The molecular, physical and mechanical properties of highly plasticized poly(vinyl chloride) membranes

M. A. Simon† and R. P. Kusy*†‡
Departments of †Biomedical Engineering and ‡Orthodontics, Dental Research Center, University of North Carolina, Chapel Hill, NC 27599-7455, USA
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Highly plasticized poly(vinyl chloride) membranes (200 parts per hundred resin, phr) form the basis of ion-selective electrodes. The effects that five different plasticizers with different chemical structures, polarities and molecular weights $\bar{M}_w$ have on modified mechanical properties such as strength, secant stiffness, toughness and ductility were examined by puncture testing. As a function of membrane thickness, strength, toughness, and secant stiffness increase, while ductility remains constant. For maximal membrane strength and toughness, plasticizer $\bar{M}_w$ should be roughly 1000. The optimal ratio of experimental plasticization level ($phr_{\mathrm{exp}} = 200$) to the minimal level required for complete plasticization (phr_{min}) was found to be ~2. A 'tube'-like model for plasticizer interaction with polymer chains is proposed to explain the vast differences in the mechanical properties of membranes.

(Keywords: poly(vinyl chloride); plasticizer; membranes)

INTRODUCTION

The unique ability to accept large amounts of plasticizer makes poly(vinyl chloride) (PVC) one of the most commercially useful polymers. Generally PVC is plasticized with 20–70 parts per hundred resin (phr) of plasticizer[1]; however, in the current system, PVC is highly plasticized at 200 phr[2]. These highly plasticized PVC films are important as membranes for ion-selective electrodes (ISEs). In ISE membranes, PVC provides the structural framework of the network. The high loading rate is necessary only so that the plasticizer can best facilitate transport of ionophore and ion–ionophore complexes through the membrane. In order to have optimal response times, the membrane must be virtually barrier free[3] and closely approximate a liquid interface. These membranes are often referred to as single-phase homogeneous mixtures or 'solvent polymeric' types[4].

Because of the relatively small amount of polymer available for structural support, the mechanical properties must be optimized or failure will occur[5]. Since the plasticizer comprises roughly two thirds of the membrane by weight, the influence that a plasticizer has on the membrane mechanical properties is important. Previously, the effect of a plasticizer on product performance has been characterized by its compatibility with PVC. Many parameters have been investigated: the Flory–Huggins interaction parameter[6–9], the Hildebrand solubility parameter[10], the sol–gel transition temperatures of PVC in plasticizer[11] and the ratios of non-polar to polar plasticizer components[11]. Knowledge of plasticizer compatibility alone does not enable prediction of plasticized PVC mechanical properties as these parameters generally indicate thermal compatibility, which does not necessarily relate to mechanical properties. One publication on plasticizer efficiency, however, incorporated dielectric spectroscopy in studying Shore A hardness, cold-crack and cold-flex temperatures of samples plasticized from 0 to 50 phr[12]. In the present paper the molecular, physical and mechanical properties of five highly plasticized (200 phr) PVC systems are investigated, which represent different chemical structures, polarities and molecular weights.

MATERIALS AND METHODS

Materials

Polymers. Two PVCs were blended in a 50/50 ratio by weight for the study (*Table 1*) as a compromise between membrane strength and processability. PVC was chosen for its ability to accept the large amounts of plasticizer necessary in its application to membrane-type ISEs. As the lifetime of solvent polymeric membrane electrodes is governed mainly by the loss of membrane components[13–15], PVC extends microelectrode life by hindering this process. PVC also yields membranes of good mechanical stability, good electromotive properties and good chemical stability[16].

Plasticizers. Dioctyl sebacate (DOS) is the currently used plasticizer in the fabrication of ISEs for clinical applications[2] (*Table 1*). Epoxidized soybean oil (ESO) and epoxidized linseed oil (ELO) are composed mainly of three biologically derived fatty acid chains. Propylene glycol dioleate (PGDO) is composed of two such chains. All fatty acid chains have been epoxidized. The advantage of these epoxidized plasticizers is their

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* To whom correspondence should be addressed

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Table 1 Polymers and plasticizers studied

Code	Material	Product	Manufacturer
Polymers			
PVC A	Low-molecular-weight PVC	Secondary standard	Scientific Polymer Products
PVC B	High-molecular-weight PVC	Secondary standard	Scientific Polymer Products
Plasticizers			
DOS	Dioctyl sebacate	DOS	Aldrich
ESO	Epoxidized soybean oil	Flexol® EPO	Union Carbide Chemicals & Plastics
ELO	Epoxidized linseed oil	Vikoflex 7190	Viking Chemical
PGDO	Propylene glycol dioleate	Vikoflex 5075	Viking Chemical
o-NPOE	*o*-Nitrophenyl octyl ether	*o*-NPOE	Fluka Chemical

potential biocompatibility. Finally, *o*-nitrophenyl octyl ether (*o*-NPOE) is a plasticizer currently favoured because of its good electrochemical properties in cation-selective electrodes[14,15]. *Figure 1* shows the most prevalent molecular structure of each plasticizer.

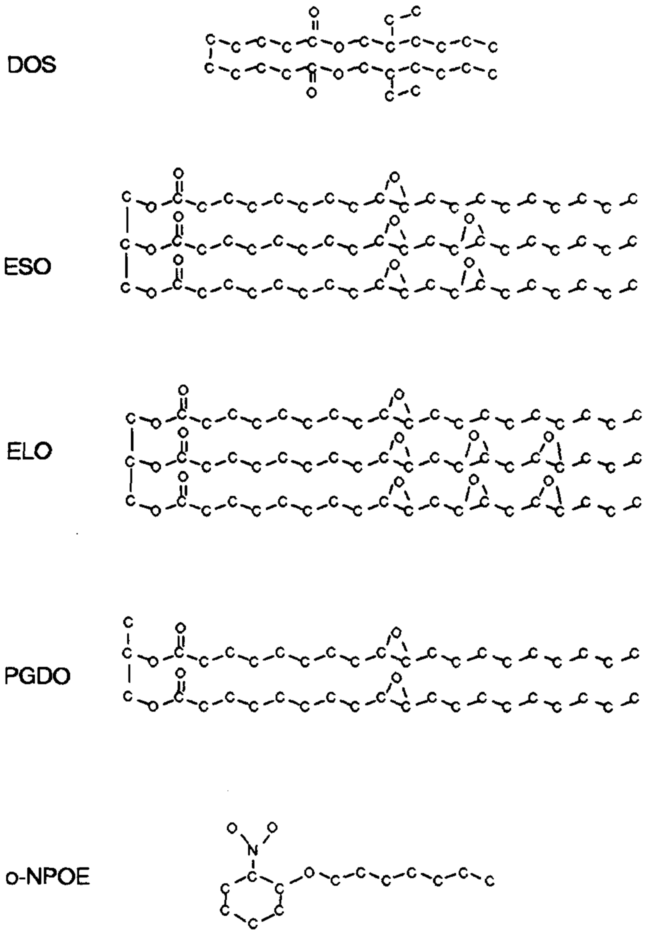

Figure 1 Molecular structures of plasticizers used in this study. Note the highly branched structures of ESO and ELO, and the polar structure of *o*-NPOE

