Influence of molecular weight distribution of polymer melts on transition from Newtonian to non-Newtonian behaviour in shear flow

Yong Hua Zang, René Muller and Daniel Froelich
Institut Charles Sadron (CRM-EAHP), 4, rue Boussingault, 67000 Strasbourg, France
(Received 11 August 1987; accepted 23 October 1987)

Dynamic moduli of high molecular weight monodisperse polystyrene melts and their binary blends have been measured as a function of frequency. The critical frequency ω_c and loss modulus $G''(\omega_c)$ corresponding to departure from Newtonian behaviour have been determined and related to the moments of molecular weight distribution. The experimental result that the product $\tau_w\omega_c$ is independent of molecular weight distribution (τ_w is the weight-average relaxation time, defined as $\tau_w=\eta_0 J_e^0$) has been interpreted by assuming: (1) the validity of the empirical Cox–Merz rule; and (2) that the transition from Newtonian to non-Newtonian behaviour in a steady shear flow occurs for a characteristic recoverable strain.

(Keywords: polymer melt rheology; polystyrene; binary blend; non-Newtonian viscosity; temporary network model; characteristic recoverable strain)

INTRODUCTION

Steady shear viscosity of polymer melts has been the subject of many investigations. It is well known that at low shear rates the viscosity η_0 is nearly constant, but decreases by several orders of magnitude if the shear rate exceeds some characteristic value $\dot{\gamma}_c$. Experimentally, it has been found that the value of $1/\dot{\gamma}_c$ is proportional to the weight-average relaxation time τ_w, which is defined as the product of the two viscoelastic constants in the terminal zone[1,2]:

$$\tau_w=\eta_0 J_e^0 \tag{1}$$

$$\tau_w\dot{\gamma}_c=C \tag{2}$$

where η_0 is the Newtonian viscosity and J_e^0 the zero shear recoverable compliance. C is a constant whose exact value depends on the way $\dot{\gamma}_c$ is defined from the flow curve.

From equation (2) it is clear that the critical condition for the transition from Newtonian to non-Newtonian behaviour depends closely on average molecular weight and molecular weight distribution (MWD) of the melt.

On the other hand, the empirical rule of Cox and Merz[3] postulates that the magnitude of the complex viscosity should be close to the steady shear viscosity for equivalent values of frequency and shear rate:

$$\eta^*(\omega)=[\eta'(\omega)^2+\eta''(\omega)^2]^{1/2}=\eta(\dot{\gamma}) \qquad \omega=\dot{\gamma} \tag{3}$$

Equation (3) can be written in another form involving dynamic modulus and shear stress:

$$G^*(\omega)=\sigma(\dot{\gamma}) \qquad \omega=\dot{\gamma} \tag{4}$$

At the critical shear rate, equation (4) defines a critical shear stress $\sigma_c(\dot{\gamma}_c)$:

$$G^*(\omega_c)=\sigma_c(\dot{\gamma}_c) \qquad \omega_c=\dot{\gamma}_c \tag{5}$$

In this study, we investigate by dynamic tests how the values of ω_c, $\tau_w\omega_c$ and $G''(\omega_c)$ (which is nearly identical with $G^*(\omega_c)$ at low frequencies) depend on average molecular weight and molecular weight distribution. Assuming that the Cox–Merz rule is verified, a tentative physical meaning is given for the corresponding results in steady shear flow.

EXPERIMENTAL

Anionically polymerized narrow MWD polystyrene samples and two series of their binary blends were investigated. Among these samples, S620 and S622[4] as well as S611 and S567[5] have already been studied in previous works. L1, L2 and L3 were synthesized and characterized by gel permeation chromatography and light scattering. The binary blends (S611–S567 and L1–L2) were obtained by dissolving the corresponding quantities of components in benzene, the solvent then being removed by freeze drying, as described in a previous paper[5]. The molecular characteristics of the samples are shown in *Table 1*.

Using a mechanical spectrometer (Rheometrics RMS-605), the dynamic moduli G' and G'' were measured as a function of frequency in a cone and plate geometry. The temperature range investigated was 120–220°C and master curves were drawn at 140°C for all samples.

