

# Diffuse versus point entanglements – homopolymers and blends

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Mechanical properties of linear polymers are frequently described via identification of the tangle of chains with an equivalent temporary network. An alternative model is presented here assuming diffuse entanglements, in keeping with the tube model. This model allows entanglement molecular weights to be predicted from knowledge of conformational characteristics of the chains. In this paper predictions of the diffuse entanglement model and of the temporary network model are compared with experimental data on critical molecular weight from viscosity and entanglement molecular weight of binary blends, and on crazing properties. Both models exhibit similar trends, although quantitative description is generally better under the assumption of diffuse entanglements.

## 1. Introduction

The importance of molecular entanglements in determining melt properties of thermoplastic polymers is well known. For instance, the stress–strain relationship in the rubbery state [1–5] and the stress–optical coefficient [3–10] have been found to correlate well using theories originally established to describe the behaviour of cross-linked rubbers. Some glassy state properties can also be explained by assuming the existence of an entanglement “network”: craze strain, crazing susceptibility and craze stability [7, 11–14] and, in particular, the geometrically necessary entanglement loss during craze formation [14, 15]. In these investigations, it is generally either explicitly or implicitly assumed that chains are constrained at definite sites called “entanglement junctions” or “entanglement points”, forming a network analogous to the permanent network in a cross-linked rubber. (Use of rubber-elasticity equations to describe the stress–strain behaviour implicitly assumes the molecular strands to be stressed at the entanglement points and to be free to assume the most probable configuration between these points.) Entanglement points have even been explicitly identified in terms of interactions between polar groups on neighbouring chains in the case of PMMA [8].

The entanglement network in thermoplastics is defined as a temporary network; discrepancies between the experimental and theoretical relationships between birefringence and strain [8, 10] and the capacity of thermoplastics to reach higher strains than the theoretical maximum strain [13, 7] are generally interpreted in terms of stress- or temperature-activated disentanglement, or of entanglement slippage.

On the other hand, the success of the “tube” model [16] in explaining certain aspects of viscoelasticity [17–19] lends support to the idea that strands of average length,  $M_e$ , are effectively confined to a tube or cage formed by neighbouring chains, or, in other

words, that the whole length of each chain is involved in interactions with its neighbours. The contour length between entanglements then appears as the length of chain such that local motion of one end is independent of constraints on the other end.

Theories of entanglements in linear polymers appear to fall into two classes: those in which strands are constrained at definite sites (localized entanglements) and those in which interactions are distributed along the chain (diffuse entanglements).

In the following sections, evidence from the literature in favour of either interpretation will be compared, and the usefulness of the two classes of theories in various applications will be assessed.

## 2. Entanglement molecular weight of bulk polymers

### 2.1. Introduction

Entanglement molecular weights,  $M_e$ , are generally determined from the plateau modulus,  $G_e$ , [20, 21], using the relation valid for cross-linked systems:

$$G_e = \rho RT/M_e \quad (1)$$

where  $\rho$  is the density,  $R$  the gas constant and  $T$  the temperature. The plateau modulus can, in turn, be obtained by integration of the loss modulus in the terminal zone [21]. These values are obtained under the assumption that the entanglement network is equivalent to a cross-linked network. Application of the rubbery-elastic stress–strain relationship to a perfect or imperfect phantom-network can be carried out by introducing a strain-dependent correction factor (Equation 50 in [5]), so that even if values of  $M_e$  obtained by use of Equation 1 are incorrect, differences in  $M_e$  between different polymers, or on modifying polymers, can be taken as correct.

As pointed out by Prevorsek and De Bona [22], most systematic studies on chain entanglement have been restricted to polymers with a relatively flexible backbone, such as aliphatic and vinyl polymers. These

TABLE 1

	$k(\text{nm mol}^{-1/2})$ [13]	$\rho(\text{g cm}^{-3})$ [23]	$M_e$ [13]	$kM_e^{1/6}(\rho N)^{1/3}$ (simple cubic)	$kM_e^{1/6}(\rho N)^{1/3}2^{-1/2}$ (b c c)
PTBS	0.060	0.95	43 400	3.04	2.71
PVT	0.068	1.04	25 000	3.24	2.89
PS	0.070	1.05	19 100	3.10	2.76
	0.0655*			3.0	2.67
PSMLA	0.073	1.06	19 200	3.35	2.99
PSAN 76/24	0.077	1.06 <sup>†</sup>	11 600	3.25	2.90
PSAN 34/66	0.084	1.07 <sup>†</sup>	6 380	3.22	2.87
PMMA	0.076	1.20	9 150	3.22	2.87
PSMMA 35/65	0.065	1.15	8 980	2.70	2.41
	0.074*			3.08	2.74
PC	0.094	1.2	2 490	3.20	2.85
PPO	0.084	1.07	4 300	3.02	2.69
	0.097 <sup>‡</sup>			3.48	3.10

\* Linear interpolation of  $k^2$ .

