

The Estimation of Mechanical Properties of Polymers from Molecular Structure

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SYNOPSIS

The use of semiempirical and empirical relationships have been developed to estimate the mechanical properties of polymeric materials. Based on these relationships, properties can be calculated from only five basic molecular properties. They are the molecular weight, van der Waals volume, the length and number of rotational bonds in the repeat unit, as well as the T_g of the polymer. Since these are fundamental molecular properties, they can be obtained from either purely theoretical calculations or from group contributions. The use of these techniques by polymer chemists can provide a screening technique that will significantly diminish their bench time so that they may pursue more creatively the design of new polymeric materials. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

The purpose of this paper was to give polymer chemists a technique for estimating the important mechanical properties of a material from its molecular structure. Hopefully, this will provide a screening tool that will significantly diminish their bench time so that they may pursue more creatively the design of new polymeric materials.

The important practical applications of polymers are generally determined by a combination of heat resistance, stiffness, strength, and cost—in short, the engineering properties of a material. Other properties may be of importance, but, if a polymer does not have a balance of these properties, its chances for commercial success are very limited. To a large extent, these properties can be associated on the molecular scale with the cohesive forces, the molecular size, and the chain mobility. The approach taken here is to relate molecular properties of the repeat unit to the properties of the polymer. Repeat unit properties can be obtained from group additivity or by simple calculations.

In the usual group contribution approach, little consideration is given to the association between molecular properties and macroproperties. The re-

sult is that for each property one wishes to calculate a new table of fragments must be used. One of the purposes of this study was to show that mechanical properties can be estimated from a very few basic molecular properties. Thus, we use semiempirical means whenever available to make these associations. This has the effect of limiting the number of tables of group contributions necessary to calculate the basic properties, it simplifies the calculation procedures, and it indicates to the theoreticians the approximate form to which their theories may be reduced.

Linking the mechanical properties to the molecular properties of a material is the equation of state. Thermodynamic relationships that involve the pressure, volume, temperature, and internal energy lead to the most fundamental equation of state. They are expressed in the following form:

$$P = \left(\frac{\partial S}{\partial V} \right)_T - \left(\frac{\partial U}{\partial V} \right)_T \quad (1)$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V = T\alpha B \quad (2)$$

Here, U is the internal energy, S is the entropy, and P , V , and T have their usual meanings, and $\alpha = 1/V[(\partial V)/(\partial T)]_P$ and $B = -V[(\partial P)/(\partial V)]_P$ are

the thermal expansion and bulk modulus, respectively.

For mechanical properties below the glass transition temperature at constant temperature and very small deformations, the entropy is assumed to be constant. Above the glass transition temperature (in the plateau region), the material behaves as a rubber and the mechanical process can be assumed to be mostly entropic. This leads to the following interesting relationships:

$$\text{Below } T_g, P = T\alpha B - \left(\frac{\partial U}{\partial V}\right)_T \quad (3)$$

$$\text{At } P = 0, T\alpha B = \left(\frac{\partial U}{\partial V}\right)_T \quad (4)$$

$$\text{Above } T_g, P = T\left(\frac{\partial S}{\partial V}\right)_T \quad (5)$$

$$\text{At } P = 0, B = \frac{1}{\alpha T}\left(\frac{\partial S}{\partial V}\right)_T \quad (6)$$

Based on these simplifying assumptions, we will proceed to develop estimates of the mechanical properties of polymers.

II. PRESSURE-VOLUME-TEMPERATURE RELATIONSHIPS

A. Volume-Temperature

It has been found by a number of investigators that there is a correspondence between the van der Waals

Table I Thermal Expansion Data

Polymer	V_w (cc/mol)	M_0 (gm/mol)	T_g (K)	ρ (gm/cc)	$\left(\frac{dV}{dT}\right)_g$ (cc/K $\times 10^4$)	$\left(\frac{dV}{dT}\right)$ (cc/K $\times 10^4$)
PE ^a	20.46	28.0	140	0.97	2.01	5.31
PIB ^a	40.90	56.1	202	0.93	1.44	5.86
PMA ^a	45.88	86.1	282	1.21	2.70	5.60
PVA ^a	45.88	86.1	304	1.18	2.12	5.83
P4MP1 ^a	61.36	84.2	302	0.84	3.83	7.61
PVC ^b	29.23	62.5	355	1.36	1.75	4.85
PS ^a	62.85	104.1	373	1.03	2.50	5.50
PMMA ^a	56.10	100.0	378	1.15	2.13	4.90
PP ^a	30.68	42.1	258	0.88	3.43	8.50
PaMS ^a	73.07	118.1	453	1.02	2.40	5.40
PET ^a	94.18	192.2	339	1.30	1.62	4.42
PDMPO ^a	69.32	120.0	480	1.03	2.04	5.13
PBD ^b	37.40	54.1	188	1.12	2.00	7.05
PEMA ^a	66.33	114.1	338	1.11	3.09	5.40
PPMA ^a	76.56	128.2	308	1.07	3.63	5.75
PBMA ^a	86.79	142.2	292	1.06	4.12	6.05
PHMA ^a	107.25	170.3	268	1.03	4.40	6.80
POMA ^a	127.71	198.4	253	1.00	4.15	6.00
PVME ^a	34.38	58.0	260	1.02	2.16	6.45
PVEE ^a	44.61	72.0	231	1.00	3.03	7.26
PVBE ^a	54.84	86.0	218	0.98	3.9	7.26
PVHE ^a	75.30	114.0	199	0.99	3.75	6.60
PCLST ^c	72.73	138.5	389	0.97	1.45	4.97
PTBS ^c	104.67	160.0	405	0.95	2.58	5.90
PVT ^c	74.00	118.0	388	1.02	1.59	3.78
PEA ^b	56.11	100.1	251	1.09	2.80	6.10
PBA ^b	76.57	128.2	224	1.11	2.60	6.00
SAN 76/24 ^c	53.78	88.7	384	1.07	2.27	4.87
PC ^b	136.21	254.3	423	1.20	2.65	5.35
PEIS ^b	94.18	192.2	324	1.33	2.00	4.55

^a Ref. 5. All the densities reported from this reference are cited at the glass transition temperature.

^b Ref. 6.

^c Internal data of The Dow Chemical Co.

volume and the molar volume of polymers.¹⁻³ Van der Waals volume is defined as the space occupied by a molecule that is impenetrable to other molecules.¹ Van der Waals radii can be obtained from gas-phase data⁴ and bond lengths can be obtained from X-ray diffraction studies. Using these data, the volume may be calculated for a particular molecule. Bondi¹ and Slonimskii et al.² calculated group contributions to the van der Waals volume for large molecules and demonstrated the additivity.

Since polymers consist of long chains, which dominate their configuration as they solidify into a glass, one might expect that they would pack quite similarly regardless of their quite different chemical natures. To determine if this hypothesis is correct, it is necessary to obtain the molar volume at some point where the polymers may be expected to be in the same equivalent state and to compare them with a measurable molecular volume such as the van der Waals volume. Two temperatures are of interest: absolute zero and the glass transition temperature. At absolute zero, all thermal motion stops and the material is in a static state. The glass transition is considered to be the point where the material begins to take on long-range motion and the properties are no longer controlled by short-range interactions.