Zero-shear Newtonian viscosity η_0 and steady-state recoverable compliance J_e^0 were calculated from the values of storage modulus G' and loss modulus G'' at low frequencies, according to the following relationships:

$$\eta_0=\lim_{\omega\to 0}\eta'(\omega)=\lim_{\omega\to 0}\frac{G''(\omega)}{\omega} \tag{6}$$

$$J_e^0=\lim_{\omega\to 0}\frac{G'(\omega)}{[G''(\omega)]^2} \tag{7}$$

0032-3861/88/040646-05$03.00

Table 1 Molecular characteristics of the samples

Sample	M_w (g mol^{-1})	M_w/M_n
L1	91000	1.15
L2	460000	1.23
L3	420000	1.15
S611	120000	1.10
S620	170000	1.05
S622	585000	1.28
S567	970000	1.19

Table 2 Values of η_0, J_e^0, ω_c, $G''(\omega_c)$ and $\tau_w\omega_c$ at 140°C for monodisperse polystyrene samples

Sample	log η_0 (Pa s)	log J_e^0 (Pa^{-1})	log ω_c (rad sec^{-1})	log $G''(\omega_c)$ (Pa)	$\tau_w\omega_c$
L1	5.92	−5.20	−1.42	4.47	0.19
S611	6.30	−5.08	−1.90	4.38	0.21
S620	6.84	−5.04	−2.42	4.40	0.24
L3	8.20	−4.80	−4.04	4.14	0.23
L2	8.37	−4.78	−4.28	4.07	0.21
S622	8.87	−4.70	−4.80	4.05	0.24
S567	9.55	−4.80	−5.35	4.18	0.25

The data for monodisperse samples are shown in *Table 2*, and those for blends in *Table 3*.

If zero-shear viscosity η_0 is plotted as a function of weight-average molecular weight M_w, the well known power law is found to be verified for monodisperse samples as well as for blends, according to the following relationship[5]:

$$\eta_0 = KM_w^{3.6} \tag{8}$$

REPRESENTATION OF RESULTS AS A FUNCTION OF MWD

As already mentioned in the Introduction, one needs a method to define in a reproducible way the critical shear rate $\dot{\gamma}_c$ or its equivalent ω_c from the flow curves or the dynamic master curves.

In this study, ω_c is arbitrarily chosen as the frequency at which $\eta'(\omega) = 0.95\eta_0$. This value approximately corresponds to the frequency at which the slope of the loss modulus *versus* frequency curve on a double logarithmic plot becomes different from one.

Values of $G''(\omega_c)$, ω_c and $\tau_w\omega_c$ (where τ_w is calculated from η_0 and J_e^0 according to equation (1)) for all monodisperse polymer melts and binary blends are shown in *Tables 2* and *3*, respectively. In *Figure 1*, it is seen that $\tau_w\omega_c$ may be considered as independent of molecular weight and molecular weight distribution. The mean and standard deviation of this parameter are:

$$\tau_w\omega_c = 0.22 \pm 0.03 \tag{9}$$

From equation (9), the following relationships can be derived:

$$G''(\omega_c) = C/J_e^0 \tag{10}$$

$$\omega_c = C/\tau_w \tag{11}$$

In a previous paper, we suggested that the weight-average relaxation time τ_w of a polydisperse melt could be calculated as a function of the weight-average relaxation times τ_{wi} of its monodisperse components[5]:

$$\tau_w = \sum \phi_i \tau_{wi} \propto Q_a \tag{12}$$

where ϕ_i is the volume fraction (here identical with the weight fraction) of component i, and Q_x is a moment of the molecular weight distribution function defined as:

$$Q_x = \int \phi(M) M^x \mathrm{d}M \tag{13}$$

From equation (12) and the well known power law for zero-shear viscosity ($\eta_0 \propto M_w^a$), the recoverable compliance J_e^0 can be calculated[5]:

$$J_e^0 \propto Q_a/Q_1^a \tag{14}$$

The critical value of the loss modulus $G''(\omega_c)$ can then be expressed as a function of MWD according to equations (10) and (14):

$$G''(\omega_c) \propto (Q_a/Q_1^a)^{-1} \tag{15}$$

whereas the value of ω_c is related to molecular weight and MWD through equations (11) and (12):

$$\omega_c \propto Q_a^{-1} \tag{16}$$

Table 3 Numerical values of η_0, J_e^0, ω_c, $G''(\omega_c)$ and $\tau_w\omega_c$ at 140°C for binary blends of monodisperse polystyrene samples