Initial characterization

Molecular weight. All materials were initially characterized via high performance gel permeation chromatography (h.p.g.p.c.) on a Waters 590 (Milford, MA) under the following conditions: flow rate, 1.0 ml min^{-1}; injection volume, 50 μl; sample concentration, 2.5×10^{-3} g ml^{-1} maximum; solvent, tetrahydrofuran (THF). The polymers were analysed with a Waters Ultrastyragel® linear analytical column, which was calibrated with 10 polystyrene standards (Shodex®, Showa Denko K. K., Tokyo) ranging in $\bar{M}_w$ from 1.32×10^3 to 3.03×10^6. A g.p.c. calibration curve was derived by using the universal calibration procedure that adapts the Mark–Houwink equations for polystyrene (PS) in THF and PVC in THF[17]. The plasticizers were analysed with a Shodex® K-Series g.p.c. column specialized for low-molecular-weight organic samples. Calibration was performed with a series of seven low-molecular-weight PS oligomer standards, ranging in $\bar{M}_w$ from 517 to 3270. Each value of $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$ and polydispersity index (*PDI*) represented the average of three sample runs.

Viscosity

The dynamic viscosity μ of each plasticizer was measured with a Brookfield Digital DV-II cone/plate viscometer (Stoughton, MA) at 25°C and a shear rate of 5170 s^{-1}. The viscometer employed a CP-40 cone with cone angle $\theta = 0.8°$ and with radius $r = 2.4$ cm.

Membrane preparation

A stock solution of PVC in THF was prepared at a concentration of 1.1 wt%. To 50 ml of solution was added 1.097 ml of each plasticizer so that at least 10 sample membranes per condition could be cast. The solutions were stirred rapidly overnight.

In the actual membrane-casting technique[18], glass rings (internal diameter = 3 cm) that had ground and polished ends were placed on a glass plate, and 3–5 ml of membrane solutions were added. To obtain uniform membrane thicknesses, the evaporation of THF was controlled for a period of 96 h by dead-weighting a stack of filter papers atop the rings.

Mechanical testing

Cast membranes were individually mounted on 0.5 cm sections of Tygon® (Norton, Akron, OH) tubing (internal diameter = 1.6 cm) using a PVC/THF glue. To stress-relax the tubing to its original as-manufactured circular condition, the tubing was heated for two minutes at 400°C using a hot air gun. Tubing sections were machined on a lathe using a copper pipe as the spindle and a razor as the cutting tool. Handwheels were employed to control razor placement, ensuring reproducible 8 cm sections with square-cut ends. Prior to testing, all mounted film samples were hydrated for 24 h in a pH 7 buffer solution to simulate actual use conditions of membranes functioning as ISEs. By using an Instron universal testing machine (Canton, MA) that was equipped with a bullet-shaped, 0.32 cm metal probe and a specially designed apparatus (*Figure 2*), sample membranes were punctured at a crosshead speed of 1.0 cm min^{-1} as their force–deflection curves were recorded.

Each membrane puncture test produced a force–displacement curve similar to the one depicted in *Figure 3*. This figure also depicts the modified definitions of several parameters that were measured from the curves: strength, secant stiffness, toughness and ductility[19]. Strength was determined by the maximum force on the force–displacement trace; secant stiffness was indicated by the force at failure divided by the displacement at failure; toughness was determined by the area under the force–displacement trace; and ductility was represented as the maximum deflection at maximum load. All parameters were plotted against membrane thickness for each sample type.

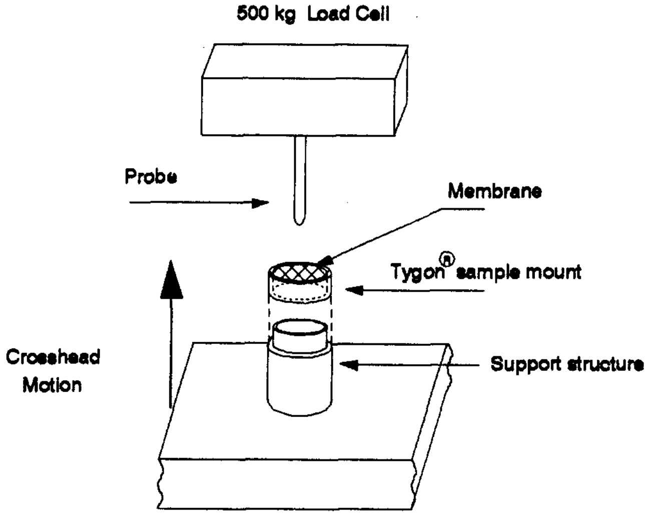

Figure 2 Schematic illustration of puncture test showing relationship of membrane assembly to support structure and probe

Thickness measurements

Since permanent deformation of the membranes occurred only locally at the site of failure, thickness measurements could be made in the undeformed regions of the membranes following puncture testing. The membranes were sectioned in half with a razor and their thicknesses measured with a Sloane Dektek 3030 profilometer (Santa Barbara, CA). The lightest stylus weight (1.0 mg) was used for a 1.6 mm scan length, which included the undeformed membrane edge.

Statistics

The four principle mechanical properties were regressed against thickness. Slopes m were obtained from the linear regressions along with the correlation coefficients r. From these r values and the number of observations n, the statistical probability p that the slope was significantly different from zero was adduced (either $p<0.01$ or $p<0.001$). Naturally, in cases in which the mechanical characteristic was independent of thickness, the outcome was not significant.

