Concentration dependence of the primitive path step length

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Recent experiments by Donald and Kramer have measured the extension ratio, λ_{craze}, for polymers in crazes under tensile strain. In this paper it is shown that $\lambda_{craze} \propto l_e^{\frac{1}{2}} i$ where l_e is the average contour length between entanglements in glassy, and not permanently crosslinked polymers and is obtained from melt elasticity experiments. It is also shown that l, the Rouse chain step length for a molten polymer, is independent of monomer density and that the average distance between entanglements, $d \propto \rho^{-\alpha}$, where ρ is the number of monomers per unit volume with $1/4 \lesssim \alpha \lesssim 1/2$. Finally these results are shown to provide confirmation for the configurational assumptions of the primitive path for reptation in which α appears as the determining factor for the concentration dependence of the relaxation modulus, the steady state viscosity and terminal relaxation time.

(Keywords: reptation; crazes; primitive path; entanglements; polystyrene; polyphenylene oxide)

INTRODUCTION

In a recent series of articles[1-3] experimental evidence has been accumulated concerning the configuration of polymer molecules in crazes. Values of M_e, the molecular weight between entanglements, have been obtained from melt elasticity experiments for the polymers concerned. From these the values of l_e, the chain contour length between entanglements, are calculated. Also, the value of d, the average distance between entanglements, is calculated using the assumption that the sections of chain between each pair of entanglements obey Gaussian statistics, in which case

$$d = k(M_e)^{1/2} \qquad (1)$$

where k is a constant obtained from light scattering or neutron scattering results[3].

That the whole polymer chain in the melt has a Gaussian, random walk configuration has been well proven by neutron scattering experiments[4,5], where it has been shown that the chain dimensions in a melt are exactly those of the chain in theta-solvent conditions, intra-chain excluded volume effects being screened out by inter-chain interactions. The random walk step length, l, is found to be about 10 monomer units[6]. It is to be noted that both the neutron scattering and crazing experiments are performed on polymers below their glass transition temperatures, care being taken to choose those which have a completely amorphous glassy state. The assumption is, here and elsewhere, that the configurational statistics of the polymers in the glassy state will be a representative frozen-in configuration of the molten state.

One may then define a maximum possible extension ratio, assuming no chain scission, λ, given by

$$\lambda = \frac{l_e}{d} \qquad (2)$$

In the experiments of Donald and Kramer[1-3] the value of the extension ratio, λ_{craze} measured in crazes produced in amorphous glassy films under tensile strain (see refs. 3 and 7 for details) was found to be described, reasonably accurately, by this equation. In one set of these experiments two perfectly miscible polymer blends were used. One was of a high molecular weight polystyrene (PS), $\bar{M}_w = 300\,000$, $\bar{M}_n = 113\,000$, blended with polyphenylene oxide (PPO), $\bar{M}_w = 35\,000$, $\bar{M}_n = 15\,000$. The other was a blend of low molecular weight polystyrene, $\bar{M}_w = 4000$, $\bar{M}_w/\bar{M}_n \leqslant 1.06$, with the same PPO. Hence, in the latter blend, the chain length of PS was very much less than the entanglement separation, as defined above, of the PPO. The two batches were prepared for a range of different weight fractions of PPO in PS (here weight and volume fraction and hence monomer fractions will be used synonomously as they are, within experimental error, identical). In the second batch the PS chains are so short that we have, effectively, a variable density matrix of PPO diluted by the short PS chains which contribute a negligible entangling effect to the PPO.