Samples	log η_0 (Pa s)	log J_e^0 (Pa^{-1})	log ω_c (rad s^{-1})	log $G''(\omega_c)$ (Pa)	$\tau_w\omega_c$
S611–10% S567	7.17	−3.34	−4.53	2.62	0.19
S611–20% S567	7.66	−3.51	−4.76	2.88	0.25
S611–40% S567	8.50	−4.07	−5.14	3.34	0.19
S611–60% S567	8.91	−4.37	−5.20	3.69	0.22
L1–10% L2	6.45	−3.80	−3.26	3.16	0.25
L1–15% L2	6.70	−3.83	−3.50	3.20	0.23
L1–20% L2	6.85	−3.92	−3.56	3.26	0.23
L1–40% L2	7.34	−4.28	−3.74	3.58	0.21
L1–60% L2	7.74	−4.40	−3.98	3.74	0.23
L1–80% L2	8.18	−4.62	−4.24	3.92	0.20

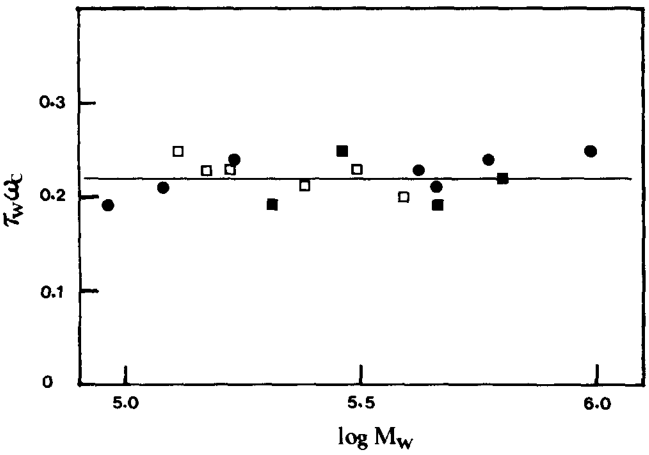

Figure 1 Product $\tau_w\omega_c$ as a function of weight-average molecular weight for monodisperse samples and blends at 140°C. (●) Monodisperse samples, (□) L1–L2 blends, (■) S611–S567 blends

Results for monodisperse melts

For polymer melts with narrow MWD, equations (15) and (16) become:

$$G''(\omega_c) \propto M_w^0 \qquad (17)$$

$$\omega_c \propto M_w^{-a} \qquad (18)$$

In *Figure 2*, log $G''(\omega_c)$ is plotted as a function of log M_w. As predicted by equation (17), this parameter is almost independent of molecular weight.

In *Figure 3*, where log ω_c is plotted as a function of log M_w, a straight line is obtained in agreement with equation (18), with a slope of −3.73 to be compared with the value of $a = 3.6$ obtained in equation (8).

Results for binary blends

For binary blends of monodisperse melts, the moments Q_1 and Q_a of the molecular weight distribution can easily be calculated:

$$Q_1 = \phi_1 M_1 + \phi_2 M_2, \qquad Q_a = \phi_1 M^a + \phi_2 M^a \qquad (19)$$

In *Figure 4*, log $G''(\omega_c)$ is plotted as a function of log Q_a/Q_1^a for two series of binary blends and, in *Figure 5*, log ω_c is plotted as a function of log Q_a for the same samples. In both cases, straight lines are obtained. The approximate values of the slopes are −1.04 and −1.02, respectively, which is close to the expected value of −1 (equations (15) and (16)).

