are shown.

Table II
Values of Fitting Parameters Obtained for $(G'(\omega)/G_N^0)^{0.5}$

polymer	A_1	B_1/B_2	C_1/C_2
PTFE-5	0.44	0.51/0.57	-1.6/+1.3
PTFE-6	0.89	0.60/1.14	-2.7/-1.3
PTFE-7	0.36	0.84/0.56	-2.4/-0.1

Table III
Zero Shear Viscosities and Molecular Weights

polymer	η_0[a]	M_w[b]	M_w/M_n
PTFE-5	14	2.3	8.2
PTFE-6	0.026	0.34[c]	2.8
PTFE-7	5.8	1.8	4.3

[a] MPa·s. [b] 10^6 g/mol. [c] The molecular weight of this sample is too low to determine the presence or absence of a low molecular component in the molecular weight distribution function (incomplete characterization of the high-frequency portion of the terminal zone). Attempts to more fully characterize this component by measuring the shear modulus at lower temperatures were fruitless due to the weak temperature dependence of the zero shear viscosity and the onset of crystallization at 330 °C.

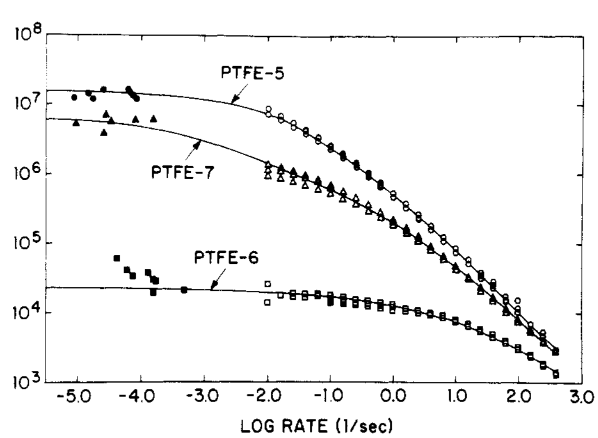

Figure 3. Shear viscosity for PTFE at 380 °C. Solid symbols represent viscosity versus shear rate data obtained from a constant-stress rheometer, and open symbols represent the complex dynamic viscosity data versus frequency. The solid line is only a visual aid. Three data sets are shown.

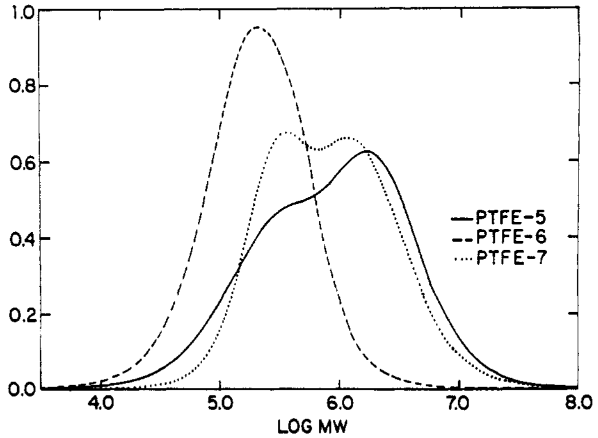

Figure 4. Differential molecular weight distributions for samples PTFE-5,-6,-7.

distribution curve is found by numerical differentiation of the square root of the reduced modulus with respect to log MW.

Lastly, the abscissa is scaled to an "absolute" weight average molecular weight, which is obtained from the relationship of the zero shear viscosity (η_0) to weight average molecular weight

$$\eta_0 = K_2(M_w)^{3.4} \qquad (4)$$

Values for the zero shear viscosity were estimated (Figure 3) from a combined plot of the frequency dependence of the dynamic viscosity and steady-state viscosity (obtained with a Rheometrics constant-stress rheometer). Values of the zero shear viscosity estimated in this fashion are given in Table III. K_2 is assigned a value of $10^{-13.5}$ from our recent efforts[17] to expand and reevaluate the previous[7] characterization of copolymers of hexafluoropropylene with tetrafluoroethylene (FEP). Thus our values for absolute molecular weights in the molecular weight distribution curves shown in Figure 4 are dependent upon the similarity of K_2 for FEP and PTFE.

