Molecular weight distribution in polymers of tetrafluoroethylene

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Molecular weight distributions of polytetrafluoroethylene (PTFE) determined by viscoelastic spectroscopy contain two (or three) components varying in average molecular weight by about an order of magnitude. The lowest molecular weight component has a 'most probable' distribution and is made only in the early stage of the polymerization. It is believed to be made in particles which are too small to contain more than one radical for an appreciable time. The intermediate and higher molecular weight components have narrower distributions characteristic of termination by combination of radicals. On the other hand, copolymers of tetrafluoroethylene and hexafluoropropylene (FEP) have a single population with a binary coupling distribution.

(Keywords: polytetrafluoroethylene (PTFE); viscoelastic spectroscopy; tetrafluoroethylene; hexafluoropropylene)

INTRODUCTION

Viscoelastic spectroscopy is a method recently developed for deducing the molecular weight distribution from the viscoelastic properties of a polymer melt[1–6]. The method has recently been applied to polytetrafluoroethylene (PTFE), using dynamic modulus for laboratory (low molecular weight) samples[6] and stress-relaxation modulus for commercial-grade (high molecular weight) samples[4]. The latter is especially significant, since most conventional techniques for determining the molecular weight distribution have not been applicable to commercial grade PTFEs (because of the lack of suitable solvent), although the number-average molecular weights have been estimated from the concentration of end groups or the standard specific gravity[7–9]. Recently, PTFEs prepared by free-radical polymerization have been reported to have bimodal molecular weight distribution in two independent studies[4,6]. The purpose of the present work is to analyse these distributions and relate them to the mechanisms of polymerization.

There are two principal varieties of PTFE[9]. The granular resin is prepared by aqueous 'suspension' free-radical polymerization and consists of large spongy particles which are usually cut up before use. The powder resin is prepared by aqueous 'dispersion' free-radical polymerization, and consists of fine powder particles coagulated from an aqueous dispersion of solid particles about 0.2 μm in diameter. The granular PTFE resin is usually used to make relatively large shapes, and the powder PTFE resin is used to make thin objects or coatings.

EXPERIMENTAL

Two commercial PTFE samples (a granular resin and a powder resin), and a series of four experimental powder resins were used. The series of four experimental powder samples were taken at various stages during an aqueous dispersion polymerization of tetrafluoroethylene, using disuccinic acid peroxide as the initiator. This series consists of sample S-1 taken at 10 min after 'kick-off', having 6.0% solids; sample S-2 at 20 min, having 10% solids; sample S-3 at 30 min, having 15% solids; and sample S-4 at the end of the run (86 min), having the final yield of 37.6% solids (see *Table 1*). Four commercial FEP resins (copolymers of tetrafluoroethylene with 7.2±0.2 mol% hexafluoropropylene) were also used for comparison with PTFE.

The stress relaxation modulus $G(t)$ curves in the melt at 370°C were measured with a Rheometrics Mechanical Spectrometer System IV, as discussed previously[4]. The $G(t)$ spectrum was used to obtain the relaxation time spectrum $H(\tau)$, which was next deconvoluted to obtain the weight fraction differential molecular weight distribution function $P(M)$. The theory and methodology have been discussed before by Wu[4].

The weight fraction differential molecular weight distribution curves are expressed, just as in g.p.c., as the normalized derivative, $P(M)=\mathrm{d}W/\mathrm{d}(\log M)$, so that the total weight is 100, i.e.,

$$\int_{-\infty}^{\infty} P(M)\,\mathrm{d}(\log M)=100 \qquad (1)$$

where W is the total weight.