RESULTS

Initial characterizations of the two polymers show that both have fairly random distributions with a $PDI \approx 2.0$ (*Table 2*). The $\bar{M}_w$ values of PVC A and PVC B are

Table 2 Molecular weight characterization of polymers

Polymer	$10^{-3}\bar{M}_n$	$10^{-3}\bar{M}_w$	$10^{-3}\bar{M}_z$	*PDI*
PVC A	106	198	316	1.9
PVC B	51	94	150	1.9

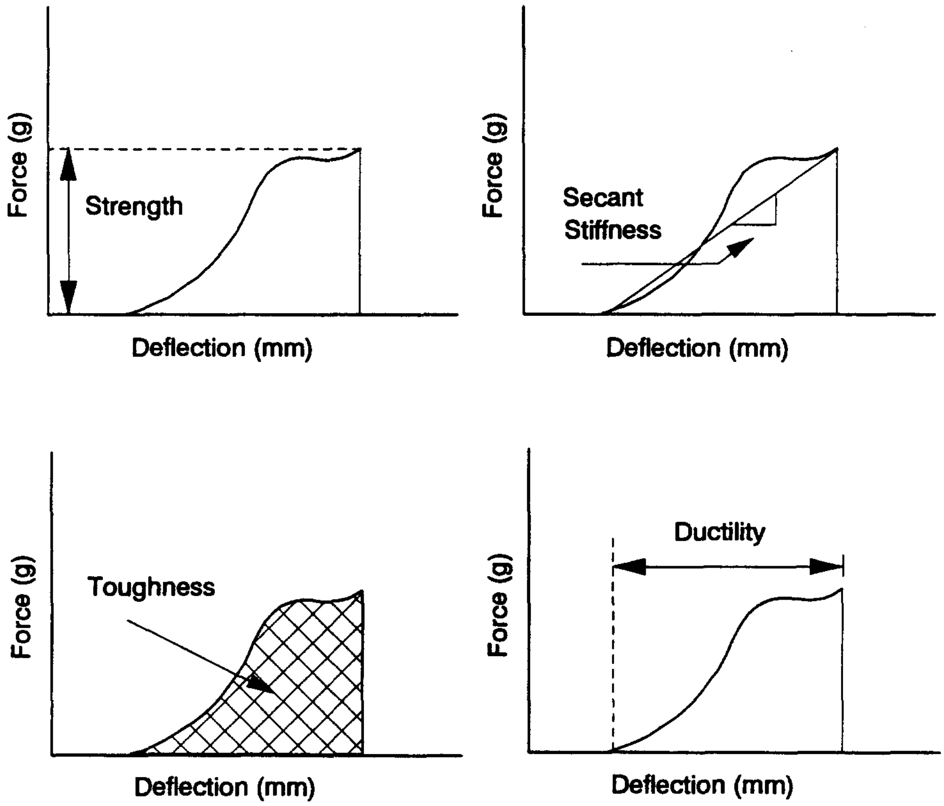

Figure 3 Typical force–deflection trace with the definitions of the four mechanical properties annotated

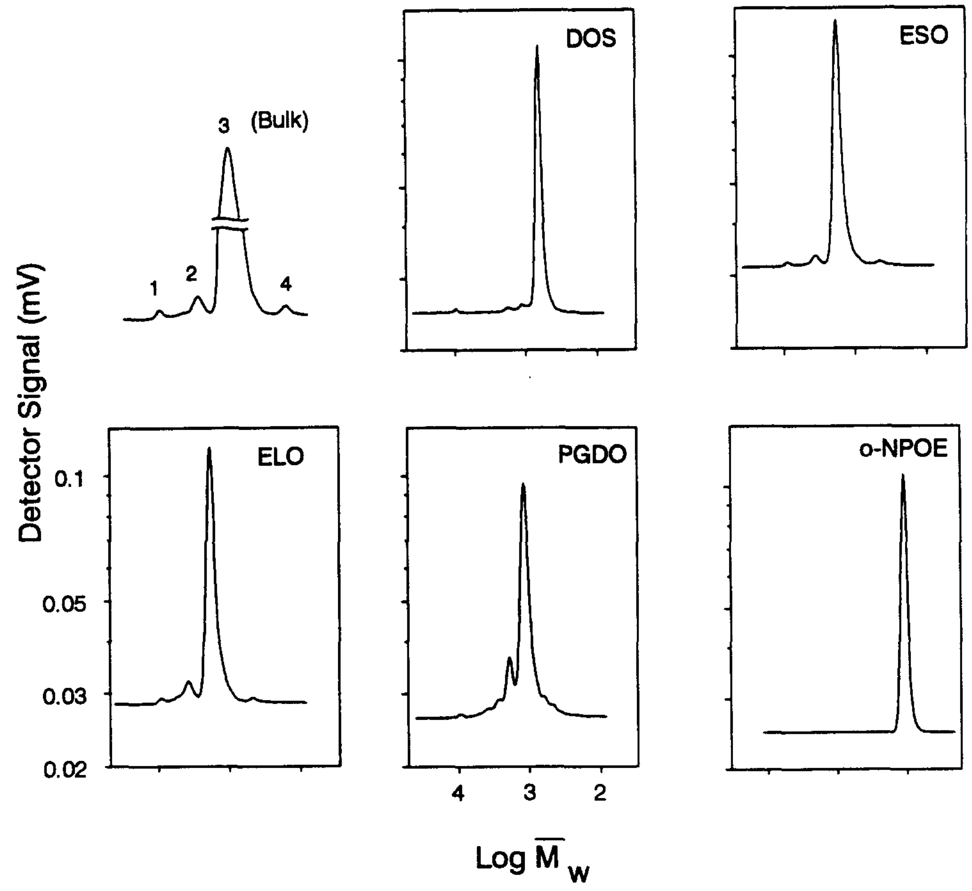

Figure 4 Plasticizer chromatograms with the peak designations highlighted (upper left) and quantified (see *Table 3*)

Table 3 Molecular weight and physical characterization of plasticizers

Code	Peak molecular weight 1	2	3 (Bulk)	4	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	*PDI*	μ (cps)
DOS	7150	928	523	–	520	525	529	1.0	16.7
ESO	6940	2840	1450	375	1320	1470	1730	1.1	329
ELO	6940	2860	1430	375	1320	1490	1770	1.1	763
PGDO	2120	1470	928	483	889	1040	1370	1.2	106
o-NPOE	–	–	177	–	184	188	210	1.0	11.9

198×10^3 and 94×10^3, respectively. The corresponding h.p.g.p.c. chromatograms for the plasticizers (*Figure 4*) show that three of the five plasticizers exhibit a four-peak distribution with the highest frequency of molecules appearing in the third peak. The *o*-NPOE is the only plasticizer to have a monodisperse distribution as well as having the lowest $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$ and μ values (*Table 3*). DOS is second lowest in $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$ and μ values, but DOS exhibits the highest peak molecular weight of all the plasticizers at 7150. PGDO follows DOS at an $\bar{M}_w$ of 1040. The highest $\bar{M}_w$ values belong to ESO and ELO, which are very similar to each other in molecular weight, although ELO has a significantly higher μ than ESO. Despite multipeaked distributions, all plasticizers are fairly monodisperse (*Table 3*).