In Table I, we have compiled the densities and the thermal coefficient, in terms of the slope of the volume-temperature curve, from several sources in the literature. We have then calculated the volume at the glass transition temperature and at 0 K using a straight-line extrapolation of the data. The results are tabulated in Table II. The data from Table II is then plotted as van der Waals volume vs. the molar volumes and fit with a straight line that was forced through zero. The results of these plots are shown in Figure 1(a)-(c).

It is apparent from the data that there is a reasonably good fit between the molar volumes at the selected equivalent states. To determine the validity of the approximation, thermal expansion data ranging from room temperature down to 14 K were obtained from the work of Roe and Simha.⁷ A fifth-degree polynomial was fit to the data (see Fig. 2) and the volume-temperature curves were then extracted from the data by using eqs. (7) and (8):

$$\alpha = aT^5 + bT^4 + cT^3 + dT^2 + eT + f \quad (7)$$

$$V_{0g} = V_{298} \exp - \int_0^{298} \alpha dT \quad (8)$$

$$V = V_{0g} \exp \int_0^T \alpha dT \quad (9)$$

Table II Molar Volumes

Polymer	V_w (cc/mol)	V_g (cc/mol)	V_{0g} (cc/mol)	V_{0r} (cc/mol)
PE	20.5	28.9	28.2	26.9
PIB	40.9	60.1	58.4	53.6
PMA	45.9	69.4	62.9	55.9
PVA	45.9	72.7	67.2	57.5
P4MP1	61.4	100.5	90.7	81.4
PVC	29.2	45.4	38.7	35.1
PS	62.9	100.9	91.2	79.6
PMMA	56.1	86.7	78.6	68.2
PP	30.7	47.5	44.1	38.3
PaMS	73.1	115.2	102.3	86.4
PET	94.2	147.6	137.1	119.0
PDMPO	69.3	116.4	104.6	86.9
PBD	37.4	44.1	42.0	36.9
PEMA	66.3	102.6	90.7	81.9
PPMA	76.6	119.2	104.9	96.7
PBMA	86.8	134.5	117.5	109.6
PHMA	107.3	165.2	145.2	134.5
POMA	127.7	184.4	165.0	168.7
PVME	34.4	54.0	50.7	44.3
PVEE	44.6	72.2	67.2	60.1
PVBE	54.8	87.4	80.1	73.8
PVHE	75.3	115.6	107.1	100.7
PCLST	72.7	143.3	135.5	116.6
PTBS	104.7	171.7	155.0	133.4
PVT	74.0	117.3	110.0	100.0
PEA	56.1	88.3	81.4	73.0
PBA	76.5	109.0	102.1	91.7
SAN 76/24	53.8	84.6	76.9	68.0
PC	136.2	220.3	197.8	162.8
PEIS	94.2	145.0	132.5	116.6

where $a, b, c, d, e,$ and f are coefficients from the fifth-degree polynomial fit, and $T =$ temperature, K.

The thermal expansion curves show very clearly the various transitions due to thermally activated molecular motions. However, when these data are integrated to give the volume-temperature curves, these transitions are smeared out into what appears to be a nearly continuous function as can be seen in Figure 3(a)-(c).

The results can be fit with a $T^{1.5}$ relationship as predicted by free-volume theory.⁸ However, from 150 K to the glass transition temperature, the data can be very nicely approximated by a straight line. These relationships are shown by the solid and dashed lines in Figure 3(a)-(c) and are described by eqs. (10) and (11). Table III summarizes the data for the six different materials:

$$V = \delta \frac{T^{1.5}}{T_g^{1.5}} V_{0g} \quad (10)$$

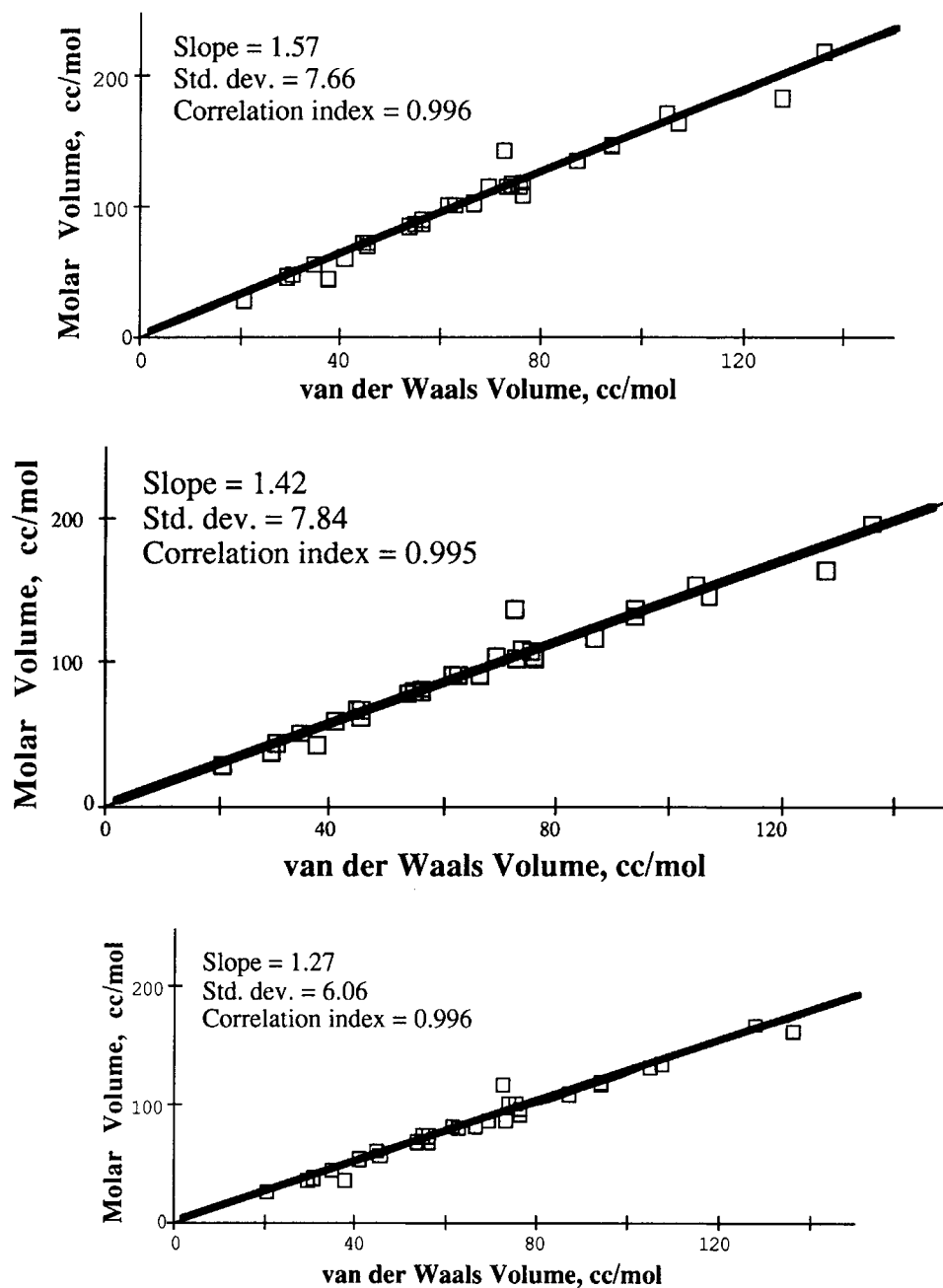


Figure 1 (a) Van der Waals volume vs. molar volume at the glass transition temperature; (b) van der Waals volume vs. molar volume for the glass at 0 K; (c) van der Waals volume vs. molar volume of the rubber at 0 K.

$$V = \delta \frac{T}{T_g} + V_{0g} \quad (11)$$

where T_g = glass transition temperature, K, and $\delta = V_g - V_{0g} = 0.15$.