SCHULZ–FLORY DISTRIBUTION FUNCTION

The Schulz–Flory distribution function gives the theoretical molecular weight distributions of free radical and condensation polymers[10],

$$\mathrm{d}W/\mathrm{d}(\ln X)=(k+1)(X/X_w)^{k+1}[\Gamma(k+1)]^{-1} \exp[-(k+1)(X/X_w)] \qquad (2)$$

where W is the weight, X the degree of polymerization, X_w the weight-average degree of polymerization, k the coupling constant (i.e., the number of independently

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Table 1 Samples taken during an aqueous dispersion polymerization of PTFE, using disuccinic acid peroxide as the initiator

Code	Time (min)	Solids (%)	Yield as fraction of final product	% Completion
S-1	10	6.0	0.104	10.4
S-2	20	10	0.184	18.4
S-3	30	15	0.292	29.2
S-4	86	37.6	1	100

growing chains required to form a dead chain), and Γ the gamma function. When $dW/d(\ln X)$ is plotted v. ln X, the maximum of the curve occurs at $X = X_w$. The number-average M_n, weight-average, and z-average M_z degrees of polymerization are related to each other by

$$X_n/k = X_w/(k+1) = X_z/(k+2) \qquad (3)$$

Equation (2) can be recast in a reduced form,

$$y = x^{k+1} \exp[(k+1)(1-x)] \qquad (4)$$

where $y = [dW/d(\log X)]/[dW/d(\log X)]_{\max}$ and $x = X/X_w$. In a log–log plot, the slope of the curve is given by

$$d(\log y)/d(\log x) = (k+1)(1-x) \qquad (5)$$

Therefore, in a log–log plot, the limiting slope at low molecular weights is given by

$$[d(\log y)/d(\log x)]_{x\to 0} = k+1 \qquad (6)$$

If each chain grows independently without coupling (i.e., $k = 1$), the 'most probable' distribution is obtained, having $M_w/M_n = 2$ and the width at half maximum is 0.74 decades. On the other hand, when two growing chains combine to form a dead chain (i.e., $k = 2$), a narrower distribution (i.e., the binary coupling distribution) is obtained, having $M_w/M_n = 1.5$ and the width at half maximum is 0.60 decades.

Figure 1 shows the log–log plots for two theoretical distributions, i.e., the most probable and the binary coupling distributions. They are distinguished by their limiting slopes at low molecular weights, the detailed shapes near the maximum and the widths at half maximum, but not by the shapes at high molecular weights, as analysed above. These theoretical patterns are used to compare with the experimental molecular weight distribution curves for the present samples.

COMMERCIAL PTFE RESINS

A log–log plot of the molecular weight distribution of the commercial granular resin is shown in *Figure 2*. Nearly all the data can be represented well by a binary coupling distribution for the main peak, and a most probable distribution for the low molecular weight shoulder, as indicated by the two solid curves in *Figure 2*. There is a high molecular weight tail remaining after subtraction of the two major populations, as shown. This tail represents a relatively small fraction of the polymer, is found in all samples (typical for all vinyl polymers made by free radical polymerization), and may reflect lower rates of termination towards the end of the polymerization.

The molecular weight distribution of the commercial powder resin is shown in *Figure 3*. The lower molecular weight peak is more prominent than in the granular resin (*Figure 2*), but the general features are similar. The lower molecular weight population has a most probable distribution, and the higher one has a binary coupling distribution. Again, there is a high molecular weight tail. Measurements on many other samples have shown that PTFE resins have a strong tendency to form a bimodal distribution, comprising a component having a weight-average molecular weight of about 5×10^6 and a most probable distribution, and a component having a weight-average molecular weight of about 5×10^7 and a binary coupling distribution[4]. Much of the variation in

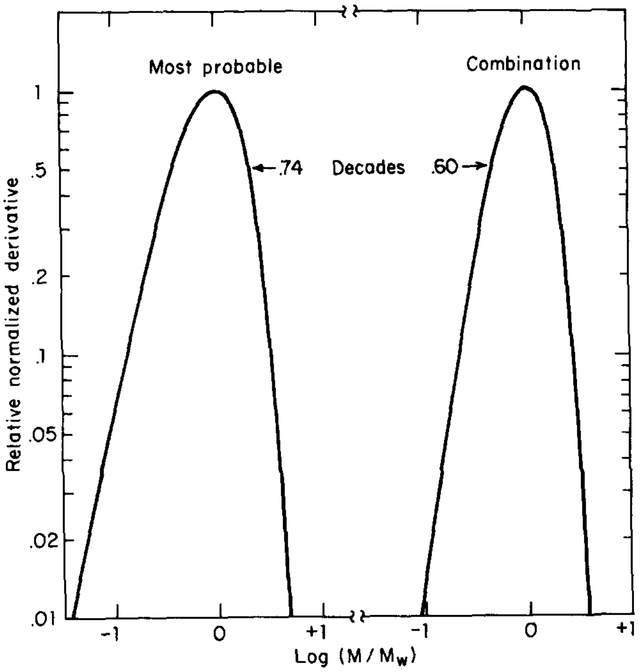

Figure 1 Theoretical molecular-weight distribution curves: most-probable and binary-coupling distributions