<sup>†</sup> Estimated from  $r_{0f}$  (see text).

<sup>‡</sup> Estimated as crystalline density/1.1.

authors investigated the effect of chain stiffness on entanglement molecular weight in polycarbonates on replacing a fraction of the carbonate groups in bisphenol A polycarbonate by terephthalate or isophthalate groups. Their somewhat unexpected result was that an increase in chain stiffness leads to an increase in entanglement density. Their interpretation of this fact was that interpenetration of molecules is higher in the case of stiff molecules than it is for flexible molecules which form a tightly packed coil [22].

## 2.2 Model

In this section a simple model estimating the degree of interpenetration from known characteristics of the chain will be given. The degree of interpenetration resulting from application of this model will then be compared with experimental values.

An estimate of chain interpenetration can be obtained by comparing the mean square end-to-end distance of a chain of molecular weight,  $M_e$ , with the average spacing of such chains. The mean square end-to-end distance,  $d_e$ , is given by

$$d_e = kM_e^{1/2} \quad (2)$$

where  $k$  is a characteristic constant, generally determined by SANS or from dilute solution properties. The occupied volume is

$$V_e = M_e/(\rho N) \quad (3)$$

where  $\rho$  is the polymer's specific mass and  $N$  is Avogadro's number, so that the mean spacing between centres of gravity of chains is:

$$a_e = A(M_e/\rho N)^{1/3} \quad (4)$$

where  $A$  is a geometrical constant equal to 1 assuming centres of gravity to be spaced on a simple cubic lattice, and equal to  $2^{1/6}$  in the case of a face-centred cubic lattice.

The basic idea, which will be checked against experimental data in the following sections, is that entanglement occurs when the degree of interpenetration characterized by the ratio  $d_e/a_e$ , reaches a specific value. This value can be obtained from literature data on chain stiffness and entanglement molecular

weights. Various interpretations of the observed value will be discussed, and predictions resulting from the assumption of constant interpenetration will be compared with predictions resulting from the assumption of interactions at specific sites and with literature data on blends.

## 2.3. Comparison with experiment

The ratio  $d_e/a_e$  is given in Table I for a series of polymers with widely varying entanglement molecular weights. It can be seen that this ratio is essentially constant, confirming the basic assumption of constant interpenetration; no systematic variation of this ratio with entanglement molecular weight can be observed. Table I calls for the following comments.

Donald and Kramer give  $k = 0.065 \text{ nm mol}^{1/2}$  for PSMMA [13] but this value appears from [23] to be appropriate for PSMA. Linear interpolation of  $k^2$  between the values appropriate for pure PS and pure PMMA gives a value of  $d/a$  consistent with other polymers (and incidentally also gives a better estimate of the maximum extension of PSMMA). A justification for this procedure is given in Section 4 (Equation 2).

The entanglement molecular weight of pure PPO is 7400 from melt elasticity measurements and 4300 from extrapolation of entanglement molecular weights in PS-PPO blends [1]. As pointed out by Donald and Kramer [12] the former value is probably too high since, because of the high glass transition temperature of PPO, some form of breakdown of the entanglement network probably occurs at the high temperature required for melt elasticity measurements.

An estimate of  $k$  for PPO can be found from the theoretical freely-rotating bond value of  $r_{0f}(\text{m}^{1/2}) = 0.0715 \text{ nm mol}^{-1/2}$  and the experimental value of  $r_0/r_{0f}$  measured in a  $\theta$  solvent, i.e. 1.36 [23] giving  $k = 0.097 \text{ nm mol}^{-1/2}$ . This is evidently too high, since it gives values of  $d/a$  inconsistent with those obtained for other polymers.

Solving Equations 2 and 4 for  $M_e$  gives:

$$M_e = A^6 B^6 / (\rho N)^2 k^6 \quad (5)$$

where  $B$  is the characteristic "universal", value of

$d_e/a_e$ , obtained from Table I. In this equation,  $M_e$  appears to depend solely on chain stiffness, through the parameter  $k$ . Relatively small changes in chain stiffness will lead to large variations in  $M_e$ . On the other hand, if the entanglement molecular weight is influenced by interactions other than topological interpenetrations, these will hardly influence the value of  $d_e/a_e$ : halving  $M_e$  will lead to a 10% decrease in  $d_e/a_e$ . In other words, Table I shows that consideration of chain stiffness alone can explain the main trends in variation of entanglement molecular weight in polymers between which this parameter varies by a factor of 20. Other effects are small and are not considered here.

