Polymer 40 (1999) 4163–4164

Polymer Communication

# The viscosity–molecular weight relationships for diolic perfluoropolyethers

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Received 9 June 1998; received in revised form 29 October 1998; accepted 29 October 1998

## Abstract

It is shown that for diolic perfluoropolyethers having short chain lengths the ‘‘anomalous’’ (non monotonic) relationship between isothermal melt viscosity and molecular weight, reported in recent papers, is not anomalous at all but fully explainable when one takes into account the fact that the glass transition of the samples $T_g$ is itself a function of the molecular weight.

For low molecular weight polymers the viscosities have to be compared not at the same $T$ but at the ‘‘normalised’’ temperature $T - T_g$.

*Keywords:* Perfluoropolyethers; Viscosity; Molecular weight

It is well known that the viscosity of molten linear polymers is a function of molecular weight, shear conditions, temperature, and pressure [1]. When the shear rate is sufficiently low (Newtonian conditions) and the pressure and temperature are constant, the molecular weight dependence of viscosity is simply given by the equations:

$$\eta = KM^a \qquad (a = 3.5 \text{ for } M > M_c) \tag{1a}$$

$$\eta = K'M^{a'} \qquad (a' = 1.0 \text{ for } M < M_c) \tag{1b}$$

$M_c$ is a critical molecular weight which is related to the molecular weight $M_e$ of the chain segment limited by two entanglements, by the approximate equation:

$$M_c \cong 2M_e \tag{2}$$

In the simplest flow model the flow units are single macromolecules below $M_c$ whereas above $M_c$, being the macromolecules entangled, the flow units are chain segments.

The temperature and pressure dependence of the newtonian viscosity of molten polymers (i.e. of the $K$ and $K'$ parameters in Eqs. (1a) and (1b)), is usually described in terms of free volume. Although the latter is difficult to define precisely, it is generally accepted that above the glass transition temperature $T_g$ it increases linearly with the difference $T - T_g$. However, the glass transition temperature $T_g$ is itself a function of molecular weight $M$:

$$T_g = T_g^\infty - C/M \tag{3}$$

where $C$ is a positive constant, and $T_g$ therefore decreases with decreasing $M$. For polydisperse linear macromolecular samples, the average value of $M$ that has to be used in the latter equation is the number-average $M_n$, which counts the chain ends, whereas in the above viscosity Eqs. (1a) and (1b) the molecular weight that has to be used is the weight average $M_w$.

The $T_g(M)$ Eq. (3) is of course a rapidly changing function of $M$ when $M < M_c$ (owing to the fact that the ‘‘excess free volume’’ of the chain ends plays a major role at very low molecular weights) but it becomes a very weak function above $M_c$, where $T_g$ is practically independent of $M$.

It is clear that when one compares the viscosity of various samples, whose $M$ differ, at a ‘‘constant temperature’’ $T$ rather than at a ‘‘constant free volume’’ (i.e. at a constant difference $T - T_g$), the results may at first sight appear rather anomalous. For example, the exponent $a$ of Eq. (1b) (but not that of Eq. (1a)) can change with changing temperature. This has been found for some hydrogenated polymers [2–4] and for a class of perfluoropolyethers investigated recently by the present authors [5]. In this latter paper the isothermal viscosity data showed that the ‘‘isothermal’’ exponent $a$ was a function of $T$, whereas the values of $a$ were independent of $T$ when plotted at a constant value of $T - T_g$ (i.e. at constant free volume).