Figure 5 displays membrane strength, secant stiffness, toughness and ductility all as functions of membrane thickness for each of the five plasticized conditions. Best-fit linear regressions are displayed. All data points were included in the regression analysis except in the case of *o*-NPOE, where one outlying point was left out of the computations.

The plasticizer that yielded the strongest membranes was PGDO, followed successively by DOS, ELO, *o*-NPOE and ESO. There is nearly a factor of two difference in strength between the ESO-plasticized membranes and the PGDO-plasticized membranes at any thickness. (Indeed, a 40 μm PGDO membrane would be comparable in strength to a 100 μm ESO membrane!) Secant stiffness results show *o*-NPOE to yield membranes with the highest stiffness, followed by PGDO, DOS, ELO and ESO. Toughness data show the same interrelationships as strength data except that the *o*-NPOE and ESO rankings are transposed; that is, membranes fabricated with *o*-NPOE now produce the least tough membranes. Finally, *o*-NPOE produces dramatically less ductile membranes than the other plasticizers, all of which show ductility characteristics

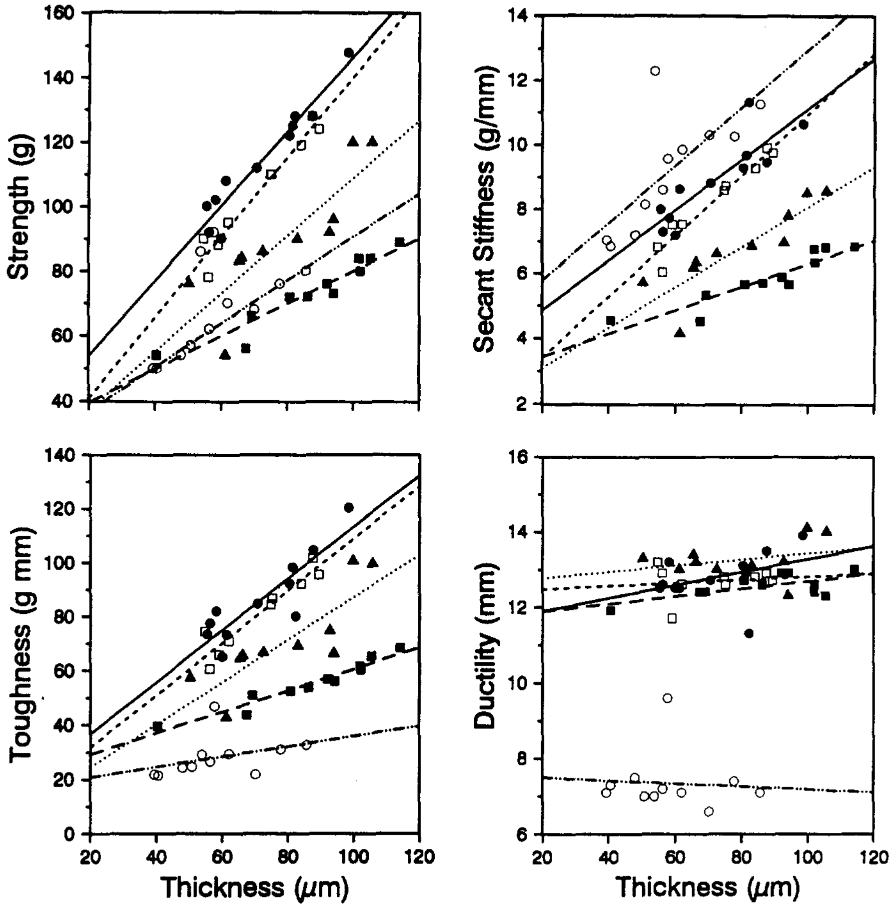

Figure 5 Mechanical properties (see *Figure 3*) as a function of membrane thickness at 200 phr plasticizer: (□) DOS; (■) ESO; (▲) ELO; (●) PGDO; (○) *o*-NPOE. Corresponding slopes *m*, correlation coefficients *r* and probabilities *p* are detailed in *Table 4*

Table 4 Regression results

		Regression slopes *m*				Correlation coefficients *r*			
	n	Strength	Secant stiffness	Toughness	Ductility	Strength	Secant stiffness	Toughness	Ductility
DOS	9	1.244	−0.064	0.965	0.004	0.975^a	0.967^a	0.944^a	0.138^c
ESO	11	0.504	−0.077	0.393	0.010	0.954^a	0.965^a	0.967^a	0.666^c
ELO	10	0.896	−0.070	0.781	0.008	0.851^b	0.822^b	0.823^b	0.295^c
PGDO	11	1.162	−0.053	1.475	0.017	0.962^a	0.884^a	0.876^a	0.378^c
o-NPOE	9	0.672	−0.081	0.087	−0.004	0.982^a	0.950^a	0.276^c	0.221^c

^{a}Significant at $p<0.001$
^{b}Significant at $p<0.01$
^{c}Not significant

similar to each other. Ductility appears to be independent of thickness in all cases, as shown by the correlation coefficients of the regression slopes that approach zero (*Table 4*).

Table 4 also shows that the regression slopes of nearly all strength, stiffness and toughness measurements are significantly different from zero, having correlation coefficients such that, with only one exception, $p \leqslant 0.01$ (see *Figure 5*).

DISCUSSION

Network models

Polymer network models were once idealized as having chemical crosslinks that served as permanent points of attachment between flexible chains[20]. However, chemical crosslinking has not been induced in the current system. Transient network models in which entanglements, or physical crosslinks, serve as temporary point-like junctions constitute another ideal network type[21]. In one transient model, PS chains were found to behave in accordance with the theory[22,23], yet solvent-dependent characteristics showed significant deviations within the same sample type. These observations show that the transient network theory is not comprehensive enough since entanglements alone are assured only in the case of very good solvents. Some adjustment to the theory must be made to account for other types of intermolecular attractions which occur in poorer solvents.