The shape of the molecular weight distribution curves is critically dependent upon the determination of the plateau modulus. We have used two different methods to generate three values of $G_N{}^0$ for PTFE. From the data of Figure 1, we can estimate that the plateau modulus should be in the range $(1.5 \pm 0.5) \times 10^6$ Pa. Additionally, from integration of the loss modulus[13] over the range $\omega = 10^{-3}$–25 rad/s for sample PTFE-5 (Figure 5) we can obtain an estimate of $G_N{}^0/2$. This procedure yields $G_N{}^0 = 1.6 \times 10^6$ Pa. These determinations of $G_N{}^0$ were carried out with the low molecular weight PTFE samples described above. We also attempted to use torsional shear in a parallel-plate geometry to measure the dynamic modulus of a very high molecular weight PTFE. The inapplicability of this geometry, in our apparatus, to high molecular weight PTFE was confirmed by our observation of increasing values of the apparent elastic modulus with decreasing strain. Even in the limit of the smallest strains used (0.1%), the apparent modulus was strain dependent; additionally, values of moduli on nominally identical samples measured under the same conditions varied by a factor of 2. The failure of this characterization method for the very high molecular weight PTFE is a direct consequence of the very high melt viscosity of this polymer, which leads to either imperfect adhesion of the melt to the parallel plates, nonlinear viscoelastic behavior, or effects due to machine compliance. For these reasons, we chose to measure the dynamic modulus of the very high molecular weight PTFE in tension; this material has sufficient elasticity to survive clamping at 380 °C. Figure 6 illustrates the dependence of Young's modulus upon frequency for this material. In calculating E', we accounted for expansion of the sample from its dimensions at room temperature to 380 °C by direct measurement of the dimensions; the dimensions had changed by 15%, which is in good agreement with the temperature dependence of the specific volume data.[18] The data in Figure 6 illustrate that the plateau value of the tensile modulus is 5×10^6 Pa. For a polymer melt,[13] $G_N{}^0 = E_N{}^0/3$, and thus we find $G_N{}^0 = 1.67 \times 10^6$ Pa.

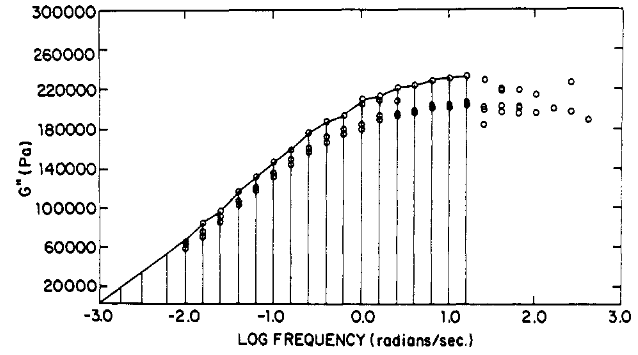

Figure 5. Loss shear modulus of PTFE-5 versus frequency with integration area outlined. Three data sets are shown.

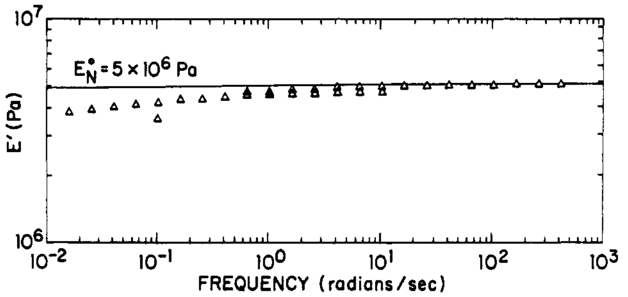

Figure 6. Elastic tensile modulus of high molecular weight PTFE versus frequency. Horizontal line is $E_N{}^0$. Data sets for two different values of strain are shown.

We believe that the three values of $G_N{}^0$ obtained as described above are in surprisingly good agreement. Although there is very little difference between any of the three values, we believe the tensile measurement to be most accurate and choose $G_N{}^0 = 1.7 \times 10^6$ Pa. This value is indicated in Figure 1.