Based on the results from these data, we feel justified in defining the slope of the volume-tempera-

ture curve as a constant over a wide range of temperatures. This approximation allows the data to be described by the Simha-Boyer⁹-type diagram as shown in Figure 4. Further, the volume can be described as being distributed in three parts: (1) the van der Waals volume or the volume considered to be impenetrable by other molecules; (2) the packing

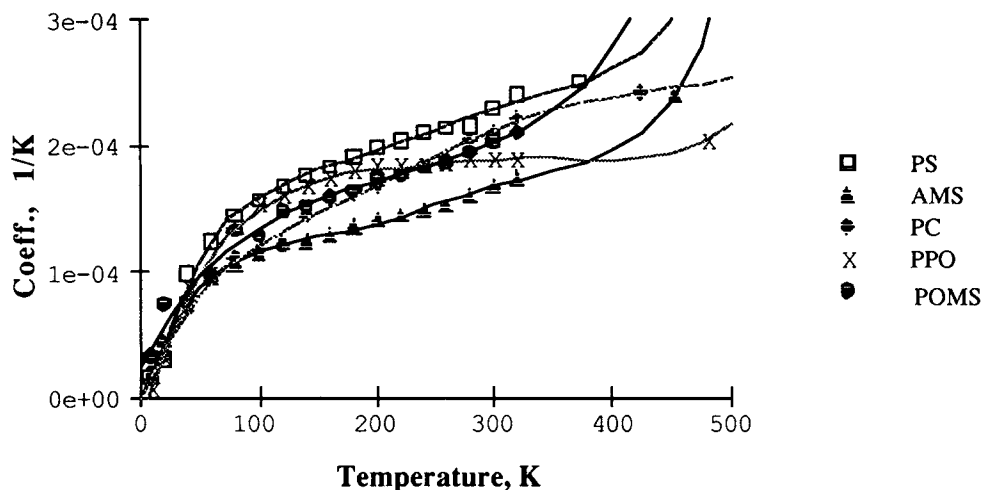


Figure 2 Thermal expansion data of Roe and Simha⁷ fit with a fifth-degree polynomial.

volume that reflects the shape and long-chain nature of the molecule; and (3) the expansion volume that is due to thermal motion of the molecules.

Using the values generated from the straight-line fit of the data in Figure 1(a)–(c), the slope and the intercept of the volume–temperature curve can be established for amorphous polymers in both the glassy and rubbery state:

$$V_g = \left(0.15 \frac{T}{T_g} + 1.42 \right) V_w \quad (12a)$$

$$V_r = \left(0.30 \frac{T}{T_g} + 1.27 \right) V_w \quad (12b)$$

The thermal expansion coefficient can thus be obtained by differentiating eqs 12(a) and (12b) and by using its standard definition:

$$\alpha_g = \frac{1}{V} \frac{dV}{dT} = \frac{1}{(T + 9.47T_g)} \quad (13a)$$

$$\alpha_r = \frac{1}{V} \frac{dV}{dT} = \frac{1}{(T + 4.23T_g)} \quad (13b)$$

The density can be estimated from the molecular weight of the repeat unit divided by the molar volume:

$$\rho = \frac{M}{V} \quad (14)$$

B. Pressure–Volume

The pressure–volume–temperature response in polymers can be determined by several molecular factors. They include intermolecular potential, bond rotational energies bond, and bond-angle distortion energies. The bond-angle distortion energies are important in anisotropic systems where aligned chains are subjected to a stress or pressure. In isotropic glasses where the bonds are randomly oriented, the properties are controlled by rotational and intermolecular potentials. In the following sections, we will separate these into entropy and internal energy terms and then try to relate this to the molecular structure using properties that can be related to the molecular structure either by direct calculation or through quantitative structure property relationships (QSPR).

In a perfect crystalline lattice, specific short-range and long-range interactions can be accounted for, but amorphous polymers by their very nature do not fit these computational schemes. Several attempts have been made at using quasi-lattice models to describe the equation of state.^{10–16} Most of these are quite limited and need additional information about reduced variables or lattice types. Computer models using molecular mechanics techniques have been devised based either on an amorphous cell, which is generated from a parent chain whose conformation is generated using rotational isomeric-state calculations,¹⁷ or on computer models that also start from RIS configurations and generate radial distribution functions.¹⁸ Both approaches use an $1/r^6$ potential function to calculate the state properties.