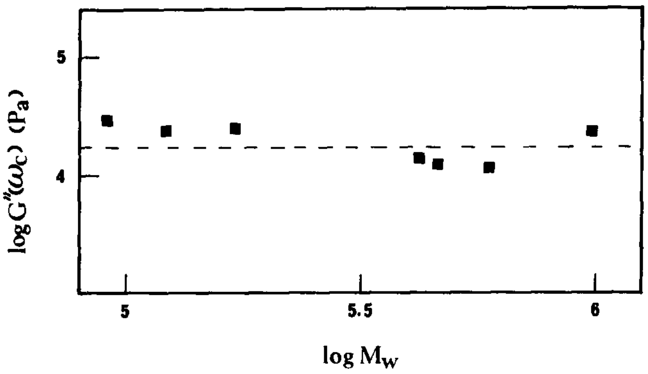

Figure 2 Critical loss modulus $G''(\omega_c)$ as a function of weight-average molecular weight for monodisperse samples

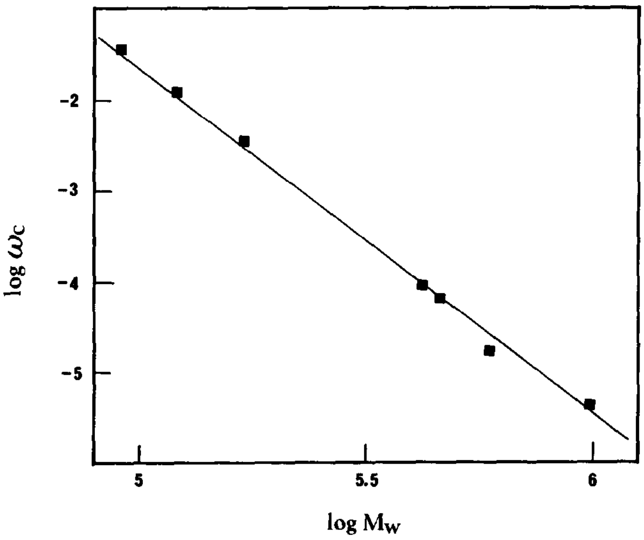

Figure 3 Critical frequency ω_c as a function of weight-average molecular weight for monodisperse samples

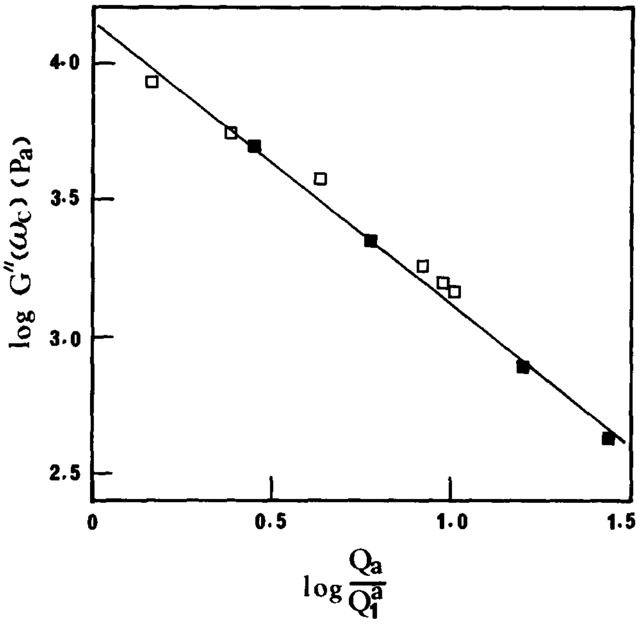

Figure 4 Critical loss modulus $G''(\omega_c)$ as a function of Q_a/Q_1^a for binary blends. (□) L1–L2 blends, (■) S611–S567 blends