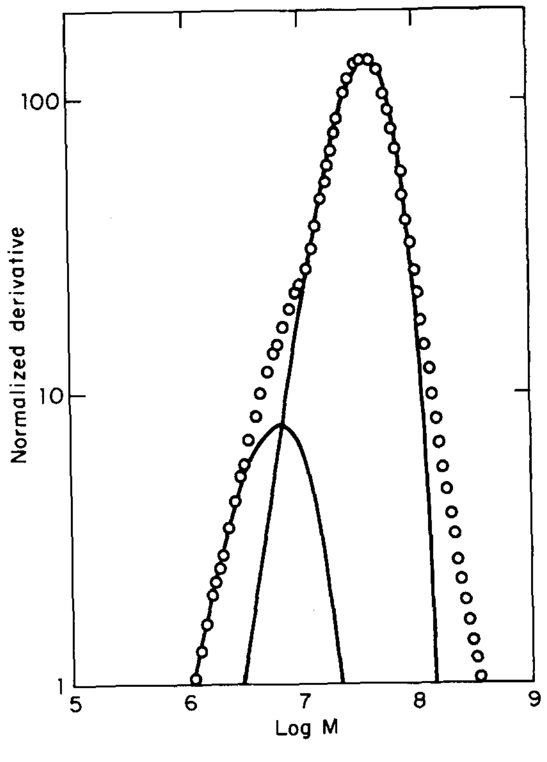

Figure 2 Differential molecular weight distribution curve for a commercial granular resin

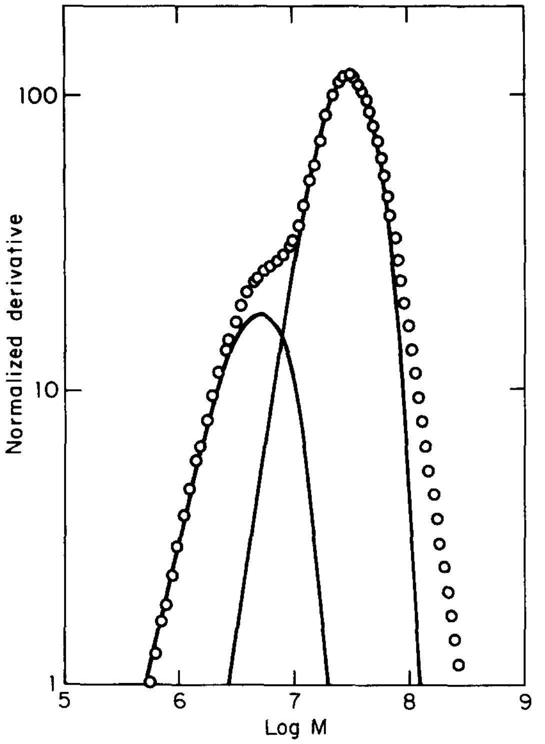

Figure 3 Differential molecular weight distribution curve for a commercial powder resin

the overall molecular weights are due to differing proportions of these two components.

PTFE POLYMERIZATION SAMPLING SERIES

The molecular weight distributions for the four powder PTFE samples taken at different stages of an aqueous dispersion polymerization are calculated from their stress relaxation modulus curves. To facilitate analysis and comparison, these curves are plotted as log $P(M)$ vs. log M in *Figure 4*, in which each curve is normalized so that its total amount corresponds to the percentage of the final resin product (see *Table 1*). For example, the final sample (S-4) has 37.6% solids, i.e., 60.2 g of polymer in 100 g of water. The first sample (S-1) has 6.0% solids, i.e., 6.25 g of polymer per 100 g of water. Therefore, the first sample is (6.25/60.2)100 = 10.4% of the final product. In other words, the polymerization process is 10.4% complete in the first sample. The final sample (S-4) is plotted so that the total amount is 100. The first sample (S-1) is plotted so that the total amount is 10.4. In such a plot, if two curves touch, it means that no polymer of that molecular weight is made in the interval between the two samples. The lines which cross are due to experimental uncertainty.