In the theoretical gap between these two models, the

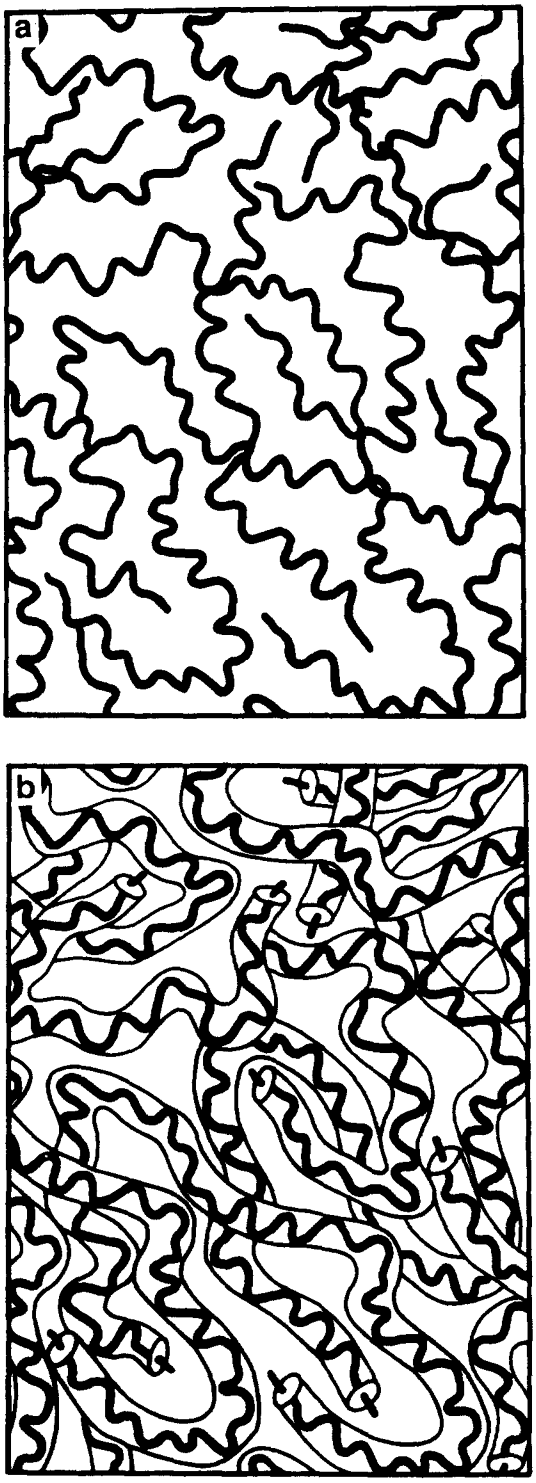

Figure 6 (a) Rendering of a physical network model of a highly plasticized PVC membrane. (b) Detailed rendering of an IPN-like model representing the optimal plasticizer level incorporated as 'tubes' surrounding the polymer chains, plus some occluded plasticizer. The outcome is an over-plasticized membrane in which $phr_{exp}/phr_{min} > 2$, with molecular spacing as shown in (a)

physical network models exist[24], in which temporary crosslinks can form in reversible gels, accounting for the formation and dissociation of non-permanent network junctions. This process of junction formation and dissociation is governed by thermodynamic equilibria. For example, PVC is a polymer known for being slightly crystalline as well as being a reversibly gelling synthetic polymer. Takahashi *et al.*[25] studied PVC by X-ray diffraction and observed two very weak rings in a diffuse background. They interpreted this as evidence for a crystallite-based gel. Since the level of crystallinity is slight in PVC (ca. 11–18%)[26] and the membranes are in effect dilute solutions that would tend to discourage crystallite formation, the presence of crystallites is not assured. In their absence, pseudo-crystalline zones that are formed by somewhat organized amorphous bundles or domains could anchor these networks within an otherwise truly amorphous structure.

The current membranes can be visualized as a physical network with polymer chains (amorphous PVC) distributed in a solvent (plasticizer) of high viscosity (*Figure 6a*). The model chains represent the average paths of the coiled polymer chains; each chain has a finer coiled structure than is represented. Mechanical properties of membranes are mainly determined by polymer chain intermolecular attractions and entanglements, since no crosslinking is present; plasticizer–plasticizer interactions contribute minimally to mechanical properties via weak viscous shearing. As *Figure 7* shows, however, with a change in plasticizer type, the mechanical properties of the membrane are altered dramatically. This confirms that plasticizers must indirectly modulate mechanical properties by profoundly affecting the manner in which polymer chains interact.

Membrane puncture testing

In present applications, *o*-NPOE is currently favoured as an ISE plasticizer because of its highly polar nature (see *Figure 1*). The *o*-NPOE molecule is rather small, with a relatively short carbon chain and a highly polar nitro grouping. In PVC applications, the polar part of the plasticizer molecule determines its solvent power for the polymer, while the non-polar part confers other properties, such as flexibility[27]. The polar nitro group contributes to the decreased strength and toughness effects, while the small non-polar part of its molecular structure has a correspondingly negative effect on the ductility of the plasticized samples. Because ductility can be defined as the displacement at some specific event on the force–displacement curve, ductility can be considered a measure of flexibility[28]. Consequently *Figure 5* shows that, while the *o*-NPOE molecule may make superior ISEs from an electrochemical standpoint, *o*-NPOE lacks flexibility as seen by its grossly inferior ductility and its large secant stiffness. Moreover, the polar group makes it second from the bottom in strength and the worst by far in toughness.

Plasticizer molecular weight effects

In order to determine the $\bar{M}_w$ effect of plasticizer on the mechanical properties of the membranes, the data were grouped into four thickness ranges: 30–50 μm = 40 μm, 50–70 μm = 60 μm, 70–90 μm = 80 μm and 90–110 μm = 100 μm. For a given data set (that is, one mechanical property and one plasticizer) all values within a thickness range were averaged. Each point in *Figure 7* represents the average of up to four samples. Ductility is constant except at low $\bar{M}_w$ (*o*-NPOE). The stiffness data behave as the inverse of ductility with high $\bar{M}_w$ plasticizers yielding less stiff membranes. It appears that an optimal $\bar{M}_w$ of roughly 1000 exists with respect to strength and toughness. In choosing a plasticizer for incorporation into an ISE membrane, strength and toughness should be maximized for membrane integrity. Because ISE applications necessitate that the membranes