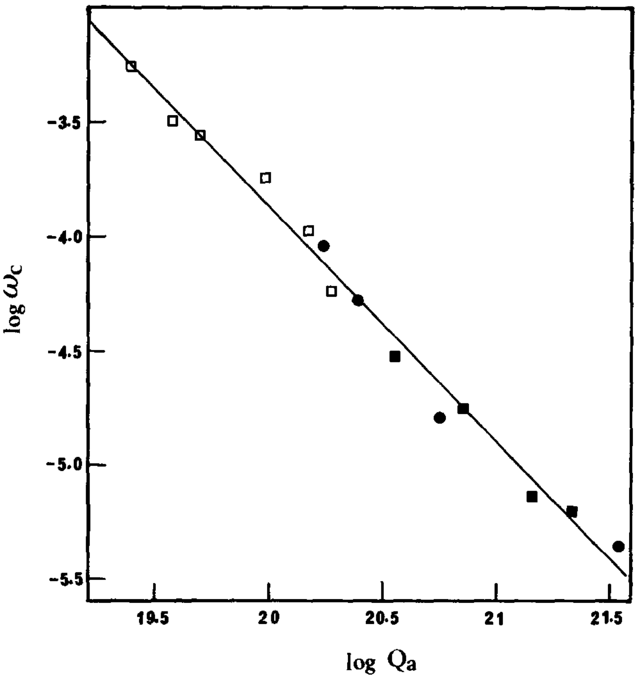

Figure 5 Critical frequency ω_c as a function of Q_a for monodisperse samples and binary blends. (●) Monodisperse samples, (□) L1–L2 blends, (■) S611–S567 blends

All data analysed here are listed in *Table 3*.

COMPARISON WITH A GENERAL MAXWELL MODEL

The results of this study show that if a critical frequency ω_c is defined as the value at which $\eta'(\omega) = 0.95\eta_0$, the product $\tau_w\omega_c$ is approximately independent of molecular weight and MWD. A similar behaviour has been observed by Prest *et al.*[6]. They found that for a frequency such as $\eta_0 J_e^0 \omega = 1$, the value of the dynamic viscosity $\eta^*(\omega)$ is generally equal to $(0.67 \pm 0.03)\eta_0$ for monodisperse as well as for polydisperse polystyrene samples.

According to the theory of Doi and Edwards (which reduces to a general Maxwell model in the linear viscoelastic range), the dynamic viscosities $\eta'(\omega)$ and $\eta^*(\omega)$ have the following expressions[7]:

$$\eta' = \frac{8G_N^0 T_d}{\pi^2} \sum_{\text{odd}}^{p} \frac{1}{p^4} \frac{1}{1+(\omega T_d)^2/p^4} \tag{20}$$

$$\eta^* = \frac{8G_N^0 T_d}{\pi^2} \sum_{\text{odd}}^{p} \frac{1}{p^4} \frac{[1+(\omega T_d)^2/p^2]^{1/2}}{1+(\omega T_d)^2/p^4} \tag{21}$$

where T_d is the longest relaxation time, related to the weight-average relaxation time τ_w by[8]:

$$T_d = \frac{10}{\pi^2}\tau_w$$

At low frequencies, the zero-shear viscosity can be calculated according to equation (20):

$$\eta_0 = \lim_{\omega \to 0} \eta' = (\pi^2/12) G_N^0 T_d \tag{22}$$

If one looks at the values of η' and η^* for the three frequencies at which the product $\tau_w\omega_c$ is, respectively, equal to 0.22, 0.5 and 1, equations (20) and (21) give:

$$\begin{aligned} \tau_w\omega_c = 0.22: &\quad \eta'(\omega_c) = 0.95\eta_0,\ \eta^*(\omega_c) = 0.98\eta_0 \\ \tau_w\omega_c = 0.50: &\quad \eta'(\omega_c) = 0.80\eta_0,\ \eta^*(\omega_c) = 0.90\eta_0 \\ \tau_w\omega_c = 1.00: &\quad \eta'(\omega_c) = 0.51\eta_0,\ \eta^*(\omega_c) = 0.71\eta_0 \end{aligned} \tag{23}$$

A satisfactory agreement with the experimental data of Prest *et al.*[6] and of this study is obtained. In fact, in the frequency range of interest (low frequencies) a Maxwell model with a single relaxation time will give very similar results, since for the Doi–Edwards model the contribution of the longest relaxation time T_d rapidly becomes predominant at low frequencies.

Finally, it should be noted that when Graessley and coworkers[9] investigated steady shear flow of monodisperse polyisoprene solutions, they defined $\dot{\gamma}_c$ as the shear rate at which $\eta(\dot{\gamma}_c) = 0.8\eta_0$ and observed that $\tau_w\dot{\gamma}_c = 0.483 \pm 0.09$, which is again in good agreement with the above calculations in the dynamic region.