All the distributions show bimodal character, but the low molecular weight component becomes progressively less prominent as the polymerization proceeds. The higher molecular weight peak occurs at essentially the same molecular weight in all samples.

The distribution for the first sample (S-1, at 10 min and 6.0% solids) is shown in *Figure 5*. The low molecular weight peak clearly corresponds to the most probable distribution. In the subsequent samples, the low molecular weight end of the distribution continues to fit this pattern, but the peak is progressively obscured by the higher molecular weight components, shown in *Figure 4*.

Unlike the commercial granular and powder resins (*Figures 2* and *3*, respectively), it is not possible to fit the data for these samples with only two standard populations. When the functions corresponding to the solid curves in *Figure 5* are subtracted from the data, a third population is revealed. This peak, shown with a dashed curve, occurs at almost the same molecular weight in all the four samples, and has the shape of a binary coupling distribution. We will call this population BCD-1 and the major peak BCD-2.

By subtracting the appropriately weighted distribution for an earlier sample from that for a later one, it is possible to compute the molecular weight distribution of the polymer made in the interval between samplings. The molecular weight distribution of the polymer made between S-1 (6.0% solids) and S-2 (10% solids) is shown in *Figure 6*. Compared with the polymer made between 0 and 6.0% solids (*Figure 5*), the BCD-2 peak has grown at the expense of the other two peaks. In the distribution for the polymer made between 10 and 15% solids (*Figure 7*) shows well-defined BCD-1 and BCD-2 peaks, while the low molecular weight most probable distribution peak appears only as a small shoulder. The distribution for the polymer made between 15 and 37.6% solids (*Figure 8*) is completely dominated by the BCD-2 peak. The BCD-1 peak appears as a shoulder, but there

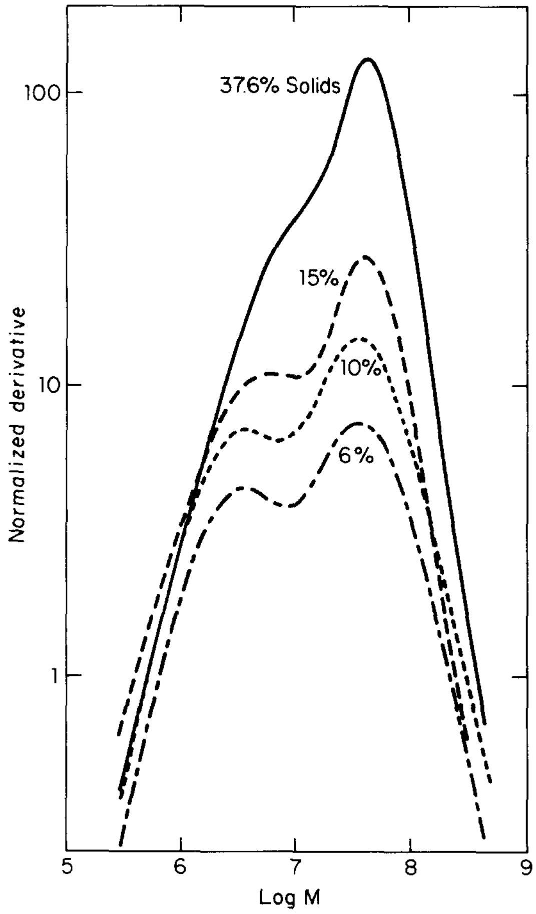

Figure 4 Differential molecular weight distribution curves for samples taken at various stages of a dispersion polymerization. Each curve is normalized to correspond to the fraction of final product. See text for explanations