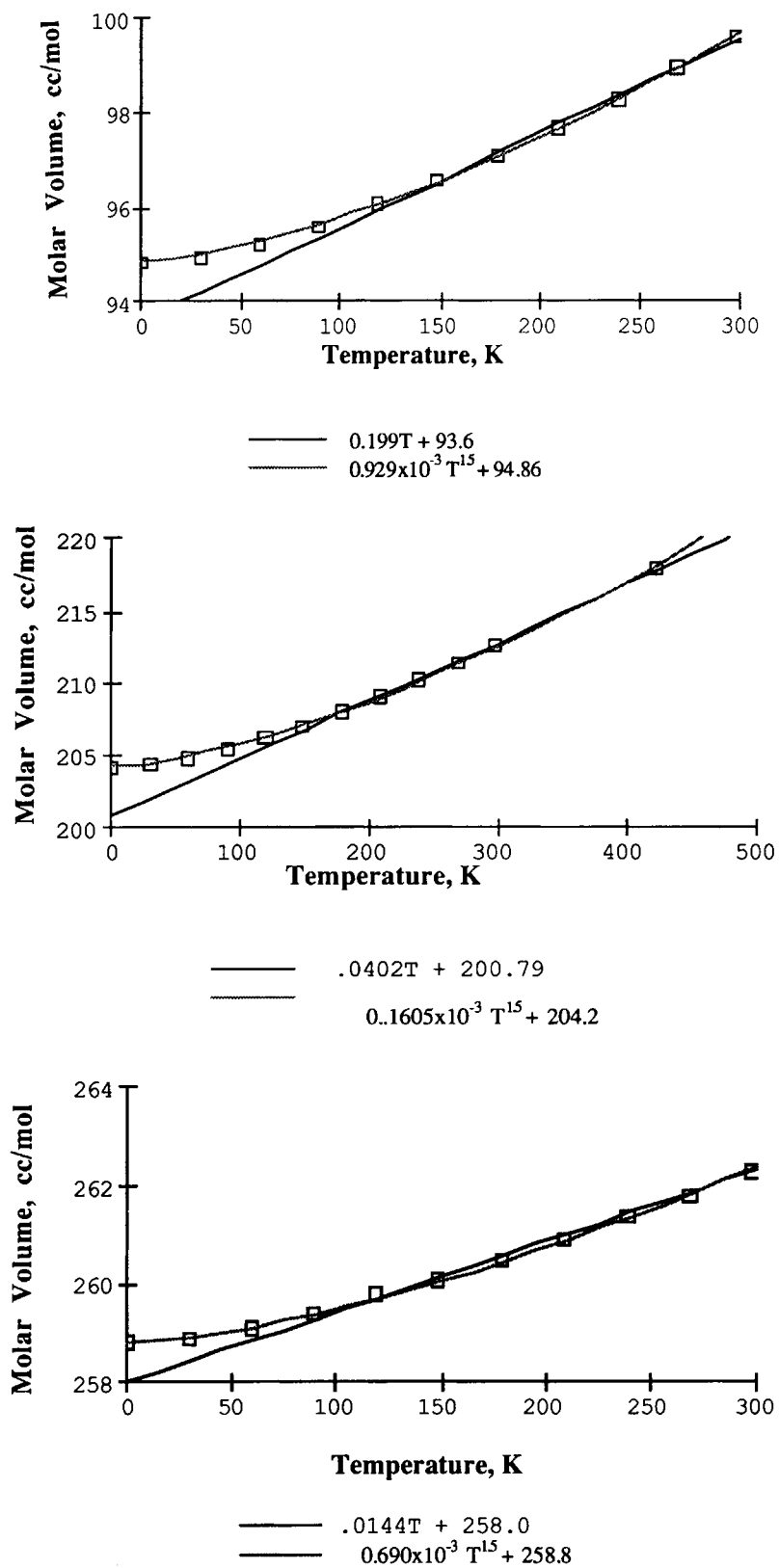


Figure 3 (a) Calculated volume-temperature data for polystyrene; (b) calculated volume-temperature data for polycarbonate; (c) calculated volume-temperature data for poly[*N,N'*(*p,p'*-oxydiphenylene)pyromellitimide] (PI).

Table III Molar Volume Calculated from the Data from Roe and Simha⁷

Polymer	$V_{0g}(T)$ (cc/mol)	$V_{0g}(T^{1.5})$ (cc/mol)	T_g (K)	V_w (cc/mol)	$\frac{V_{0g}(T)}{V_w}$	$\frac{V_{0g}(T^{1.5})}{V_w}$
PS	93.6	94.85	373	62.85	1.49	1.51
PC	200.8	204.2	423	136.2	1.47	1.50
PPO	106.2	107.4	475	69.32	1.53	1.55
POMS	109.8	110.9	409	74.00	1.48	1.50
PaMS	93.6	112.9	443	73.07	1.53	1.55
PI	258	258.8	630	185.2	1.39	1.40
CHDMT	215.5	218.7	365	149.2	1.44	1.46

Here, we will divide the polymer molecule into suitable submolecules (repeat units) that will then be assumed to be surrounded by a mean field at a distance r . We will also assume that the volume of the repeat unit can be described in terms of its van der Waals volume. The field potential will be described by a Lennard-Jones¹⁹ potential function:

$$e = e_0 \left[2 \left(\frac{r_0}{r} \right)^6 - \left(\frac{r_0}{r} \right)^{12} \right] \quad (15)$$

Thus, the molar volume is related to the intermolecular distance r as follows:

$$V = \frac{Nr^3}{C} \quad (16)$$

where N is Avogadro's number and C is a constant that corrects for the geometry of the submolecule. On substituting the ratio of the volumes, one arrives at the following relationship between volume and intermolecular distance:

$$\frac{V}{V_0} = \left(\frac{r_0}{r} \right)^3 \quad (17)$$

The total potential energy of a system containing N repeat units is

$$U = Ne \text{ and at the minimum } U_0 = Ne_0 \quad (18)$$

Equations (15) and (18) combine to define the contribution to the internal energy U from the intermolecular potential:

$$U = U_0 \left[2 \left(\frac{V_0}{V} \right)^2 - \left(\frac{V_0}{V} \right)^4 \right] \quad (19)$$

Taking the partial of U with respect to V and substituting into the thermodynamic equation state for P below the glass transition temperature yields

$$P = \left(\frac{\partial S}{\partial V} \right)_T - \frac{4U_0}{V} \left[\left(\frac{V_0}{V} \right)^2 - \left(\frac{V_0}{V} \right)^4 \right] \quad (20)$$

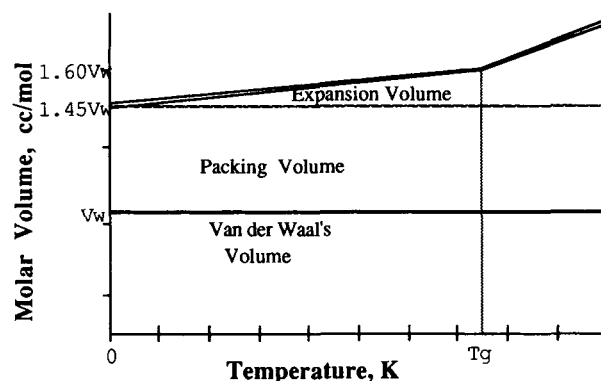
At zero pressure and constant temperature,

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{4U_0}{V_T} \left[\left(\frac{V_0}{V_T} \right)^2 - \left(\frac{V_0}{V_T} \right)^4 \right] \quad (21)$$

$$P = 4U_0 \left[V_0^2 \left(\frac{1}{V^3} - \frac{1}{V_T^3} \right) - V_0^4 \left(\frac{1}{V^5} - \frac{1}{V_T^5} \right) \right] \quad (22)$$

where V is the molar volume, cc/mol; V_T , the molar volume at the temperature of interest, cc/mol; V_0 , the molar volume at the minimum in the potential well; and U_0 , is the depth of the well

The bulk modulus is defined by $-V[(\partial P)/(\partial V)]_T$. Taking the derivative of eq. (22) and multiplying by V gives

**Figure 4** Volume-temperature diagram.

$$B = \frac{4U_0}{V} \left[\left(\frac{5V_0}{V} \right)^4 - \left(\frac{3V_0}{V} \right)^2 \right] \quad (23)$$

Haward²⁰ used a form of this equation to predict the relationship between the volume and the bulk modulus of poly(methyl methacrylate).

Pressure-volume data were obtained from Kaelble²¹ was fit to eq. (23) using regression analysis to solve for the value of U_0 . The factor V_0 was assumed to be the molar volume of the glass at 0 K ($1.42V_w$). The solid line shows the fit to the data in Figure 5(a)-(c).