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PII: S0032-3861(98)00760-5

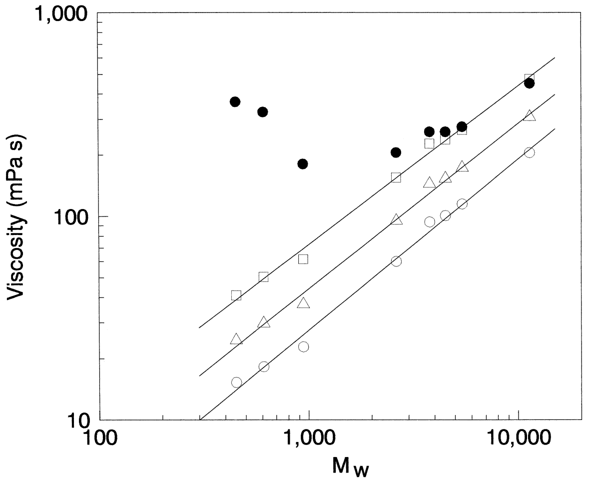

Fig. 1. Iso-free volume viscosities at $T - T_g = 130°C$ (□), 140°C (△) and 150°C (○) plotted as a function of the weight average molecular weight $M_w$; isotherm viscosities determined at 10°C (●) are also shown.

In some recent papers Danusso and coworkers [6,7] have investigated the interesting family of random copolymeric perfluoropolyethers whose chains terminate with two –OH groups:

$$HOCH_2\ CF_2\ O(CF_2\ CF_2\ O)_p(CF_2\ O)_q\ CF_2\ CH_2\ OH \qquad (4)$$

Strangely enough, for the above samples the constant $C$ in Eq. (3) is negative rather than positive. In other terms $T_g$ decreases with increasing $M$. This peculiar result has to be attributed to the presence, in those macromolecular chains, of strong interacting polar ends, whose ‘‘concentration’’ in the polymer decreases with increasing molecular weight. In free volume terms, the peculiarity can be interpreted as evidence that the chain ends do not contribute but subtract additional free volume to the polymer.

In one of the papers [6] it was shown that the isothermal viscosity (measured at 30°C) of fractions of number average molecular weight $M_n$ in the range between 350 and 18 000, when plotted against $M_n$ had also an ‘‘anomalous’’ behaviour. The $\eta(M)$ curve was in fact going through a minimum at $M_n$ values slightly over 1 000.

In a more recent work Tieghi et al. [8] have again investigated perfluoropolyethers samples whose chains terminate with two –OH groups. Viscosity measurements were carried out at several different temperatures (from 10°C to 60°C), on fractions whose $M_n$ was ranging from 400 to 9 050.

It was found that the $\eta(M_n)$ curves show again an ‘‘anomalous’’ minimum at all temperatures. In order to interpret these results Tieghi et al. [8] introduce into Eq. (1b) a molecular weight dependence of $K'$ of an assumed form, writing it as:

$$\frac{\eta}{M} = K'(M,T) \rightarrow \log_{10}\left(\frac{\eta}{M}\right) = A(T) + \frac{B(T)}{M} \qquad (5)$$

The rather complex final equation obtained by Tieghi et al. [8] is the following:

$$\log_{10}\eta = (a + \log_{10}M + c/M) + (b + d/M)(1/T) \qquad (6)$$

which contains the four constants $a$, $b$, $c$ and $d$.

In the present paper the Occam razor rule is applied to the above problem by showing that no additional ‘‘entities’’ have to be introduced in the theory in order to explain the ‘‘anomalous’’ $\eta(M)$ dependence of the isothermal viscosities of –OH terminated perfluoropolyethers. What one has to do is only to take into account the well known $M$ dependence of glass transition temperature (strong when $M < M_c$), and therefore to compare the experimental viscosity data at constant value of $T - T_g$, rather than at constant $T$. In other words in order to compare viscosities the temperature has to be first ‘‘normalized’’, being the normalized variable simply $T - T_g$.

To show that, we have used the Tieghi et al. data in the following way. From the previous paper [7] in which the $T_g(M_n)$ dependence was reported, we have calculated the $T_g$ of the samples of any given $M$, and have then plotted simply the viscosity data of the Tieghi paper as $\log\eta$ vs. $(T - T_g)$. From the plot the viscosities at three values of $T - T_g$ (130°C, 140°C and 150°C) were derived. They are shown as a function of $M_w$ in Fig. 1. Three parallel lines are obtained, which can be compared with the ‘‘isothermal’’ $\eta(M)$ plot at $T = 10°C$, which goes through a minimum.

The slopes of the lines are close to 1.0 (the actual average value is about 0.81) and they are basically temperature independent, as expected from Eq. (1b).

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