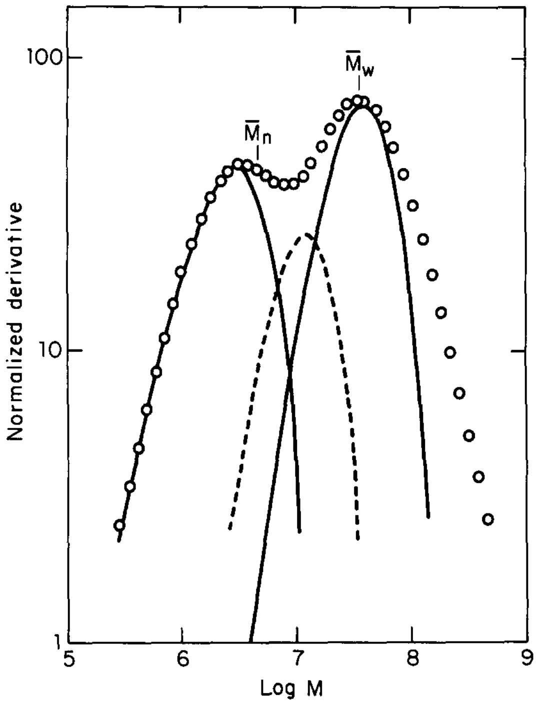

Figure 5 Differential molecular weight distribution of the sample (S-1), taken at 6.0% solids after 10 min (i.e., at 10.4% completion)

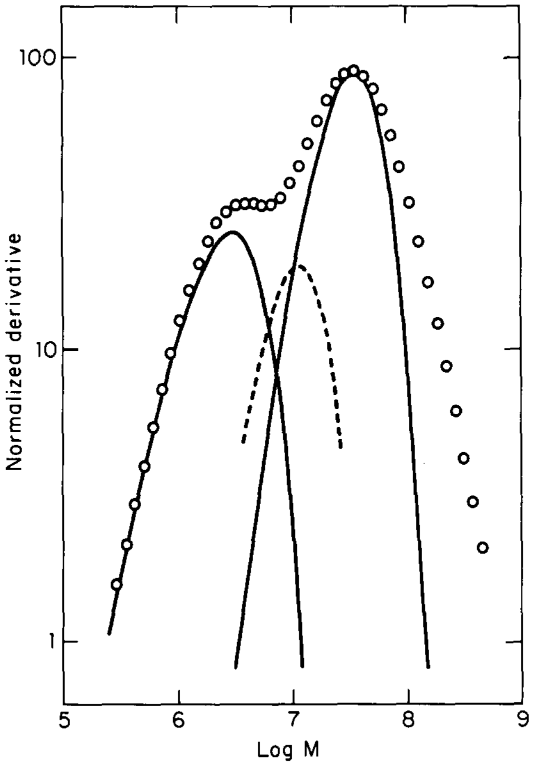

Figure 6 Differential molecular weight distribution of the polymer made between 6 and 10% solids (i.e., between 10 and 20 min, or between 10 and 18% completion)

is no detectable contribution from the low molecular weight most probable distribution population.

The results of this series suggest that the low molecular weight population which has a most probable distribution is formed only in the early stages of the polymerization, mostly below 10% solids ($\sim$20% completion of the polymerization process). This material appears to have a weight-average molecular weight of about 2.5×10^6. The BCD-1 population appears to have