PHYSICAL MEANING OF PARAMETER *C* IN A STEADY SHEAR FLOW

If the empirical Cox–Merz rule is assumed to be verified, the counterpart of $G''(\omega_c)$ in steady shear flow will be the critical stress at which the viscosity begins to decrease. The results obtained in this study mean that the critical shear stress σ_c should be constant for high molecular weight monodisperse polymer melts, but should decrease with increasing polydispersity (just as $G''(\omega_c)$ does). Actually, this behaviour has been observed experimentally[10].

To understand the physical meaning of the constant value of the product $\tau_w\omega_c$, equation (9) can be rewritten in the following form (if the Cox–Merz rule is still assumed to be verified):

$$\tau_w\omega_c = \tau_w\dot{\gamma}_c = J_e^0\sigma_c(\dot{\gamma}_c) = \gamma_R^c = C \tag{24}$$

Equation (24) shows that the parameter $C = \tau_w\omega_c$ represents a characteristic recoverable strain γ_R^c, whose value is approximately independent of MWD.

INTERPRETATION IN TERMS OF A TEMPORARY NETWORK MODEL

Numerous theoretical approaches to rheological behaviour of linear high molecular weight polymer melts are based on the temporary network model[2,6,11–13]. According to Lodge's elastic liquid theory[12], temporary junctions between chains, which can be thought of as entanglements, are continually formed and released during the flow, but entanglement density (or average spacing between entanglements) is not a function of shear rate. This picture leads to a shear rate (or shear stress) independent viscosity.

The representation of a polymer melt as a dynamic entanglement network with a shear rate dependent density of junctions has been elaborated by different authors[14,15]. Generally, they assume that the concentration of entanglements decreases with increasing shear rate, which results in the shear-thinning behaviour.

Keeping the general ideas of the network models, it can be assumed that the macroscopic recoverable strain originates from the deformation of the entanglement network, which is in turn related to the deformation of the network strands between coupling junctions. On the other hand, equation (23) shows that as soon as the recoverable strain overshoots some critical value γ_R, the viscosity begins to decrease. In terms of the temporary network model, we can therefore hypothesize that the transition from Newtonian to non-Newtonian behaviour occurs for a given deformation of the chain segments between entanglement junctions. Actually, when this deformation exceeds a given value (of the order of C), a certain number of junctions will be released, leading to the above mentioned strain-induced disentanglement effect (which is an additional effect with respect to the thermally induced entanglement–disentanglement process).

Finally, it is desirable to show that the MWD dependence of zero-shear recoverable compliance is not in contradiction with the temporary network concept.

One has to explain at least qualitatively why, for temporary networks, recoverable compliance increases with polydispersity, although the average molecular weight between entanglement junctions is constant, whereas for networks with permanent junctions (crosslinked networks), compliance depends only on molecular weight between junction points.

In fact, if a crosslinked network is submitted to a constant shear rate for a time t, all the applied deformation is recoverable:

$$\gamma_R = \gamma = t\dot{\gamma} \tag{25}$$

From classical rubber elasticity theory[16]:

$$J_N = \frac{\gamma}{\sigma} = \frac{\gamma}{G\gamma} \propto M_c^{-1} \tag{26}$$

where M_c is the average molecular weight between crosslinking points.

For a polymer melt, equation (24) shows that steady-state recoverable strain (at low shear rates) depends on the product of applied shear rate and weight-average relaxation time τ_w (instead of total time of flow t for a crosslinked network), which can be thought of as the average entanglement lifetime:

$$\gamma_R = \tau_w \dot{\gamma} \tag{27}$$

Going back to the MWD dependence of the weight-average relaxation time:

$$J_e^0 = \frac{\gamma_R}{\sigma} = \frac{\tau_w \dot{\gamma}}{\eta_0 \dot{\gamma}} \propto \frac{Q_a}{Q_1^a} \tag{28}$$

Equations (27) and (28) show how the increase of recoverable compliance with polydispersity can be understood in the framework of the temporary network model.