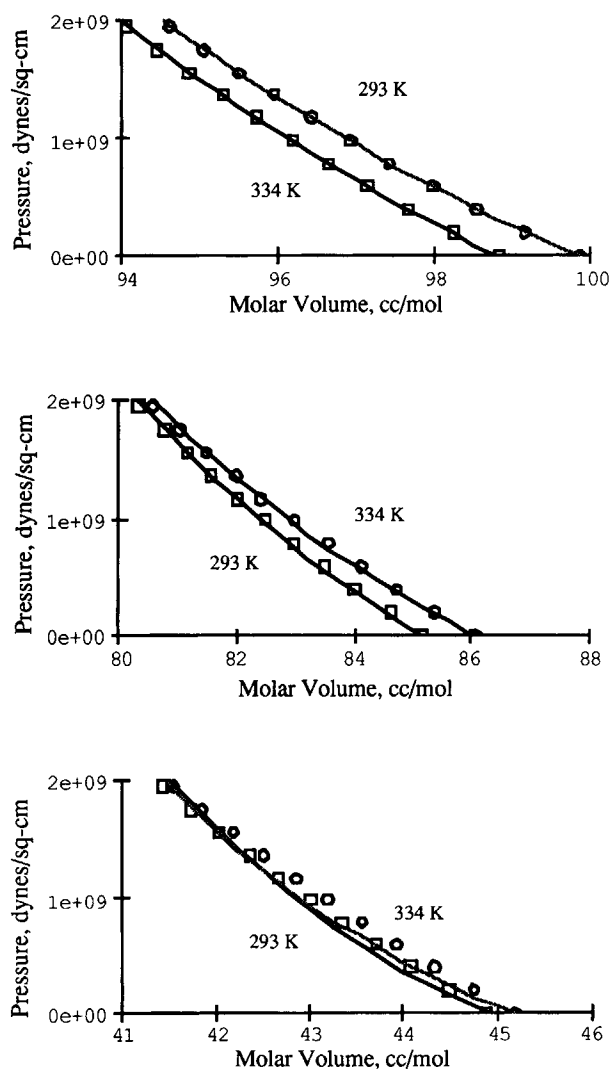


Figure 5 (a) Pressure-volume data²¹ for polystyrene; (b) pressure-volume data²¹ for poly(methyl methacrylate); (c) pressure-volume data²¹ for poly(vinyl chloride).

Table IV U_0 as Calculated from the Pressure-Volume Data

Polymer	U_0 (293) (j/mol)	U_0 (334) (j/mol)	U_{coh} (exp) (j/mol)	Ratio (U_0/U_{coh})
PS	7.30E4	7.12E4	3.43E4	2.15
PMMA	5.09E4	4.79E4	2.93E4	1.74
PVC	3.31E4	3.09E4	1.72E4	1.92

Table IV shows the values of U_0 that were obtained from the fit of the data along with the molar cohesive energy as calculated from the data of Fedors²² and van der Waals volume from Bondi¹ and Slonimski et al.² as compiled in Ref. 23. The ratio of U_0 to the cohesive energy for these three polymers averages 1.94, or approximately 2. We will show later from the analysis of the mechanical properties that this ratio, U_0/U_{coh} , is indeed very close to 2.

III. MECHANICAL PROPERTIES

A. The Modulus and the Stress-Strain Curve

1. Volume-Strain Relationships

The important moduli for engineering applications are the shear modulus G and the tensile modulus E . They are related to the bulk modulus B in the following manner:

$$E = 3B(1 - 2\nu) = 2G(1 + \nu) \quad (24)$$

E and G may be evaluated from the bulk modulus using eq. (23) if the value ν (Poisson's ratio) is known. Poisson's ratio is defined as the ratio of the lateral contraction in the y and z directions as a tensile stress is applied in the x direction and it accounts for the change in volume during the deformation process. Stress and strain can be introduced into the calculations as volume changes by using the following relationships:

$$\frac{dV}{V} = d\epsilon_x + d\epsilon_y + d\epsilon_z \quad (25)$$

$$P = \frac{1}{3}(\sigma_x + \sigma_y + \sigma_z) \quad (26)$$

$$\nu = -d\epsilon_y/d\epsilon_x = -d\epsilon_z/d\epsilon_x \quad (27)$$

where the subscripts x , y , and z denote the stresses and strains in three principal directions.

In the case of a material being stretched uniaxially in the x direction, eq. (25) can be solved for the strain in terms of Poisson's ratio and the volume by using eq. (27):

$$\epsilon = \int d\epsilon = \int_{V_T}^V \frac{1}{(1-2\nu)V} dV \quad (28)$$

Using the results of eqs. (26) and (28) with the assumption that the stress is zero in all directions, except in the x direction, eq. (22) can now be solved in terms of stress and strain where V_ϵ is the volume-dependent strain:

$$\sigma_x = 12U_0 \left[\left(-\frac{V_0^4}{V_\epsilon^5} + \frac{V_0^2}{V_\epsilon^3} \right) - \left(-\frac{V_0^4}{V_T^5} + \frac{2}{V_T^3} \right) \right] \quad (29)$$

Similarly, substituting eqs. (24) and (28) into eq. (23), the tensile modulus is obtained:

$$E = 24(1-2\nu)U \coth \left[5 \frac{V_0^4}{V_\epsilon^5} - 3 \frac{V_0^2}{V_\epsilon^3} \right] \quad (30)$$

The value of V_T can be estimated from van der Waals volume and the glass transition temperature using eqs. (10), (11), or (12), and U_0 may be estimated using the approximation that it is two times the cohesive energy. However, without a relationship between Poisson's ratio and the molecular structure, we are unable to calculate the tensile or shear moduli.

2. Poisson's Ratio.

Our model as presently constituted does not contain any information about the directional properties of the system. However, just as the bulk modulus varies as $1/V$ in eq. (23), one might expect that a simplified unidirectional (tensile) moduli would vary as the area being stressed. Using this analogy, Poisson's ratio can be equated to E/B from eq. (25). The result of this relationship can be stated as follows:

$$\nu = 0.5 - k\sqrt{A} \quad (31)$$

The value A can be thought of as the molecular cross-sectional area and is defined here as the area of the end of a cylinder whose volume is equal to the van der Waals volume of the repeat unit and has a length of the repeat unit in its all trans-conformation:

$$A = \frac{V_w}{N_A l_m} \quad (32)$$

where l_m is the length of the repeat unit in its fully extended conformation and N_A is Avogadro's number. The fully extended conformation corresponds to the all-*trans*-conformation and can be calculated by assuming ideal tetrahedral bonding around the carbon atoms in the polymer backbone and using simple trigonometric relationships. Table V gives the calculated A for a number of polymers for which we have data.

The data from Table V is plotted in Figure 6 and is represented by the circular symbols. The line in Figure 6 was obtained by fitting the data to a square-root argument using regression analysis. The statistical fit represented by eq. (33) has a standard deviation of 0.019 and a correlation index of 0.998:

$$\nu = -2.37 \times 10^6 \sqrt{A} + 0.513 \quad (33)$$

To estimate the stress-strain relationship as a function of temperature, we must have both Poisson's ratio and the volume as a function of temperature. The temperature-volume relationships can be calculated from eq. (12a).