Reference will now be made to the recently developed model of reptation to describe the motion of molten polymers and how this may be related to the results described above.
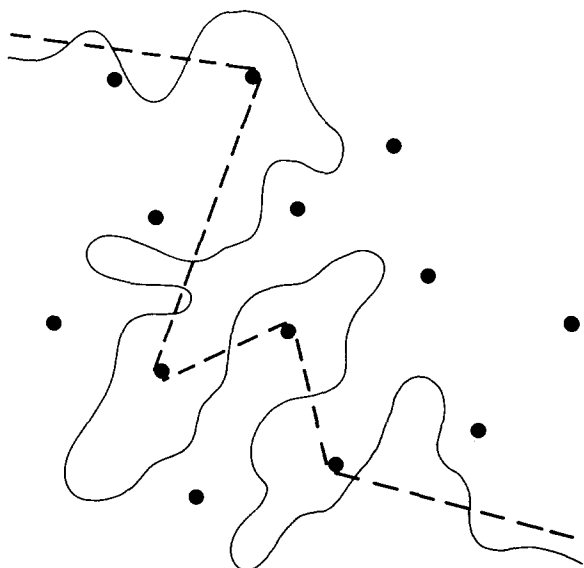
Figure 1 Schematic diagram of the primitive path model for reptation. Dashed line indicates the primitive path random walk created from the topological entanglements of the original chain (solid line)

THEORY

In the reptation model[8-10] the notion of entanglements in a molten polymer is developed into the construction of a tube, around any one particular polymer chain created by the average effect of the topological obstacles caused by adjacent chains. One particularly elegant way of visualizing the topology of this tube is to imagine the meandering chain pulled taut. The resulting path, known as the primitive path, is also that of the tube (see *Figure 1*). This path is assumed to be a random walk with an average path segment length given by d, the mean entanglement separation. It is to be noted that this path length is assumed to be equivalent to the tube width in the Doi–Edwards model[9,10].

This model has been shown to give very good agreement with the behaviour of the bulk properties of polymers, e.g. relaxation moduli, viscoelasticity, normal stresses, etc.[10-12]. Numerical values are consistent with the use of the entanglement separation values, d, obtained from melt elasticity experiments. There is, however, considerably less experimental evidence to support the model at the molecular level. One notable exception to this is the experimental work[13] supporting the theoretical prediction that the diffusion coefficient $D \propto N^{-2}$, where N is the number of units per chain.

Other molecular assumptions made in the tube model concerning the configurations of the primitive path are that

(i) the step length of the primitive path, d, is independent of the polymer chain length;

(ii) the step length will depend on the number concentration of monomers, ρ, as a power law, hence

$$d \propto N^0 \rho^{-\alpha} \tag{3}$$

(iii) random walk behaviour describes the chain between pairs of entanglements.

To evaluate α, four predictions have been produced, based on the configurational statistics of the tube model, each evaluating the effects of inter-chain contacts along

the tube in different ways. De Gennes[14], by simply counting contacts, predicted $\alpha = \frac{1}{2}$. Doi[15], using a simple scaling argument, produced $\alpha = 1$. Edwards[16], in an early paper, evaluated the effects of constraints using a topological invariant and obtained $\alpha = \frac{1}{4}$. Most recently, however[17] this calculation has been re-evaluated to avoid the problem of a divergence in the integration, yielding a value $\alpha = \frac{1}{2}$. In the original reptation papers of Doi and Edwards[9] the value $\alpha = \frac{3}{4}$ was actually used. Below we shall show how the crazing work described above provides experimental evidence for these assumptions, and can indicate a value for α. Since the dependence of d on ρ has direct implications for macroscopic quantities such as viscosity, terminal relaxation time and relaxation modulus, an experimental method of determining α is important.