Discussion

In comparison with many other polymers, PTFE possesses many unusual properties, such as chemical inertness, high thermal stability, solvent resistance, high lubricity, and a low dielectric constant, which are attributable to its basic chemical structure.[3] These properties are thought to be due to the strength of the C–F bond, shielding of the carbon backbone by the fluorine substituents, and the weak secondary forces that exist between adjacent polymer chains. Additionally, virgin (never melted) PTFE has very unusual rheological properties that are similar to those observed in low molecular weight liquid crystals.[19] These properties are believed to be due to the extended chain structure of the extended and folded ribbon morphologies observed in the virgin polymer.[20] This morphology has been attributed to both the temperature of the polymerization[20] and the presence of surfactant in the aqueous polymerization medium.[10,11,20] From these observations[10,11] a molecular weight dependent polymerization mechanism has been proposed, which implies a bimodal molecular weight distribution for PTFE whose shape is dependent upon the relative concentration of surfactant to PTFE. Thus our results of bimodal molecular weight distributions (Figure 4) are in qualitative agreement with previous electron microscopy[20] and thermal analyses.[12] At the present time we do not have sufficient data to comment on whether the observed bimodality of the molecular weight distribution is confirmed to be intimately associated with the different morphologies formed during the polymerization. Note that the shapes of the molecular weight distribution curves are dependent upon determination of the proper value for G_N^0 and the validity of eq 1 but are not dependent upon the value of K_2 used.

Determination of the proper value for G_N^0 is critical for not only the determination of the shape of the molecular weight distribution curve, but also for understanding the role that chain stiffness plays in the formation of the extended chain morphology during the polymerization process. From our value of G_N^0 and a value[18] of the density at 380 °C of 1.4614 g/cm^3, we calculate[13] that the molecular weight between entanglements is 4667 g/mol, which corresponds to the number of chain atoms between entanglements (N_e) of 93. This may be compared to a previously determined value of 132 for PTFE,[21] 119 for FEP,[7] and also a value of $N_e = 90$ for polyethylene.[13] Thus it appears that at least in terms of N_e the flexibilities of PTFE, FEP, and PE are very similar.

Similar flexibility for PE and PTFE might be thought to be at variance with the physical properties of the two polymers. A number of observations indicate that PE and PTFE should not be expected to be of grossly different flexibility: comparison of calculated values of characteristic ratios, similar tendencies to form chain-extended structures during polymerization, and entropy of fusion. The characteristic ratio of PTFE has not been determined with great certainty, but is estimated to lie in the range 10–15 at 25 °C.[22] This may be compared to values of 6.7 (140 °C) or extrapolated values of 5.3 (380 °C) or 7.5 (25 °C) for polyethylene.[23] This would indicate that PTFE is somewhat stiffer than PE but not greatly so. This similarity and the apparent inconsistency of this finding with the substantially different physical properties of PTFE as compared to PE have been noted before.[23] One such example of an apparent inconsistency is the ability of only TFE to form extended chain structures during polymerization, but recent results have shown that these same types of structures may also be formed during the polymerization of ethylene.[24] Another example is the apparent imperviousness of PTFE to solvents, but this is only a manifestation of the relative unfamiliarity of nonaqueous and nonhydrocarbon solvents[4,25,26] and the high melting point of fluoroalkanes[27] compared to alkanes.[28] Thirdly, it had been believed that the large difference in the entropies of fusion of PE and PTFE supported the idea that the polymers differed greatly in stiffness; however, more recently it has been shown that the entropies of fusion of PE and PTFE are very similar.[9] Therefore this argument as to the inherent stiffness of PTFE is obviated.