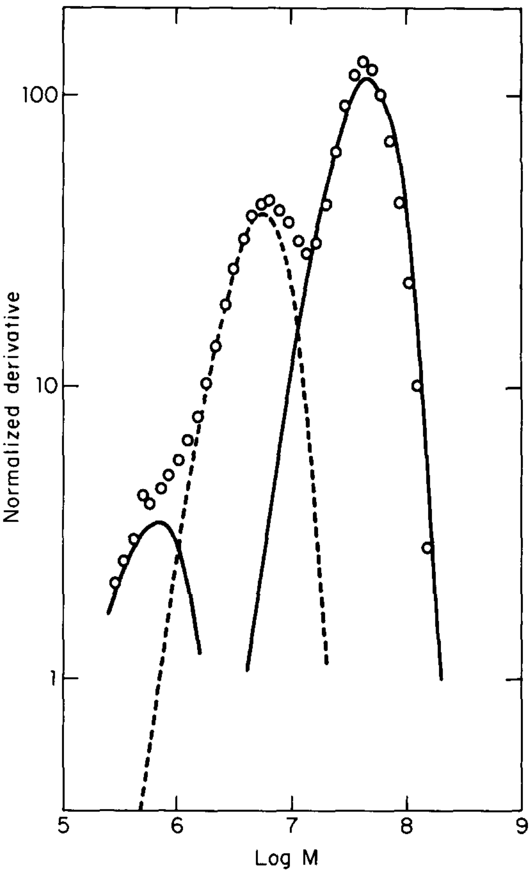

Figure 7 Differential molecular weight distribution of the polymer made between 10 and 15% solids (i.e., between 20 and 30 min, or between 18 and 29% completion)

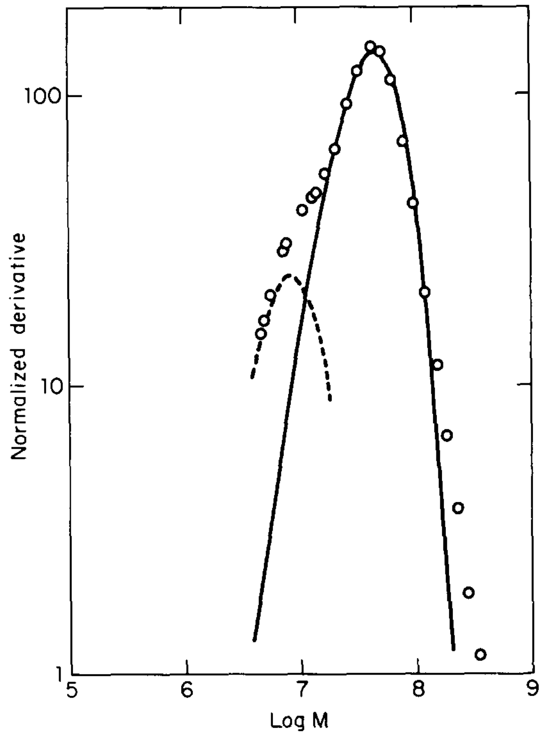

Figure 8 Differential molecular weight distribution of the polymer made between 15 and 37.6% solids (i.e., between 30 and 86 min corresponding to between 29 and 100% completion)

a weight-average molecular weight of about 10^7 and is thought to be formed throughout the polymerization as a relatively minor component.

On the other hand, the BCD-2 population has a weight-average molecular weight of about 5×10^7. Its importance increases throughout the polymerization process. By the end, it has become the dominant component. All of the samples show some evidence of a high molecular weight tail. However, this feature appears to be less significant in the polymers made after 10% solids (i.e., about 20% completion) than in the earlier ones.

COMMERCIAL FEP RESINS

Earlier, the molecular weight distributions for four commercial FEP resins were determined from dynamic modulus curves in the melt, and found to conform essentially to the binary coupling distribution[3]. The molecular weight distribution for one of these copolymers (i.e., FEP-2) is compared with the theoretical binary-coupling distribution in *Figure 9*. The agreement is excellent, except for a high molecular weight tail. Unlike PTFEs, however, the FEP resins show no signs of bimodal character. Interestingly, alternating copolymers of tetrafluoroethylene and ethylene were recently found also to have essentially binary coupling distributions by a light scattering method[11].

An interesting feature of the distributions for all of the FEP resins which have been examined is that the limiting slopes in the log–log plots of normalized derivatives vs. molecular weight at low and at high molecular weights have equal magnitude but opposite sign. The data can be approximated empirically by

$$y = 2/(x^n + x^{-n}) \qquad (7)$$

where n is the limiting slope [d log y/d log x] at $x \rightarrow 0$, $-n$ is that at $x \rightarrow \infty$, and x and y have been defined in equation (4). We do not know the reason for this phenomenon.