The stiffness constant  $k$  can be linked with structural characteristics in the following manner. The mean square end-to-end distance,  $d$ , of a sequence of  $n_e$  stiff segments of length,  $l$ , having valence angle  $(\pi/2 - \theta)$  and azimuthal angle  $\Phi$  is given, to a good approximation when  $n_e$  is large and  $\langle \cos \Phi \rangle$  is small, by:

$$\begin{aligned} d^2 &= n_e l^2 \frac{1 + \cos \theta}{1 - \cos \theta} \frac{1 + \langle \cos \Phi \rangle}{1 - \langle \cos \Phi \rangle} \\ &= \frac{n_e v_0}{Sl} l^2 \frac{1 + \cos \theta}{1 - \cos \theta} \frac{1 + \langle \cos \Phi \rangle}{1 - \langle \cos \Phi \rangle} \\ &= \frac{M_e}{\rho N S} \frac{l}{S} \frac{1 + \cos \theta}{1 - \cos \theta} \frac{1 + \langle \cos \Phi \rangle}{1 - \langle \cos \Phi \rangle} \end{aligned} \quad (6)$$

and

$$k^2 = \frac{d^2}{M_e} = \frac{l}{\rho N S} \frac{1 + \cos \theta}{1 - \cos \theta} \frac{1 + \langle \cos \Phi \rangle}{1 - \langle \cos \Phi \rangle} \quad (7)$$

where  $v_0$  is the stiff segment volume and  $S$  its average cross section, and  $\langle \cos \Phi \rangle$  is the average value of  $\cos \Phi$ . A large value of  $k$  could result from a long stiff segment and a low value of  $S$ , i.e. no bulky side groups (e.g. polycarbonate) or from a high value of  $\langle \cos \Phi \rangle$ , i.e. hindered internal rotation with trans sequence favoured over gauche (e.g. PMMA).

Equation 7 allows quantitative evaluation of Prevorsek and De Bona's [22] results on substituted polycarbonates. On replacing a carbonate group by a terephthalate (isophthalate) group the stiff segment length is increased by a factor of roughly 2.8 [2], the stiff segment molecular weight is increased from 127 to 358 (358) and the average cross-sectional area is unchanged (increased by a factor of 1.4), so that, assuming unchanged valence angles in chain-redirecting groups, and assuming unchanged hindrance to internal rotation,

$$k_T^2 = 2.8 k_C^2 \quad (8)$$

and

$$k_I^2 = \frac{2}{1.4} k_C^2 = 1.4 k_C^2 \quad (9)$$

where the suffixes C, T and I refer to carbonate, terephthalate and isophthalate, respectively.

Assuming additivity of squared end-to-end distances, for a random copolymer containing weight fraction  $w_1$  of polymer 1 and  $w_2$  of polymer 2, the mean square end-to-end distance of a sequence of molecular

TABLE II

$w_2$	Terephthalate		Isophthalate	
	$M_e$ [12]	$M_e$ (exp)	$M_e$ [12]	$M_e$ (exp)
0	2450	2426	2450	2426
0.1	1490	1232	2180	1600
0.3	671	770	1740	1500
0.5	357	850	1420	1500

weight,  $M_e$ , is given by:

$$\begin{aligned} d_e^2 &= k_1^2 (w_1 M_e) + k_2^2 (w_2 M_e) \\ &= [k_1^2 + (k_2^2 - k_1^2)w_2] M_e \end{aligned} \quad (10)$$

or

$$k^2 = k_1^2 + (k_2^2 - k_1^2)w_2 \quad (11)$$

Introducing Equation 11 into Equation 5, and eliminating unknown constants by use of  $M_{el}$ , the entanglement molecular weight of pure polymer 1, one obtains:

$$M_e = M_{el} / [1 + (k_2^2/k_1^2 - 1)w_2]^3 \quad (12)$$

Prevorsek and De Bona's experimental values of  $M_e$  [22] are compared with the values resulting from application of Equation 12 in Table II. An average literature value of 2450 was taken as the entanglement molecular weight of PC.

The correspondence between experimental and calculated values is reasonable for replacement by terephthalate groups, less so for replacement by isophthalate groups. In both cases experimental values of  $M_e$  decrease faster than calculated for low weight fractions; this could simply be an indication that  $\langle \cos \Phi \rangle$  is modified, in contradiction to the simplifying assumptions used. For replacement by terephthalate, at a weight fraction of 0.5 the calculated entanglement molecular weight is reduced to little more than one stiff segment, so that use of Equations 1 and 7 is open to question. It is interesting to note, however, that higher weight fractions could not be investigated because of crystallization, which could be thought of as the limiting behaviour of "entangled" polymers when the entanglement molecular weight decreases to a sufficiently low number of stiff segments.

The results summarized in Table II can be interpreted in terms of the topological nature of entanglements and confirm the basic idea that  $d_e/a_e$  is approximately a "universal" constant, i.e. that entanglement occurs at a universal value of interpenetration. It would be far more difficult to interpret these results in terms of localized interactions at specific sites since it is difficult to understand how introduction of a small fraction of terephthalate or isophthalate groups, similar in nature to the bisphenol A group, could increase the number of interactions to such a degree.

## 2.4. Interpretation

Various interpretations of the value found for  $d_e/a_e$  can be considered.