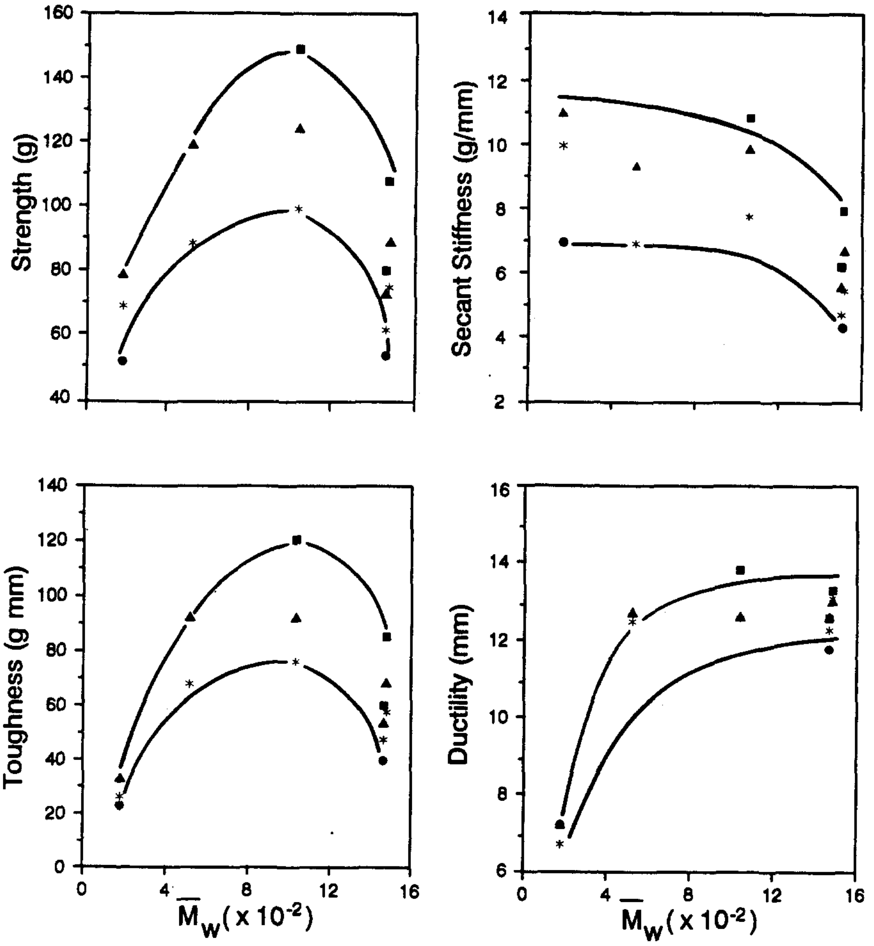

Figure 7 Mechanical properties (see *Figure 3*) as a function of plasticizer weight average molecular weight ($\bar{M}_w$, see *Table 3*) and membrane thickness: (●) 40 μm; (*) 60 μm; (▲) 80 μm; (■) 100 μm. The inscribed envelopes suggest that optimal mechanical properties at 200 phr are achieved at $\bar{M}_w \approx 1000$, i.e. when PGDO is the plasticizer

display some rigidity and are deformable, stiffness and ductility are thus also important parameters to optimize. Consequently, when considering all parameters together at 200 phr, plasticizers above and below the $\bar{M}_w$ value of 1000 yield less optimal membrane properties. As the plasticizer varies, polymer–plasticizer interactions may account for this.

Current theories regarding the diffusion of polymer chains in an entangled polymer matrix suggest three different mechanisms based on the relative molecular weights of the polymer and matrix: reptation[29], constraint release[30–33] and Stokes–Einstein diffusion[34]. Green and Kramer[35] used forward-recoil spectroscopy to study the matrix effects on diffusion of long PS polymer chains in a PS matrix. In the case of long chains in a low-molecular-weight matrix where the matrix was non-entangled, the researchers found that the long chains diffused as coils in a viscous medium. In an entangled matrix, reptation and constraint release were applicable. The dependence of their tracer diffusion coefficient on chain molecular weight suggested that the entangled matrix effectively screened the hydrodynamic interactions between chain segments. In the current system, the plasticizer of lowest molecular weight must yield a non-entangled matrix owing to its small and compact structure. However, ESO and ELO, with higher molecular weights and higher degrees of branching, may in fact yield entangled matrices. If so, a similar shielding of polymer chains from one another could account for the decreased mechanical properties observed for these plasticizers.

Plasticization level

Membranes can also be weakened by an excessive amount of plasticizer. The stoichiometry between plasticizer and PVC is not thoroughly defined. There are attachment points, and certainly there must be arrangements most suitable for both plasticizer and PVC that are at the lowest energy states. Since PVC forms a helix with structural units of about 16.5 Å long[36], the formula weight for one helical unit is 875. In order to block each polar group on the PVC, the minimal required amount of plasticizer for complete plasticization phr_{min} must be

$$phr_{\text{min}} = \frac{\bar{M}_w}{875} \times 100 \qquad (1)$$

The actual experimental level used in this study, $phr_{\text{exp}} = 200$, is well above the minimal level required for the plasticizers studied, that is in all cases the membranes are over-plasticized: $phr_{\text{exp}}/phr_{\text{min}} > 1$ (*Figure 8*). However, even at this rate of plasticization, all membranes were optically clear and appeared to be fully integrated.

The phr_{min} levels provide some basis to judge the degree of over-plasticizing that exists for each plasticizer at the current highly plasticized level of $phr_{\text{exp}} = 200$. When