RESULTS

If we assume that the segments of polymer chain between any pair of entanglements follow a random walk, then
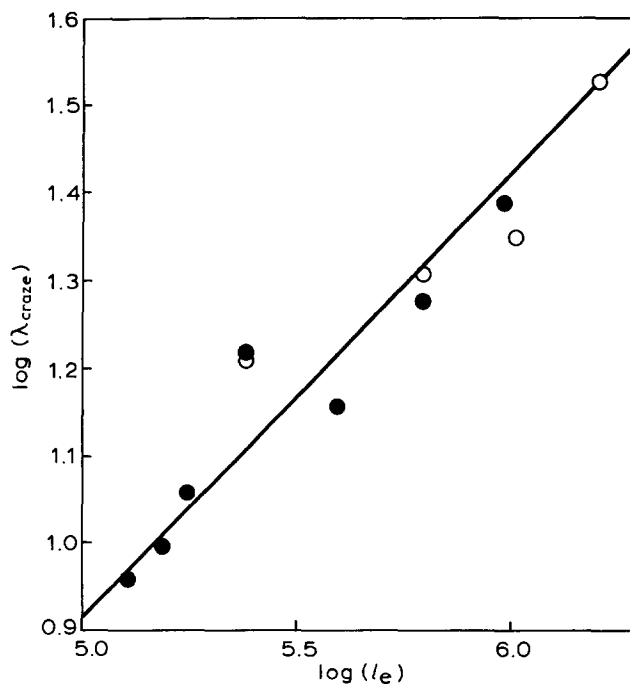
$$d^2 = N_e l^2 \tag{4}$$

where N_e is the number of chain steps, each of length l, between entanglements. By definition the contour length, l_e, between entanglements is given by

$$l_e = N_e l \tag{5}$$

Hence, from equations (2), (4) and (5) we obtain

$$\lambda = (N_e)^{1/2} = \left(\frac{l_e}{l}\right)^{1/2} \tag{6}$$

In *Figure 2* the measured values log (λ_{craze}) (see *Table 1*) are plotted against the values of log (l_e) obtained from melt

Figure 2 Log-log plot of λ_{craze} against l_e for low (O) and high (●) molecular weight PS in PPO. Solid line is for $\lambda \propto l_e^{1/2}$

Table 1 Results extracted from ref. 1 for high molecular weight PS ($\bar{M}_m$ = 300 000, $\bar{M}_n$ = 113 000) and PPO ($\bar{M}_w$ = 35 000, $\bar{M}_n$ = 15 000) and for low molecular weight PS ($\bar{M}_w$ = 4000, $\bar{M}_w/\bar{M}_n$ 1.06) with PPO; showing values of l_e, λ_{craze} and ρ

High Mol. Wt. PS/PPO:

λ_{craze}	l_e (Å)	ρ (PPO)
4.0	400	0
3.6	330	0.1
3.2	270	0.25
3.4	220	0.5
2.9	190	0.75
2.7	180	0.90
2.6	165	1.00

Low Mol. Wt. PS/PPO:

λ_{craze}	l_e (Å)	ρ (PPO)
—	1650	0.1
4.6	500	0.33
3.9	410	0.4
3.85	330	0.5
3.4	220	0.75

elasticity experiments. As can be seen, the results fit very well to

$$\lambda_{craze} \propto l_e^{1/2} \tag{7}$$

Thus, the entanglement values obtained indirectly from melt elasticity experiments are consistent with extension ratios obtained in the crazing experiments, providing evidence supporting both the assumption of random walk statistics between pairs of entanglements and the validity of using data from the melt with that in the glassy state. Both types of PS–PPO blend exhibit this behaviour since, irrespective of any ρ dependence of l_e in the two batches, random walk statistics will apply between entanglements irrespective of whether they are due to PPO or PS chains. The results for the two blends must also lie on the same line in *Figure 2* since, as ρ (PPO) approaches 1, we must arrive at the same value of l_e (or λ) in both cases.

The absolute value of l can also be obtained from

$$\log(\lambda_{craze}) = \tfrac{1}{2}\log(l_e) - \tfrac{1}{2}\log(l) \tag{8}$$

The line drawn yields $\log(l) = 3.2$, hence $l = 25$Å for PPO. This compares very favourably with previous estimates[6] that the free chain random walk step length will be about 10 monomer units, and is related to the flexibility and length of these units.

Using the experimental values of ref. 1 (see Table 1) for λ_{craze} and l_e for pure PPO, we have, from equation (6)

$$l = l_e/\lambda_{craze}^2 \tag{9}$$

with $l_e = 165$Å and $\lambda_{craze} = 2.6$. This gives $l = 24.4$Å, consistent with the extrapolated result above. This formula may be applied to the complete set of PPO chains in low molecular weight PS giving $l = 24$, 28, 24, 19 and 24Å respectively.