First, the characteristic ratio is approximately 3: the end-to-end vector of a strand of molecular weight,  $M_e$ , is approximately three times the average spacing between centres of gravity of these strands. In other

words, neighbouring chains interacting with one end of the strand are not in direct contact with chains interacting with the other end of the strand. The entanglement molecular weight then appears as the smallest value such that motion of one end of the strand is independent of constraints on the other end, i.e. such that both ends can be considered to be firmly embedded in the medium. In this interpretation, the "strand" does not begin or end at any definite point along the chain length; in particular, a chain slightly shorter than  $M_e$  is not "unentangled", but rather "partially entangled", and there are no "dangling ends": the first "entanglement length" starts at the chain end.

A second possible interpretation can be given by estimating the total number of strands in the volume pervaded by a reference strand. An estimate of the pervaded volume is given by (fcc):

$$V = \frac{(2s)^3}{2^{1/2}} = \frac{2}{3^{3/2}} d^3 \quad (13)$$

so that the number of strands in this volume is, on average:

$$\begin{aligned} n &= \frac{2}{3^{3/2}} k^3 M_e^{3/2} (\rho N / M_e) \\ &= 0.38 k^3 M_e^{1/2} \rho N \end{aligned} \quad (14)$$

This works out as approximately 12. This could be taken to mean that each strand interacts with twelve others. This, however, is too simplistic. Firstly, only part of the reference strand is present in the volume given by Equation 13. This is also true of all other chains, so that the total number of strands partly present in the pervaded volume is far greater than twelve. On the other hand, the reference strand cannot, of course, be present everywhere in the pervaded volume, so that it interacts with far fewer than the total number of strands. On the whole, this interpretation is somewhat unenlightening. However, it will be useful to remember (see Section 5) that the pervaded volume must reach a certain value for a strand to be considered entangled.

A third interpretation, due to Rault [24], is based on the ratio of the occupied volume to the pervaded volume: according to Rault, this ratio, equal to  $M_e / (\rho N d^3)$ , works out as approximately 3% which is close to the value of the free volume at the glass transition.

It should be pointed out, however, that the numerical value of this ratio depends sharply on the radius used to define the pervaded volume. Assuming a gaussian chain of  $n$  statistical segments of length  $l_0$ , the probability of finding the  $m$ th segment at a distance smaller than  $r$  from the origin is

$$\begin{aligned} P(r, m) &= \frac{4}{\pi^{1/2}} \left[ -\frac{1}{2} \left( \frac{3}{2m} \right)^{1/2} \frac{r}{l_0} e^{-(3/2m)(r^2/l_0^2)} \right] \\ &\quad + \operatorname{erf} \left[ \left( \frac{3}{2m} \right)^{1/2} \frac{r}{l_0} \right] \end{aligned} \quad (15)$$

For  $r^2 = nl_0^2$  the average probability for the  $n$

segments works out as 0.84, so that the sought ratio is

$$\frac{0.84 M_e / \rho N}{\frac{4}{3} \pi k^3 M_e^{3/2}} = 6.3 \times 10^{-3} \quad (16)$$

whereas for  $r^2 = s^2 = nl_0^2/6$  the average probability is 0.27 and the ratio is

$$\frac{0.27 M_e / \rho N}{\frac{4}{3} \pi k^3 M_e^{3/2} / 6^{3/2}} = 3 \times 10^{-2} \quad (17)$$

The value corresponding to the free volume at the glass transition (0.025) would be obtained for a sphere having a radius slightly larger than the radius of gyration, so that the correspondence seems accidental.

In conclusion, data on bulk homopolymers and copolymers are in support of the diffuse, topological nature of molecular entanglements, and of a universal value of the degree of interpenetration of entangled strands.

### 3. Binary blends – homopolymers

#### 3.1. Critical molecular weight

In this section, data on viscosity and on crazing sensitivity of binary mixtures of narrow fractions of polystyrene will be examined in the light of the ideas expressed in the preceding section. A relationship will first be sought between entanglement molecular weight and weight fraction of high molecular weight compound.

First consider a polymer of molecular weight  $M_1$  in solution in a solvent or polymer of molecular weight low enough to assume negligible contribution to the entanglement network. Equation 5 can be written:

$$M_{es} = M_{e0} \left( \frac{\rho_0}{\rho_s} \right)^2 \left( \frac{k_0}{k_s} \right)^6 \quad (18)$$

where subscript 0 refers to the bulk polymer, subscript  $s$  to the solution and  $\rho_s/\rho_0$  is the weight fraction of polymer 1, i.e.  $w_1$ .

If the solvent acts as a  $\theta$  solvent,  $k_0 = k_s$  and Equation 18 predicts the entanglement molecular weight to be proportional to  $w_1^{-2}$ .