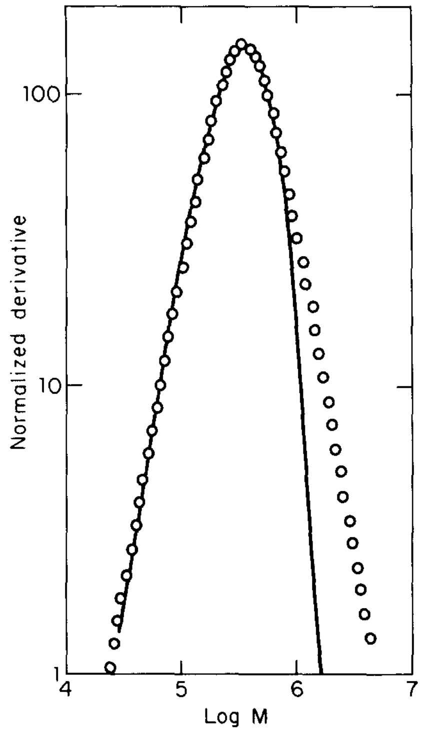

Figure 9 Differential molecular weight distribution of a commercial FEP resin (FEP-2). See ref. 3 for description of the material

DISCUSSION

Tetrafluoroethylene is polymerized in water at 60–90°C to form particles having a very high degree of crystallinity[9]. It seems probable that the polymerization is essentially confined to the particle surfaces. It is thought that the well-defined populations found in the molecular weight distribution of PTFE must have been formed in different kinds of polymerization domains. The abstraction of fluorine atoms by free radicals is not expected to occur appreciably. Therefore, termination should occur predominantly by combination of radicals, rather than by disproportionation or chain transfer.

From these considerations, it is found that the population of relatively low average molecular weight with a most probable distribution is formed in particles which are too small to accommodate more than one free radical for an appreciable time. The higher molecular weight material with a binary coupling distribution is formed in larger particles, in which more than one chain radical can grow. This type of polymerization completely dominates the later stages of the reaction.

Bimodal molecular weight distributions have been reported in the dispersion polymerizations of styrene[12] and of copolymers of vinylidene fluoride with 30 mol% TFE[13]. In the styrene system, part of the reaction occurs in small emulsion particles and the remainder in larger suspension particles. The emulsion polymerization leads to a component having a most probable distribution. The material produced in the suspension particles has a narrower distribution, indicating that at least part of termination is by combination of chain radicals. Because an organic soluble initiator (such as lauroyl peroxide) was used, the polymer made in the larger suspension particles had a lower average molecular weight than that made in the smaller emulsion particles which the initiating radicals reached less frequently having had to diffuse through the water. Contrarily, in PTFE the use of a water-soluble initiator leads to the opposite situation, resulting in a higher average molecular weight in the larger particles. In both cases, the polymer made in the smaller particles has the most probable distribution, and that made in the larger particles has the narrower binary-coupling distribution.

In contrast to PTFE, the as-polymerized particles of FEP resin are only about one-third crystalline[14,15]. Because it is known that this polymer can absorb substantial amounts of small perfluorocarbon molecules[16], it is believed that the polymerization is not limited to the surfaces of the particles. The single-moded molecular weight distribution for FEP suggests that all particles are equivalent sites for polymerization, and that termination occurs mainly by binary coupling of chain radicals.

CONCLUSION

The molecular weight distributions of PTFE and FEP resins provide clues to the mechanisms of polymerization. They support the belief that termination occurs by combination of free radicals. In PTFE, multiple populations in the molecular weight distribution are believed to be associated with different kinds of particles as sites of polymerization. A population of relatively low average molecular weight having a most probable distribution is made only in the early stages of the reaction and is attributed to polymerization on very small particles. On the other hand, populations of much higher average molecular weights are formed by combination of chain radicals in larger particles, which have binary coupling distribution and are formed predominantly in the later stages of polymerization. In contrast, the FEP resins have single-moded molecular weight distributions, characteristic of binary coupling distribution.

Recently, a light scattering technique was used to determine the molecular weight distribution of a low molecular weight PTFE resin[17]. This technique has not been applied to commercial grade high molecular weight PTFE resins studied in the present work, because of the difficulty of finding a suitable solvent. It would be interesting to apply this technique to commercial grade PTFE resins, and compare the results with those of the present work.

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