Table V Poisson's Ratio and Molecular Cross-sectional Area

Polymer	Poisson's Ratio	Molecular Cross-sectional Area (cm ² × 10 ⁻¹⁶)
Polycarbonate	0.401 ^a	19.8
PS	0.354 ^a	41.1
ST/MMA 35/65	0.361 ^a	38.0
Poly(<i>p</i> -methyl styrene)	0.341 ^a	48.4
SAN 76/24	0.366 ^a	33.8
PSF	0.441 ^a	20.1
PDMPO	0.410 ^b	27.6
PET	0.430 ^b	14.0
POMS	0.345 ^a	46.4
Arylate 1 : 1 : 2	0.433 ^a	19.2
Phenoxy resin	0.402 ^a	19.2
PMMA	0.371 ^a	37.2
PTBS	0.330 ^a	68.5
PVC	0.385 ^a	18.5
Poly(amide-imide)	0.380 ^a	18.6

^a Internal data of The Dow Chemical Co. Poisson's ratio was measured using an MTS biaxial extensometer no. 632.85B-05 in conjunction with an MTS 880 hydraulic testing machine. The tests were performed under the conditions of ASTM D638, using type 1 tensile specimens. The crosshead speed was 0.2 in./min. All samples were compression-molded and then annealed at (T_g + 30 K) for 24 h.

^b Data obtained from Ref. 24.

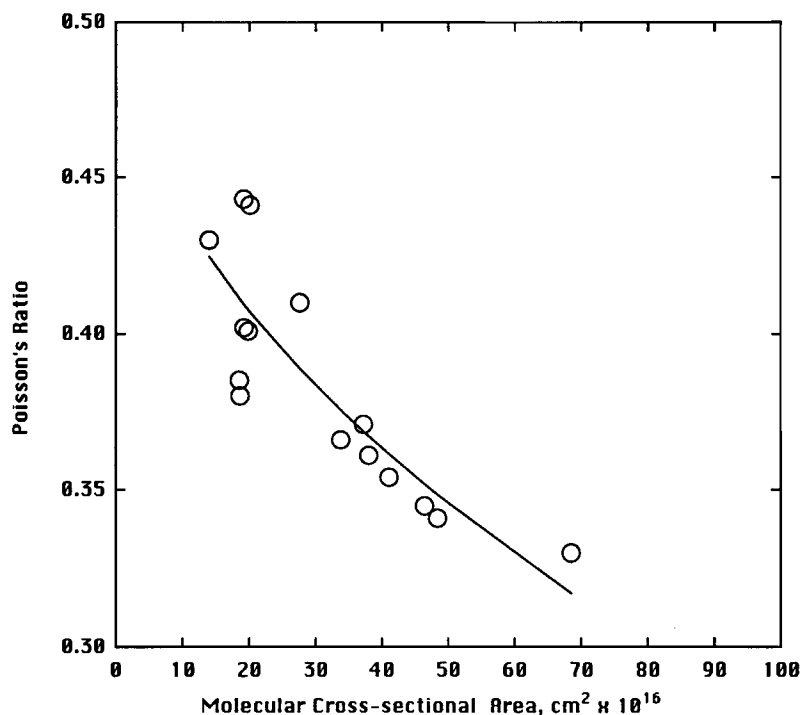


Figure 6 Poisson's ratio as a function of molecular area.

Poisson's ratio increases very slowly as a function of temperature to within 20° of the glass transition temperature with only very minor deviations due to low-temperature transitions. Just above the glass

transition temperature, Poisson's ratio is assumed to approach 0.5 so that the volume is conserved in the rubbery state. Based on the data and the previous assumption, a fitting function was developed to es-

Table VI Poisson's Ratio as a Function of Temperature

PC		PS		PMMA		PVT		ST/MMA		PVC		POMS	
<i>T</i>	ν	<i>T</i>	ν	<i>T</i>	ν	<i>T</i>	ν	<i>T</i>	ν	<i>T</i>	ν	<i>T</i>	ν
173	0.386	173	0.352	173	0.339	297	0.341	296	0.361	173	0.364	173	0.348
193	0.390	193	0.352	193	0.340	313	0.342	313	0.364	193	0.371	193	0.344
213	0.395	213	0.348	213	0.342	333	0.350	333	0.368	213	0.373	213	0.344
233	0.398	233	0.353	233	0.346	353	0.359	353	0.376	233	0.379	233	0.346
253	0.401	253	0.353	253	0.351	173	0.327	173	0.339	253	0.382	253	0.342
273	0.402	273	0.354	273	0.358	193	0.328	193	0.340	273	0.383	273	0.340
293	0.401	296	0.354	296	0.361	213	0.328	213	0.342	293	0.385	293	0.345
313	0.399	313	0.355	313	0.364	233	0.332	233	0.346	313	0.388	313	0.343
333	0.400	333	0.356	333	0.368	253	0.334	273	0.358	333	0.405	333	0.348
353	0.399	353	0.359	353	0.376	273	0.337	253	0.351	354	0.500	353	0.352
373	0.398	373	0.500	387	0.500	373	0.500	382	0.500	373	0.370	373	0.370
393	0.398												
413	0.401												
423	0.500												

Poisson's ratio was measured using an MTS biaxial extensometer no. 632.85B-05 in conjunction with an MTS 880 hydraulic testing machine. The tests were performed under the conditions of ASTM D638 using type 1 tensile specimens. The crosshead speed was 0.2 in./min. All samples were compression-molded and then annealed at (T_g 30 K) for 24 h.

estimate the relation between temperature and Poisson's ratio. Table VI gives Poisson's ratio as a function of the temperature for seven polymers. The fitting function for these data is as follows:

$$\nu_T = \nu_0 + 50 \frac{T}{T_g} \{ 1.63 \times 10^{-3} + \exp[0.459(T - T_g - 13)] \} \quad (34)$$

where ν_T is Poisson's ratio at temperature T , and ν_0 can be calculated from substituting in the value at room temperature for ν_T , which can be determined from eq. (33). The results of using this fitting equation are shown in Figures 7(a)–(c).

3. Tensile Modulus

Employing Poisson's ratio and the experimental tensile moduli, U_0 was calculated from eq. (30). The average of the ratio of U_0/U_{coh} was 2.06 for all 18 polymers in Table VII. The final column of the table shows the calculated values of the tensile modulus using $U_0 = 2.06 U_{\text{coh}}$. When compared with the experimental data (see Fig. 8), the results give a correlation index of 0.988 and a standard deviation of the regression of 0.334.

The final form for the room-temperature modulus in units of Pascals is

$$E = 24.2 \times 10^6 U_{\text{coh}} \left(1 - 47.4 \times 10^6 \sqrt{\frac{V_m}{N_A l_m}} \right) \times \left[5 \left(\frac{T_g}{9.47T + T_g} \right)^4 - 3 \left(\frac{T_g}{9.47T + T_g} \right)^2 \right] \quad (35)$$

The temperature modulus curve can be calculated by substituting the volume and Poisson's ratio temperature relationships from eqs. (11) and (33) into eq. (30). The results of this calculation are shown for polystyrene in Figure 9.