In a good solvent, the coil will expand and, if  $d_g$  and  $d_\theta$  are the coil end-to-end distance in a good and  $\theta$  solvent [25],

$$d_g = d_\theta w_1^{-1/8} \quad (19)$$

or

$$k_0 = k_s w_1^{-1/8} \quad (20)$$

Equation 18 then becomes:

$$M_{eg} = M_{e0} w_1^{-5/4} \quad (\text{good solvent}) \quad (21)$$

$$M_{e\theta} = M_{e0} w_1^{-2} \quad (\text{theta solvent}) \quad (22)$$

As pointed out by de Gennes [25], in a binary mixture the low molecular weight component acts as a good solvent if the ratio of molecular weights is sufficiently large.

On the other hand, if point entanglements are assumed, and if every contact between two polymer molecules has a constant probability of entanglement

$$M_{ep} = M_{e0}/w_1 \quad (23)$$

TABLE III

$w_1$	$M_c$	$M_c w_1^{5/4}$	$M_c w_1^2$	$M_c w_1$
1 (melt, 165°C)	32 000*	32 000	32 000	32 000*
0.312 (in PS 2400, melt, 217°C)	100 000*	23 320	9 730	31 200
0.55 { in <i>n</i> -butyl benzene, 30°C	74 550	35 310	22 550	41 000*
0.255 {	149 000	27 000	9 690	38 000*
0.415 { in di-octyl phthalate, 25°C	62 650	20 870	10 790	26 000*
0.310 {	83 870	19 400	8 060	26 000*

\*[39].

†[20].

An estimate of  $M_c$  can be obtained from the break in viscosity–molecular weight data. This gives the critical molecular weight  $M_{c0}$ , which is larger than  $M_c$  by a polymer-dependent factor [20]. In a given polymer–solvent system, however, it can be hoped that variations in  $M_c$  will closely reflect variations in  $M_{c0}$ . There is some uncertainty in determining  $M_c$  from viscosity data, especially in a mono-disperse polymer for which the low molecular weight portion of the graph has a distinct downward curvature.

Data of  $M_c$  for polystyrene in solution and in a binary mixture are given in Table III, together with estimates of  $M_{c0}$  from Equations 21 to 23. Evidently, the combination of diffuse entanglements and neglect of coil expansion is totally inadequate. Equation 23 appears to offer a more adequate description of variation of  $M_c$  than Equation 21; however, uncertainties in experimental data do not allow us to choose between the two. It should be pointed out that in the derivation of Equations 21 to 23 it was assumed that the low molecular weight component does not participate at all in the entanglement network, so that the values of  $M_c$  predicted by these equations are expected to be overestimated (i.e. the values of  $M_{c0}$  predicted from experimental values of  $M_c$  should be underestimated).

### 3.2. Craze properties

It was observed some years ago by Wellinghoff and Baer [11, 26] that stable crazes occur in monodisperse PS at molecular weights above 37 500; this is roughly  $2 \times M_c$ . However, in a binary blend 1% high molecular weight PS ( $M = 67 \times 10^4$ ) in a matrix of low molecular weight PS ( $M = 10^4$ ) was sufficient for highly fibrillated crazes to grow in thin films (50 to 600 nm thickness) and even 0.1% of high molecular weight component was sufficient to stabilize craze growth [26]. Since the end-to-end distance obtained using  $k$  from Table I (50 nm) is somewhat smaller than the average spacing between molecules at this concentration (100 nm), it was concluded that “entanglement interactions are not completely necessary for fibre formation”.

This would be true in the case of a  $\theta$  solvent, but for a good solvent, by applying Equation 21, taking  $M_c = 67 \times 10^4$  and  $M_{c0} = 19 \times 10^2$ , a weight fraction of 5.8% is found. This would be the lowest weight fraction at which an entanglement network could be formed by molecules of  $M = 67 \times 10^4$  in a low molecular weight solvent. The “solvent” in this case is a polymer of  $M = 10^4$ , which is not much lower than the entanglement molecular weight in the bulk.

Although polystyrene of this molecular weight cannot form an entanglement network, it can help in entangling the high molecular weight component; in other words, the ratio  $d/a = B$  necessary for formation of an entanglement network may drop slightly at low concentrations. Introducing Equation 20 into Equation 5 and solving for  $w_1$ ,

$$w_1 = \left(\frac{M_0}{M}\right)^{4/5} \left(\frac{B}{B_0}\right)^{24/5} \quad (\text{good solvent}) \quad (24)$$

or

$$w_1 = \left(\frac{M_0}{M}\right)^{1/2} \left(\frac{B}{B_0}\right)^3 \quad (\theta \text{ solvent}) \quad (25)$$

For  $M_0 = 19 100$ ,  $M = 570 000$  and  $B/B_0 = 2/3$ ,  $w_1 = 0.8\%$  in a good solvent and 5% in a  $\theta$  solvent. At  $B_0/B = 2.5$  (i.e.  $B \simeq 1$ ) these values drop to 0.07% and 1.1%, respectively. At this concentration the end-to-end distance is practically equal to the mean spacing of the molecules. The value found for a good solvent is remarkably close to the concentration (0.05%) at which an occasional fibril was found to span cleaved deformation zones in low molecular weight PS [11].