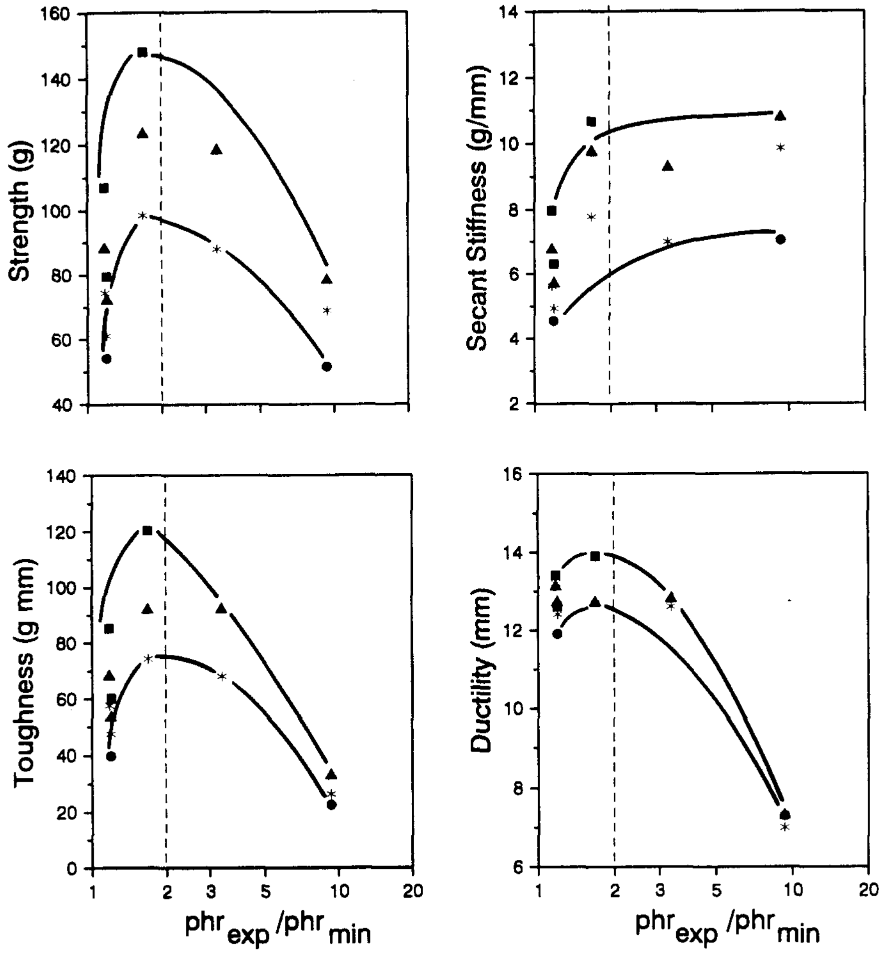

Figure 8 Mechanical properties (see *Figure 3*) as a function of relative plasticizer level (phr_{exp}/phr_{min}; see equation (1) and *Table 3*) and membrane thickness: (●) 40 μm; (*) 60 μm; (▲) 80 μm; (■) 100 μm. Here the inscribed envelopes suggest that optimal mechanical properties are achieved at $phr_{exp}/phr_{min} \approx 2$, i.e. when PGDO is the plasticizer

the mechanical properties *versus* the plasticizer ratio phr_{exp}/phr_{min} were plotted for the four thickness ranges (40, 60, 80 and 100 μm), the overall optimal mechanical properties were attained at a ratio $phr_{exp}/phr_{min} \approx 2$, which corresponds to PGDO. This level represents an appropriate compromise between the minimal level required to separate the polymer chains sufficiently to obtain membrane flexibility and separating them excessively, allowing too little chain–chain interaction both by intermolecular attractions and by entanglements. In contrast, the plasticizer that resulted in the most extreme case of over-plasticization was *o*-NPOE (*Figure 8*), with over nine times the minimum required level. Perhaps if a factor of two over phr_{min} had been used, the optimal mechanical properties of an *o*-NPOE-plasticized PVC would have been achieved, too.

Plasticizer dynamic viscosity

One property of a plasticizer that may affect the ease of intermolecular chain interaction is dynamic viscosity. By analysing the grouped data with respect to plasticizer viscosity (see *Table 3*), the anomalous behaviour of *o*-NPOE is again apparent (*Figure 9*). It is clear, however, that plasticizer viscosity has no definitive role in the determination of the present mechanical properties. Further plots were generated that examined membrane mechanical properties *versus* a normalized viscosity parameter (to eliminate the effect of differing phr_{exp}/phr_{min} ratios) and the plasticizer Hildebrand solubility parameters (which were calculated from molecular group contributions). These efforts, too, showed no ability to predict the mechanical properties of membranes.

Towards an IPN-like model

An interpenetrating polymer network (IPN) is one example of a physical network model. True molecular interpenetration can occur only in the case of mutual solubility. If there is some phase separation but both networks are continuous throughout the whole sample, then some phase interpenetration must exist, at least at the supermolecular level as molecular groups. Research has been done on IPN-like systems that incorporate physical crosslinks or entanglements rather than chemical crosslinks[37,38]. An analogy can be made of the current system to a semi-IPN with one crosslinked polymer and one linear polymer. PVC is analogous to the crosslinked polymer with physical entanglements of the long amorphous chains serving as the crosslinks; plasticizer is analogous to the linear polymer. In that the membranes contain the plasticizer and exhibit some structural strength on deformation, PVC is shown to be soluble and continuous throughout the membrane. Plasticizer continuity is assured by the levels of plasticization

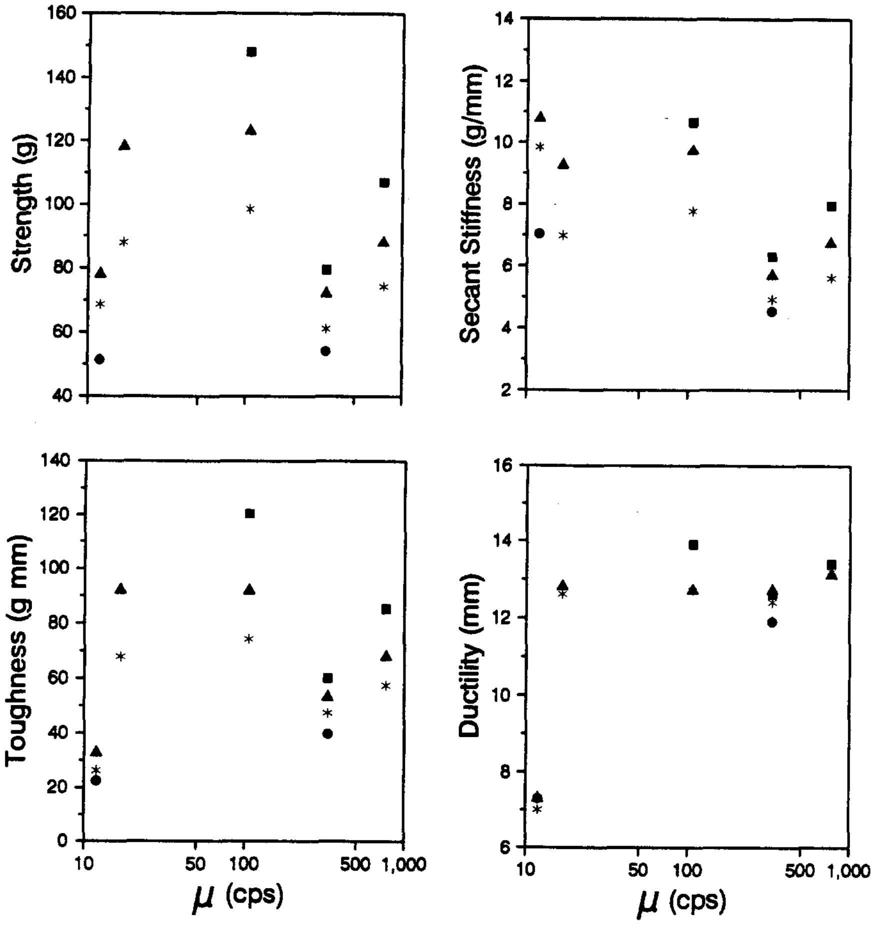

Figure 9 Mechanical properties (see *Figure 3*) as a function of plasticizer dynamic viscosity (μ; see *Table 3*) and membrane thickness: (●) 40 μm; (*) 60 μm; (▲) 80 μm; (■) 100 μm. In this case, no clear trends emerge at 200 phr

employed; the plasticizer molecules must contact each other throughout the sample. The ratio indicated by this research, namely $phr_{exp}/phr_{min} \approx 2$, suggests that there must be a sufficient number of plasticizer molecules available to block PVC polar groups and another portion of equivalent size to enhance chain sliding. When $phr_{exp}/phr_{min} > 2$, there must be some occluded plasticizer that serves no constructive mechanical function. To illustrate this interrelationship, *Figure 6b* shows each polymer chain surrounded by a 'tube' of plasticizer, the amount that is necessary for optimizing mechanical properties. In addition, some occluded plasticizer is depicted to illustrate the condition $phr_{exp}/phr_{min} > 2$. As the plasticizer phase increases, the 'tubes' containing polymer chains and their attendant plasticizer molecules become increasingly screened from one another, permitting less interaction between the polymer phases, and resulting in decreased strength and toughness. These same outcomes occur if $phr_{exp}/phr_{min} < 2$, i.e. when the tubes are not filled, or the required amount of lubricity is not available. Further work is necessary to elucidate the model in general and the unusual behaviour at $phr_{exp}/phr_{min} < 2$ in particular.