B. Deformation Mechanisms

There are two dominant modes of deformation in polymers: shear yielding and crazing. Although neither process is entirely understood at the molecular level, it is the intent here to attempt to correlate these mechanisms with the molecular structure using existing theories and empirical relationships.

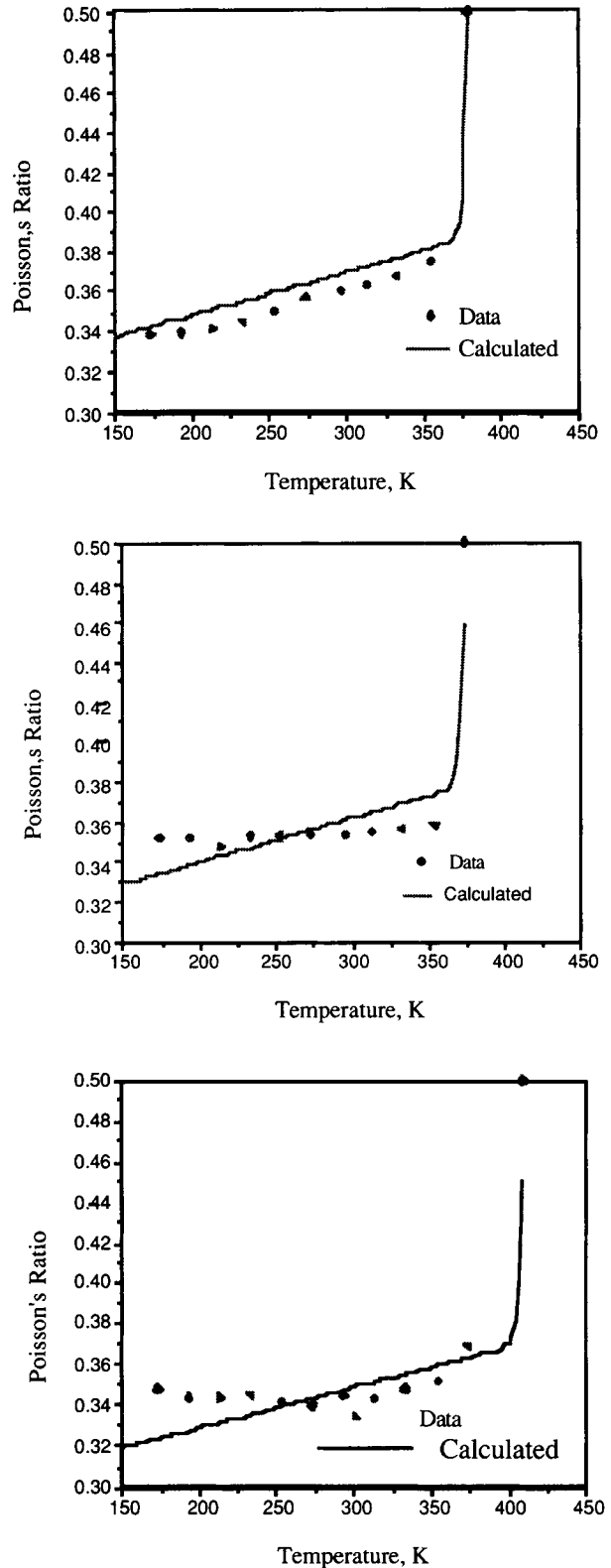


Figure 7 (a) Poisson's ratio as a function of temperature for poly(methyl methacrylate); (b) Poisson's ratio as a function of temperature for polystyrene; (c) Poisson's ratio as a function of temperature for polycarbonate.

Table VII Tensile Modulus Data

Polymer	Expt Modulus (GPa)	V_w (g/mol)	M_w (g/mol)	l_m (cm)	T_g (K)	$E_{coh} \times 10^{-4}$ (j/mol)	Poisson's Ratio	Calcd Modulus (GPa)
o-CIST	4.0 ^b	72.7	138.5	2.21	392	5.19	0.32	4.16
ST/MMA 65/35	3.5 ^b	58.0	101.4	2.21	373	3.61	0.36	2.91
ST/aMS 52/48	3.8 ^b	65.7	111	2.21	408	4.16	0.33	3.48
PAMS	3.1 ^b	68.5	118	2.11	443	4.31	0.32	3.1
PC	2.3 ^b	136.2	254	10.75	423	9.24	0.40	2.27
PS	3.3 ^b	62.9	104	2.21	373	4.03	0.35	3.20
PMMA	3.2 ^b	56.1	100	2.11	378	3.38	0.37	2.62
SAN 76/24	3.8 ^b	51.3	84.6	2.21	378	3.79	0.37	3.19
PPO	2.3 ^c	69.3	120	4.6	484	4.47	0.41	1.95
PET	3.0 ^c	90.9	192	10.77	346	12.06	0.43	3.11
PSF	2.5 ^c	234.3	443	18.3	463	19.20	0.44	1.66
PVC	2.6 ^c	28.6	62	2.55	358	1.99	0.39	2.52
PTBS	3.0 ^b	104.7	160	2.21	405	4.75	0.33	2.61
PHEN	2.3 ^b	162.6	277	10.70	363	12.50	0.40	2.59
PES	2.6 ^d	111.9	224.1	10.40	503	9.32	0.42	2.24
PEC 1 : 1	2.3 ^b	194.7	596	2.51	448	23.50	0.44	2.44
ARYL 1 : 1 : 2	2.1 ^d	338.7	644	31.20	463	28.50	0.44	1.71
PVT	3.1 ^b	74.0	118	2.21	388	4.50	0.34	3.26

^a All data for cohesive energy was obtained from Fedors (see Ref. 22) with the exception of the value of SO_2 where a value of 26,000 was used.

^b Internal data of The Dow Chemical Co. The data were obtained under conditions of ASTM D-638 using type 1 tensile bars and a 200 : 1 extensometer.

^c Ref. 25.

^d Ref. 26.