## 4. Blends of compatible polymers

### 4.1. Entanglement molecular weights

Compatibility of blends of PPO and PS has convincingly been demonstrated by SANS [27–29]; the radius of gyration of PS in the blend was, within experimental scatter, the same as in the homopolymer. In Wignall *et al.* [27] the molecular weight of PS was comparable with that of PPO.

The variation of entanglement molecular weight (determined from the plateau modulus) with composition in blends of PPO with PS was found by Prest and Porter [1] to follow Equation 26

$$M_e = \frac{M_{e0}}{1 + 3.2w_1} \quad (26)$$

where  $M_{e0}$  is the entanglement molecular weight of polystyrene and  $w_1$  the weight fraction of PPO. The two polymers were of comparable molecular weights, so that they are expected to behave approximately like  $\theta$  solvents for each other.

An average value of  $d^2$  in the blend can be obtained assuming additivity:

$$d^2 = w_1 d_1^2 + w_2 d_2^2 \quad (27a)$$

$$= w_1 (k_1^2 M_c) + w_2 (k_2^2 M_c) \quad (27b)$$

$$= k^2 M_c \quad (27c)$$

TABLE IV Relative decrease of entanglement molecular weight with weight fraction of PPO in PPO/PS blends

$w_2$	Equation 26 (exp)	Equation 29 (diffuse)	Equation 31 (localized)	
0.05	1.16	1.12	1.008	1.07
0.2	1.64	1.52	1.12	1.48
0.4	2.28	2.20	1.48	2.52
1	4.2	5.38	4	9
Me (PPO)	4550	3550	4780	2100

Identifying Equation 27c with Equation 27b:

$$k^2 = w_1 k_1^2 + w_2 k_2^2 \quad (28)$$

Introducing Equation 28 into Equation 18, and rearranging, the following expression is found in the case of diffuse entanglements:

$$M_e = \frac{M_{e02}(\rho_{02}/\rho)^2}{[1 + (k_1^2/k_2^2 - 1)w_1]^3} \quad (29)$$

On the other hand, assuming entanglements to occur at specific sites, the number of entanglements per unit volume should vary as:

$$N \sim w_1^2 f_1^2 + w_2^2 f_2^2 + w_1 w_2 f_1 f_2 \quad (30)$$

where  $f_{1,2}$  are proportional to the probabilities that a contact between chains will result in an entanglement. Under this hypothesis, the entanglement molecular weight would be inversely proportional to  $N$ . Since  $M_e$  must reduce to the value for each pure polymer when  $w_1$  (or  $w_2$ ) = 0,  $f_1^2/f_2^2$  can be identified with  $M_{e2}/M_{e1}$ , so that, neglecting changes in specific volume,

$$M_e = \frac{M_{e1}}{w_1^2 + w_2^2(M_{e1}/M_{e2}) + w_1 w_2(M_{e1}/M_{e2})^{1/2}} \quad (31)$$

The denominators in Equations 26, 29 and 31 are compared in Table IV. In Equation 29, the average values for  $k$  from Table I are used for both polymers, and volume changes are neglected. In Equation 31, two values of  $M_{e1}/M_{e2}$  are tried:  $M_{e1}/M_{e2} = 4$ , giving approximately the same value of  $M_e$  for pure PPO as that found by extrapolation of experimental values in 1; and  $M_{e1}/M_{e2} = 9$ , giving a reduction in  $M_e$  with weight fraction of PPO comparable with experiment, but giving an unreasonably low value of  $M_e$  for pure PPO. Also, Equation 31 is strongly nonlinear, in contrast with experiment. Equation 29 gives a good fit with experiment although all ratios are somewhat too low; however, the volume of mixing of PPO with PS is known to be negative [29]; taking the change in density into account would result in a better fit.

Evidence from variation of entanglement molecular weight in blends therefore lends support to the hypothesis of diffuse entanglements.

## 4.2. Crazing

Craze extension ratios in a wide variety of materials have been shown to correlate well with the maximum extension ratio computed as  $l_e/d$ , where  $l_e$  is the chain contour length between entanglements and  $d$  the mean square end-to-end distance [13]. An interesting extension of this work was the investigation into properties of crazes in blends of PPO with low or high  $M_w$  PS

[12]. The materials used were PPO ( $M_w = 35000$ ,  $M_n = 15000$ ), PS ( $M_w = 300000$ ,  $M_n = 113000$ ) and monodisperse PS ( $M_w = 4000$ ,  $M_w/M_n \leq 1.06$ ).