This provides explicit experimental evidence that the Gaussian step length is unaffected by monomer concentration ρ. In other words, we remain in the equivalent

of theta-solvent conditions over a wide range of concentration.

Rearranging (2), (4) and (5) we obtain

$$\lambda = \frac{N_e l}{d} = \frac{d^2}{l^2} \cdot \frac{l}{d} = \frac{d}{l} \tag{10}$$

So, from assumption (ii) we have

$$\lambda \propto \rho^{-\alpha} \tag{11}$$

A plot of $\log(\lambda_{craze})$ against $\log(\rho)$ is given in *Figure 3*. The results for low molecular weight PS indicate a value of α somewhere between $\tfrac{1}{4}$ and $\tfrac{1}{2}$. By contrast, in the long chain PS batches all the chains are entangled by both PS and PPO chains and cannot distinguish between the two so that there is little, if any, ρ dependence.

Finally, it is to be noted (see *Table 1*) that the range of values of l_e lie between 165Å and 500Å. In other words, the number of Gaussian steps, length l, between entanglements lies between 6 and 20. Even with such a small number of steps the results obtained are consistent with a random walk, with a step length equal to the step length of the whole chain, operating between pairs of entanglements.

CONCLUSION

In this paper experimental evidence has been given providing further confirmation for the configurational assumptions used in the reptation model. These results are also consistent with the assumption that the configurational statistics of a glassy polymer are a representative frozen-in configuration from the melt. The value of the step length of the primitive path d is found to be about five times the Rouse chain step length l of the original chain, in agreement with melt elasticity results for
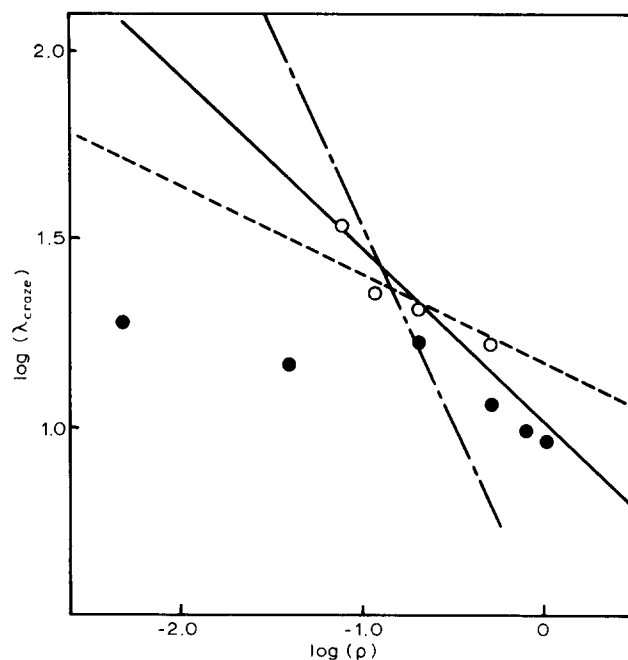
Figure 3 Log–log plot of λ_{craze} against ρ (PPO) for low and high molecular weight PS. Values of $\alpha = 1$, 1/2, 1/4 are indicated by (– – – –), (———) and (- - - - -) lines respectively. λ_{craze}, high mol. wt. ●, low mol. wt. ○

different polymers, namely polyethylene and poly-styrene[11,18]. Furthermore, l is shown to be independent of the effective (entangled) concentration of chains.

Finally, the value for the power law dependence of d on monomer concentration is also found to lie between $\frac{1}{2}$ and $\frac{1}{4}$. This result is believed to be the most direct attempt so far made on estimating α, based as it is on a method of varying the polymer melt concentration, the value of which is crucial to many of the power-law predictions of the reptation model for the concentration dependence of such quantities as the steady state viscosity, relaxation modulus and terminal relaxation time[9].

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