The most salient apparent difference between commercial PTFE and commercial linear high-density PE is that the melt viscosity of the fluorinated homopolymer is so large that the material is largely intractable, whereas PE, even of ultrahigh molecular weight, is tractable in the melt. This apparent contradiction has been the basis[3] for speculation that the unique properties of PTFE melts are primarily due to the presence of fluorine rather than hydrogen being attached to the carbon backbone as opposed to arguments based on molecular weight. Therefore, we attempt here to generate a comparison of the melt viscosities of PE and PTFE (at equivalent degrees of polymerization). The zero shear viscosities of the PTFE samples are given in Table III. The zero shear viscosities of a series of fractionated linear PEs at 190 °C have been reported,[29] and the zero shear viscosity of $M_w = 2.62 \times 10^5$ is 1.6 MPa·s. In the absence of any data at 380 °C, we extrapolate to this temperature using the temperature dependence of the zero shear viscosity of PE over the range 195–280 °C previously reported[30] and extrapolate the data of ref 29 to $M_w = 6.44 \times 10^5$ (the degree of polymerization (23 000) at this molecular weight is the same as that of PTFE-5 of molecular weight 2.3×10^6). These extrapolations yield a zero shear viscosity at 380 °C for PE of 0.55 MPa·s; this is contrasted to the value found for PTFE-5 of 14 MPa·s (Table III). This comparison, which is qualitative at best, indicates that the melt viscosity of PTFE is not grossly different than that of PE when compared at equivalent degrees of polymerization and temperature; therefore, the apparent intractability of commercial high molecular weight PTFE is, to a large extent, attributable to the extremely large degree of polymerization of this polymer. Thus the flow properties and N_e of PE and PTFE are not greatly dissimilar. We are presently carrying out additional experiments with both homo- and copolymers of TFE to further address this point and to further elucidate the role that the surfactant plays in determining the molecular weight distributions in these two polymers.

Determination of absolute values of molecular weights is dependent upon the accuracy of the value of K_2 in eq 4. We have used a value that we previously determined for FEP at 300 °C.[17] The use of such a value might be quite questionable if the entanglement spacing of the two polymers were not so similar and the activation energy for flow not so small. Comparison of molecular weights found here to those anticipated from the polymerization stoichiometry and the DSC results is self-consistent. Additionally, the weight average molecular weight of one of these polymers (PTFE-5) has been recently determined[31] by light scattering, and the value of M_w found ($M_w = 2.1 \times 10^6$) is very similar to our results ($M_w = 2.3 \times 10^6$).

Conclusions

Rheological characterization of low molecular weight PTFEs has shown that previous reports of bimodal molecular weight distributions (formed during polymerization) inferred from DSC characterization are correct. Additionally, the number of chain atoms between entanglements has been found to be similar to PE and FEP. These findings reinforce previous[24] reports that the unusual morphology and processing properties of virgin PTFE are not an inherent property of the monomer or the equilibrium chain architecture but are primarily due to a very special polymerization process that produces polymer of an extremely large degree of polymerization and in a highly chain-extended form.

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Note Added in Proof. We have recently recalculated the MWDs from the data reported here using a different least-squares fitting routine. This new fitting routine allows a more objective judgment of the goodness of fit of the calculated curve to the data.[17] For PTFE this procedure gives essentially the same results as reported here, whereas for FEP copolymers the MWDs obtained with the two different procedures are found to be quite different.[17]

Registry No. PTFE, 9002-84-0.

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Theory of the Grafted Polymer Brush

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ABSTRACT: We calculate the free energy of surfaces coated with grafted polymers in a solvent. We use a self-consistent field (SCF) method appropriate for weak excluded-volume interactions and at moderately high surface coverage. We give the exact solution for the "classical limit" of our SCF equations which shows that, at high molecular weight, the concentration profile approaches a parabolic form rather than the step-function suggested by Alexander and de Gennes. Accordingly, the energy required to slightly compress the brush varies as the cube of the compression distance. An extension of the method to the good-solvent, semidilute regime is described.

Introduction

Polymers attached by one end to a substrate and immersed in solvent are a system of practical importance. Colloidal particles may be kept in suspension by grafting polymers onto their surfaces; the attached polymer layers repel each other and may keep the colloidal particles from aggregating. Equilibrium conformations of, and forces between, such polymer "brushes" have thus been the object of both theoretical[1–4] and experimental[5,6] study.

Previous theoretical treatments[1,2] of polymer brushes have employed either Flory arguments of global energy balance or scaling arguments which treat each polymer as a sequence of "blobs". In the former, the equilibrium height at fixed surface coverage is obtained by balancing the pairwise excluded-volume interaction with the free energy to stretch a typical chain away from the grafting