The approximate excluded volume parameter  $\xi = N_1^{1/2}/N$  was introduced by de Gennes [25] as an indicator of expansion of a molecule of  $N_1$  units in a solution of molecules of  $N$  units: the chain is ideal if  $\xi \ll 1$ . What the unit should be is not quite clear, but it appears logical to take a statistical segment, i.e.  $M_e/\lambda_{max}^2$ , giving approximately 1000 for PS and 500 for PPO. For PS chains in a blend of high  $M_w$  PS with PPO,  $\xi = 300^{1/2}/70 = 0.25$ ; no coil expansion is expected in this system. For PPO in low molecular weight PS,  $\xi = 70^{1/2}/4 = 2.1$ ; expansion of PPO is therefore expected. The chain contour length between entanglements in the high molecular weight blend is

$$l_e = \left[ \left( \frac{l}{M} \right)_1 w_1 + \left( \frac{l}{M} \right)_2 w_2 \right] M_e \quad (32)$$

and the mean square end-to-end distance is given by Equations 27 and 28 so that, substituting  $b_{1/2}$  for  $(l/M)_{1/2}$

$$\lambda_{max} = \frac{l_e}{d} = \frac{1 + (b_1/b_2 - 1)w_2}{k/k_2} \left( \frac{M_e}{M_2} \right)^{1/2} \lambda_{max_2} \quad (33)$$

where subscript 1 refers to PPO and 2 to PS.

Introducing Equation 18 into Equation 33, Equation 34 is obtained in the case of ideal behaviour and Equation 35 in the case of coil expansion. (Numerical coefficients are taken from Table I or [13]; identity of  $b_2/b_1$  with  $k_2^2/k_1^2$  is accidental)

$$\lambda_{max} = \frac{1 + 0.75 w_2}{(1 + 0.75 w_2)^2} \lambda_{max_1} \quad (34)$$

$$\lambda_{max} = \frac{1 + 0.75 w_2}{[(1 - w_2)^{3/4} + 1.75 w_2]^2} \lambda_{max_2} \quad (35)$$

Equation 34 corresponds to essentially the same interpretation as that given by Kramer [14], although  $k$  for the blend was found by linear instead of quadratic interpolation. Although the justification for quadratic interpolation is clear, in practice the difference is numerically very small.

Equations 34 and 35 are compared with Donald and Kramer's [12, 13] results in Fig. 1a, using  $\lambda_{max} = 4$  for pure PS. The fit is excellent for  $w_2 < 0.5$  but predicted values for  $\lambda_{max}$  are too low for  $w_2 > 0.5$ . It has been shown that annealing has no measurable effect on craze growth kinetics [30]. However, annealing is known to increase the yield stress, which is also the stress at the craze tip, and craze strain has been shown to increase with the stress acting during craze growth [31], so that an increase in craze strain on annealing is not unexpected. Equations 34 and 35 were therefore recalculated using  $\lambda_{max_1} = 2.6$  (experimental value). Equation 34 is remarkably consistent with data for both annealed and unannealed samples. Equation 35 underestimates  $\lambda_{max}$ , thus confirming that the blend exhibits ideal behaviour.

In the PPO-low molecular weight PS blend, the polystyrene molecules will behave like a good solvent for PPO; also, since the polystyrene molecular weight is well below the entanglement molecular weight, only

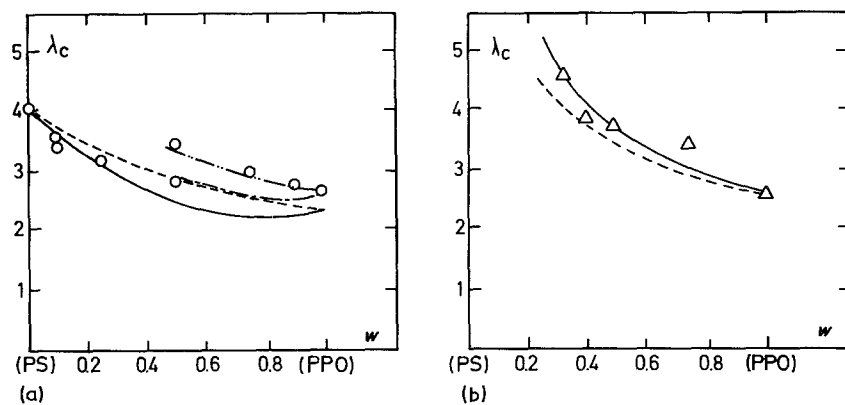


Figure 1 Variation of craze strain with composition in PPO-PS blends. (a) PPO + high molecular weight PS.  $\circ$ , experimental [12]. (b) PPO + low molecular weight PS.  $\Delta$ , experimental [12]. Curves: theory (see text).

PPO will take part in the entanglement network. Equations 21 to 23 give the appropriate concentration dependence of entanglement molecular weight for delocalized and point entanglements, respectively. The chain contour length scales like  $M_e$  and the end-to-end distance is given by Equation 19, so that the maximum strain becomes:

$$\lambda_{\max} = \lambda_{\max_1} w_1^{-1/2} \quad (36)$$

$$\lambda_{\max} = \lambda_{\max_1} w_1^{-3/8} \quad (37)$$

Equation 36 is appropriate for delocalized entanglements and Equation 37 for point entanglements. These equations are compared with experimental results in Fig. 1b taking  $\lambda_{\max_1} = 2.6$  since all results were obtained on annealed samples. There is not a great deal of difference between the two, although the assumption of point entanglements gives predictions which are systematically too low.