CONCLUSIONS

For PVC membranes containing 200 phr plasticizer we can conclude the following.

1. There is an optimal choice of plasticizer $\bar{M}_w$ to yield over-plasticized PVC membranes with maximal strength and toughness. This $\bar{M}_w$ is roughly 1000. Ductility of the membranes remains constant throughout the range except at very low plasticizer $\bar{M}_w$ values.
2. The high polarity of the *o*-NPOE molecule resulted in behaviour very different from the other plasticizer molecules when over-plasticized PVC membrane mechanical properties were tested. The *o*-NPOE was the least effective plasticizer from the mechanical property standpoint, yielding membranes with the highest stiffness, and lowest toughness and ductility. The PGDO was the best, yielding membranes with the highest strength, toughness and ductility.
3. The optimal level of plasticizer must be twice the minimum required for total plasticization. Using such a ratio represents the best compromise between separating the polymer chains sufficiently to obtain membrane flexibility and separating them excessively to minimize chain–chain interactions by either intermolecular attractions or entanglements.

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REFERENCES

1 Nass, L. (Ed.) 'Encyclopedia of PVC', Vol. 1, Marcel Dekker, New York, 1976, p. 445
2 Johnson, T. A., Engle, C. L., Kusy, R. P., Knisley, S. B., Graebner, C. A. and Gettes, L. S. *Am. J. Physiol.* 1990, **258**, H1224
3 Horvai, G., Graf, E., Toth, K., Pungor, E. and Buck, R. P. *Anal. Chem.* 1986, **58**, 2735
4 Thomas, J. D. R. *Anal. Chim. Acta* 1986, **180**, 289
5 Kusy, R. P. and Buchanan, J. W. *Microbeam Anal.* 1989, 63
6 Flory, P. J. *Chem. Phys.* 1949, **17**, 223
7 Anagnostopoulos, C. E. and Coran, A. Y. *J. Polym. Sci.* 1962, **57**, 1
8 Anagnostopoulos, C. E., Coran, A. Y. and Gamrath, H. R. *Mod. Plast.* 1965, **43**, 141
9 Patel, S. V. and Gilbert, M. *Plast. Rubber Proc. Appl.* 1986, **6**, 321
10 Hildebrand, J. H. and Scott, R. L. 'The Solubility of Non-Electrolytes', 3rd Edn, Vol. 17, Reinhold, New York, 1949, p. 223
11 Ramos-de Valle, L. and Gilbert, M. *Plast. Rubber Proc. Appl.* 1990, **13**, 151
12 Kisbenyi, M. *J. Polym. Sci. C* 1971, **33**, 113
13 Oesch, U. and Simon, W. *Anal. Chem.* 1980, **52**, 692
14 Ammann, D. 'Ion-Selective Microelectrodes', Springer-Verlag, Berlin, 1986, p. 55
15 Ammann, D. 'Ion-Selective Microelectrodes', Springer-Verlag, Berlin, 1986, p. 88
16 Moody, G. J. and Thomas, J. D. R. in 'Ion-Selective Electrodes in Analytical Chemistry' (Ed. H. Freiser), Vol. 1, Plenum Press, New York, 1978, Ch. 4
17 Brandrup, J. and Immergut, E. H. (Eds) 'Polymer Handbook', 2nd Edn, Wiley, New York, 1975, p. IV-14
18 Craggs, A., Moody, G. J. and Thomas, J. D. R. *J. Chem. Educ.* 1970, **51**, 541
19 Peng, T., Kusy, R. P., Garner, S. C., Hirsch, P. F. and DeBlanco, M. C. *J. Bone Min. Res.* 1987, **2**, 249
20 Flory, P. J. *Polymer* 1979, **20**, 1317
21 De Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979, p. 219
22 Wiltzius, P., Haller, H. R., Cannell, D. S. and Schafer, D. W. *Phys. Rev. Lett.* 1983, **51**, 223
23 Wiltzius, P., Haller, H. R., Cannell, D. S. and Schafer, D. W. *Phys. Rev. Lett.* 1983, **51**, 1183
24 Burchard, W., Stadler, R., Freitas, L. L., Möller, M., Omeis, J. and Mühleisen, E. in 'Biological and Synthetic Polymer Networks' (Ed. O. Kramer), Elsevier, London, 1986, p. 3
25 Takahashi, A., Nakamura, T. and Kagawa, J. *Polym. J.* 1972, **3**, 207
26 Maron, S. H. and Filisko, F. E. *J. Macromol. Sci.* 1972, **B6** (2), 413
27 Ritchie, P. D. (Ed.) 'Plasticizers, Stabilizers, and Fillers', Plastics Institute, Iliffe Books Ltd, London, 1972, p. 139
28 Kusy, R. P., Dilley, G. J. and Whitley, J. Q. *Clin. Mater.* 1988, **3**, 41
29 De Gennes, P. G. *J. Chem. Phys.* 1971, **55**, 572
30 Doi, M. and Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* 1978, 1789
31 Doi, M. and Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* 1978, 1802
32 Graessley, W. W. *Adv. Polym. Sci.* 1982, **47**, 67
33 Klein, J. *Macromolecules* 1986, **19**, 105
34 Daoud, M. and De Gennes, P. G. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 1971
35 Green, P. F. and Kramer, E. J. *Macromolecules* 1986, **19**, 1108
36 Sears, J. K. and Touchette, N. W. in 'Encyclopedia of Polymer Science and Engineering' (Ed. J. I. Kroschwitz), 2nd Edn, Supplement, Wiley Interscience, New York, p. 593
37 Klemper, D. and Frisch, H. L. *Polym. Lett.* 1970, **8**, 525
38 Kresge, E. N. in 'Polymer Blends' (Eds D. R. Paul and S. Newman), Vol. 7, Academic Press, New York, 1978, Ch. 20