CONCLUSIONS

The general conclusion to be drawn from this study is that the transition from Newtonian to non-Newtonian behaviour occurs at a given recoverable strain, which is independent of molecular weight distribution. A tentative explanation of this result on a molecular level may be given by recalling an experimental behaviour observed on chemically crosslinked rubbers. For permanent networks, it has been shown that the deformation of the crosslinking points is nearly affine (with the macroscopic deformation) only at small strains, but markedly non-affine (in fact lower than the macroscopic deformation) at large strains. On the other hand, at constant macroscopic strain, the higher the molecular weight between crosslinks, the more pronounced the difference between macroscopic and microscopic deformation (the higher the non-affinity of displacement of crosslinking points)[17]. For uncrosslinked melts, we may similarly hypothesize that, for low shear rates, deformation of chain segments between entanglements is small and affine with the macroscopic recoverable strain. At the same time, the average spacing between entanglements is not affected by the flow, leading to shear rate independent entanglement density and constant viscosity. When the critical shear rate $\dot{\gamma}_c$ is exceeded, the deformation of chain segments reaches the critical recoverable strain ($\gamma_R \approx 0.22$), for which the chain tension causes some of the junction points to be disentangled (strain-induced disentanglement effect). For the remaining entanglements which have a higher average spacing, it may be assumed, by analogy with the crosslinked rubbers, that the deformation of the chain segments between these entanglements is lower than the macroscopic recoverable strain. At the same time, entanglement density is decreased and viscosity becomes a decreasing function of shear rate.

Finally, if one assumes that the strain-induced disentanglement process actually occurs at a given tension of chain segments between entanglement points, one should observe: (1) that the critical recoverable strain has a universal value independent of molecular structure (average molecular weight, MWD, and branching) – this point seems to be verified by the experimental results of Graessley *et al.*[9] and this study; and (2) that if a chain segment with an average molecular weight $\approx M_e$ is labelled within a principal chain (for instance a (PSH)–(PSD)–(PSH) polystyrene copolymer with a deuterated sequence), the deformation of this segment (as measured by SANS experiments) should be directly proportional to shear stress only for shear rates lower than $\dot{\gamma}_c$, and a different behaviour should be observed at higher shear rates. The present study suggests that such an experiment would be helpful in understanding the non-Newtonian behaviour on a molecular basis.

ACKNOWLEDGEMENTS

The authors are indebted to Dr J. Bastide, Dr F. Boué and Dr C. Picot for helpful discussions and remarks. Dr J. L. Barea has participated in several experiments for this work. We are grateful to one of the referees for his remark on the *conjecture* of non-affinity, which has not yet been definitely established.

REFERENCES

1 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn., Wiley, New York, 1980
2 Graessley, W. W. *Adv. Polym. Sci.* 1974, **16**, 1
3 Cox, W. P. and Merz, E. H. *J. Polym. Sci.* 1958, **28**, 619
4 Zang, Y. H., Muller, R. and Froelich, D. *Polymer* 1986, **27**, 61
5 Zang, Y. H., Muller, R. and Froelich, D. *Polymer* 1987, **28**, 1577
6 Prest, W. M., Porter, R. S. and O'Reilley, J. M. *J. Appl. Polym. Sci.* 1970, **14**, 2697
7 Doi, M. and Edwards, S. F. *J. Chem. Soc. Faraday Trans.* 1978, **74**, 1802, 1818
8 Graessley, W. W. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 27
9 Graessley, W. W., Masuda, T., Roovers, J. E. L. and Hadjichristidis, N. *Macromolecules* 1976, **9**, 127
10 See, for example, Vinogradov, G. V. and Malkin, A. Ya. 'Rheology of Polymer', Mir Publishers, Moscow, 1980, Ch. 2, pp. 172, 210
11 Green, M. S. and Tobolsky, A. V. *J. Chem. Phys.* 1946, **14**, 80
12 Lodge, A. S. 'Elastic Liquids', Academic Press, New York, 1964
13 Yamamoto, M. *J. Phys. Soc. Japan* 1957, **12**, 1148
14 Graessley, W. W. *J. Chem. Phys.* 1967, **47**, 1942
15 Buche, F. *J. Chem. Phys.* 1968, **48**, 4781
16 Treloar, L. R. G. 'The Physics of Rubber Elasticity', 3rd Edn., Clarendon Press, Oxford, 1975
17 Candau, S., Bastide, J. and Delsanti, M. *Adv. Polym. Sci.* 1982, **44**, 27