Another comparison between the two assumptions can be made by estimating the minimum concentration  $w_m$  for a network to exist. In the point entanglement picture, each molecule should be at least twice the entanglement molecular weight for a network to exist, so that, from Equation 23

$$w_m = 2 M_{e0}/M_n \quad (38)$$

(The appropriate molecular weight is the number average molecular weight since Equation 38 expresses the fact that there must be as many entanglement points as chain ends.) This works out as  $w_m = 0.53$ .

Assuming diffuse entanglements, a chain is entangled with the network if constraints at either end are independent of each other and if each chain interacts with enough other chains. Thus, only one "entanglement length" per chain is required. The critical concentration is given by:

$$w_m = (M_{e0}/M_n)^{4/5} \quad (39)$$

which works out as  $w_m = 0.37$ . This value is remarkably close to the concentration (between 0.33 and 0.4) at which crazes were found to become very fragile [12].

Although in this system both models predict similar values of the critical concentration, the assumption of diffuse entanglements gives a better fit with experiment.

## 5. Discussion

Evidence from a variety of experiments is in favour of diffuse rather than localized entanglements. However, a wealth of information has been obtained in the past by assuming the entanglement network to be equivalent to a temporary cross-linked network. One might query the usefulness of information obtained in this way.

The first question to be answered is: what is the significance of entanglement molecular weights obtained from the plateau modulus assuming a network of equivalent temporary crosslinks, if no such crosslinks exist? A qualitative answer can be obtained from Flory and Erman's work [32] on elasticity of constrained networks: in this theory, applicable to cross-linked rubbers, diffuse entanglements are assumed to act solely through constraints on fluctuations of junctions. This theory cannot, of course, be extrapolated to the case where only diffuse entanglements exist, since if there are no junctions there can be no constraints on fluctuations of junctions. However, it should be noted that this theory predicts the contribution to the elastic force of diffuse entanglements to be of a magnitude comparable with that of the phantom network at zero strain. Whether the modulus is assumed to be due to a temporary (phantom) network alone, a temporary network with diffuse entanglements, or diffuse entanglements alone, the order of magnitude of the entanglement molecular weight obtained will not be altered. In other words, comparisons between entanglement molecular weights obtained from the plateau modulus can be accepted as valid; absolute values should not be taken too literally. It should be noted that the fact that absolute values of entanglement molecular weights are unknown does not invalidate the conclusions of Section 2: the ratio  $d_e/a_e$  is relatively insensitive to  $M_e$ ; is equivalent to multiplying  $d_e/a_e$  by 1.12.

Values of  $M_e$  obtained from the plateau modulus are clearly reasonable, since they yield estimates of the natural draw ratio which are comparable with experimental values for a wide variety of polymers [13].

The apparent increase of  $M_e$  with strain, obtained, for example, from data on birefringence [8, 10], should also be viewed with caution. As shown by Erman and Flory [5], in a network with constraints due to diffuse

entanglements, the stress-optical coefficient decreases with strain. In an entirely different approach taking account of two components of strain (orientational and extensional) Brown and Windle have shown that the development of birefringence with strain can be described adequately, both in the rubbery [33] and glassy states [34] without assuming an increase in entanglement molecular weight on drawing. (Although the entanglement molecular weight does not appear explicitly in Brown and Windle's theory, constant  $M_e$  should logically be equivalent to constant limiting draw ratio due to the extensional mode.) Relationships between draw ratio and entanglement molecular weight obtained via identification of orientation-strain data with rubber-elasticity theory should not be taken too literally; that there is an increase is, however, apparent from the fact that the maximum recoverable extension of thermoplastics is limited by the molecular weight of the whole chain [35]. In keeping with the views expressed in Section 2, this could be attributed to the fact that deformation of the pervaded volume is not affine, so that a given strand interacts with fewer chains with increasing strain. (At full extension it interacts with at most six neighbours.) A publication discussing this point in more detail is in preparation. The fact that the conformation of the whole chain is active in determining the entanglement characteristics of a polymer is also apparent from the work of Wool and co-workers on crack-healing phenomena in polymers [36–38]: the full strength of the virgin material is only recovered once interpenetration over a distance comparable with the random coil dimensions of the whole chain has occurred.

## 6. Conclusions

A model for diffuse entanglements has been proposed, giving an adequate description of a variety of phenomena. This description is never worse, and in most instances is better, than that resulting from the point entanglement or temporary network model. It allows prediction of the entanglement molecular weight from knowledge of chain characteristics, in particular chain stiffness.

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