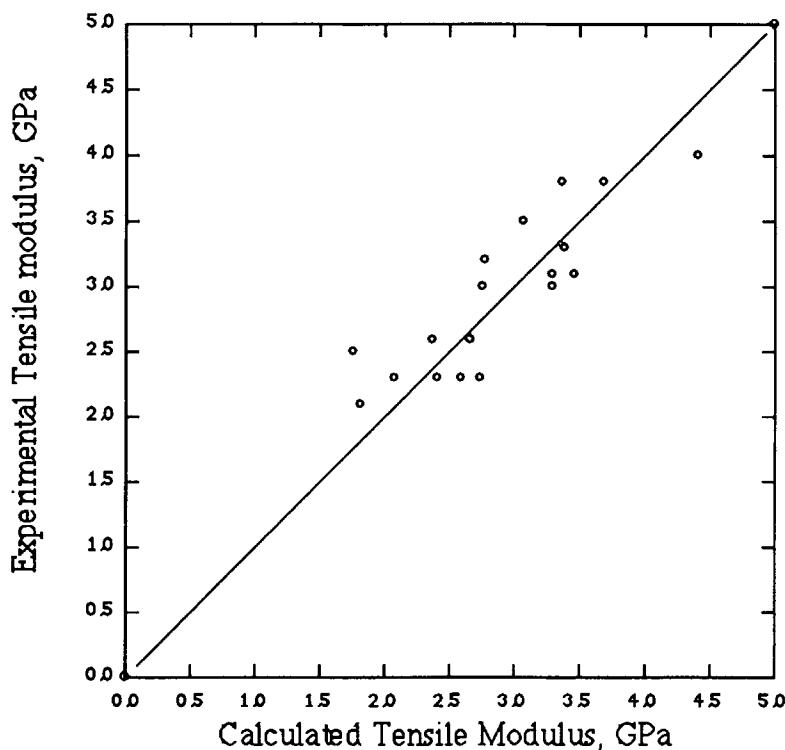


Figure 8 Comparison of experimental modulus with calculated tensile moduli.

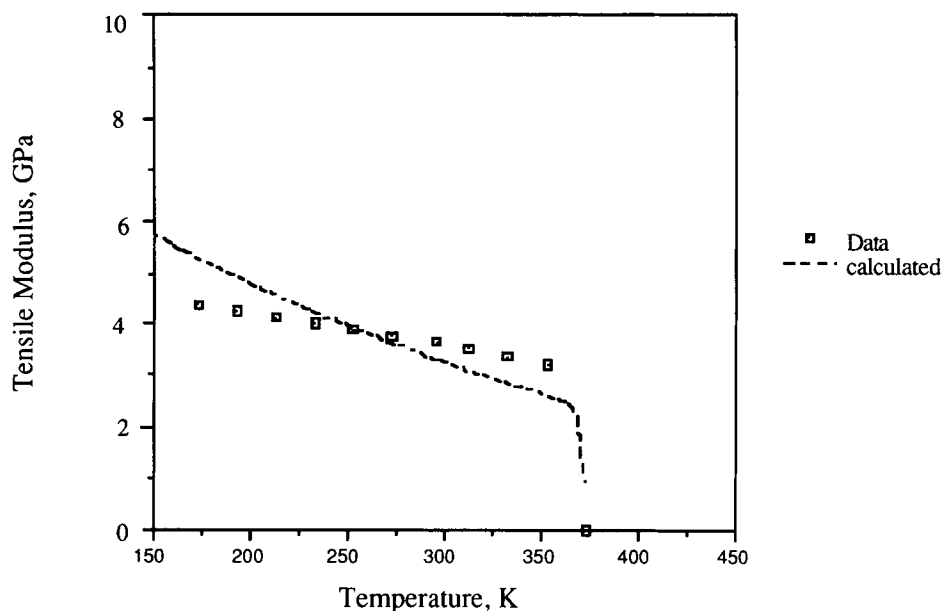


Figure 9 Tensile modulus of polystyrene as a function of temperature.

1. Shear Yielding

There have been many attempts to describe the yield strength from the molecular point of view.²⁷⁻³¹ None of these relates well to basic molecular parameters. However, a good correlation between modulus and yield strength has been noted by several researchers.³²⁻³⁴ Brown³⁵ suggests the following as an approximate equation for the yield point:

$$\tau_y = \kappa G(P, T) + \frac{kT}{V_s} \ln\left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0}\right) \quad (36)$$

where the value of κ is a constant for amorphous linear polymers, $G(P, T)$ is the shear modulus that depends on P and T , and V_s and $\dot{\epsilon}_0$ are material parameters involving an activation volume and a reference strain rate. Table VIII gives the tensile modulus and the tensile yield strength of a number of materials rather than the shear modulus.

On the assumption that the time-dependent term is much smaller than the first term of eq. (36), the data from Table VIII were fit by a straight line using regression analysis. The results of the fit are shown in Figure 10. The fit of the line to the data gives a standard deviation of 0.968 MPa and a correlation index of 0.976. It is interesting to note that the semicrystalline polymers as well as the amorphous polymers can be represented in this way, thus mak-

Table VIII Tensile Modulus and Yield Strength

Polymer	Tensile Modulus (GPa)	Yield Strength (MPa)	Ratio
HDPE ^a	1.0	30	0.030
LDPE ^a	0.2	8	0.040
PP ^a	1.4	32	0.023
PS ^b	3.3	76	0.023
PVC ^a	2.6	48	0.019
PTFE ^a	0.4	13	0.033
PMMA ^b	3.2	90	0.028
PC ^b	2.3	62	0.027
NY6/10 ^d	1.2	45	0.038
PET ^c	3.0	72	0.024
CA ^a	2.0	42	0.021
CLST ^b	4.0	90	0.025
SAN ^b	3.8	83	0.022
PPO ^c	2.3	72	0.031
PHEN ^c	2.3	66	0.029
PSF ^c	2.5	69	0.028
PES ^c	2.6	84	0.032
NY 6 ^a	1.9	50	0.263
NY 6/6 ^a	2.0	57	0.029

^a Ref. 24.

^b Internal data of The Dow Chemical Co. obtained from a biaxial test conducted in simultaneous tension and compression. The yield point was obtained by extrapolation using a Von Mises criteria.

^c Ref. 36.

^d Ref. 34.

ing the relationship universal for all polymers.³⁵ Equation (29) can now be rewritten in terms of tensile stress as follows:

$$\sigma_y = .025E + \frac{k}{T} \left(\frac{\epsilon}{\dot{\epsilon}_0} \right) \quad (37)$$

The other material constants change to account for the tensile component of stress rather than for the shear component. The temperature dependency of the yield stress can be determined from the temperature dependency of the modulus.

2. *Crazing*

Because the stress to initiate a craze depends on local stress concentrators, it is very difficult to analyze from a molecular viewpoint. In fact, as of yet, there appears to be no quantitative method of relating crazing to molecular structure.

However, the relationship between materials that craze and materials that shear yield has been correlated with entanglement spacing by Donald and Kramer.^{37,38} Using their results, a criterion can be established, based on the contour length of the en-

tanglement to predict if a material will craze or shear yield. If the contour length turns out to be greater than approximately 200 Å, the material will mostly likely craze. If the contour length is less than 200 Å, then shear yielding is expected. The contour length can be calculated from entanglement spacing that can be obtained from dynamic mechanical data (see section on entanglements). Wu³⁹ correlated the crazing stress σ_c with the entanglement density as follows:

$$\log_{10}(\sigma_c) = 1.83 + 0.5 \log_{10} \left(\frac{\rho}{M_e} \right) \quad (38)$$

3. *Brittle Fracture*

At sufficiently low temperatures, all glassy polymers behave in a brittle manner, but as the temperature approaches the glass transition temperature, they generally become ductile. The tensile stress to fracture at which the material exhibits no ductile failure mechanisms, i.e., crazing or shear yielding, is termed the brittle stress. Usually, this stress is never realized, except in highly cross-linked systems or at extremely low temperatures, because some ductile

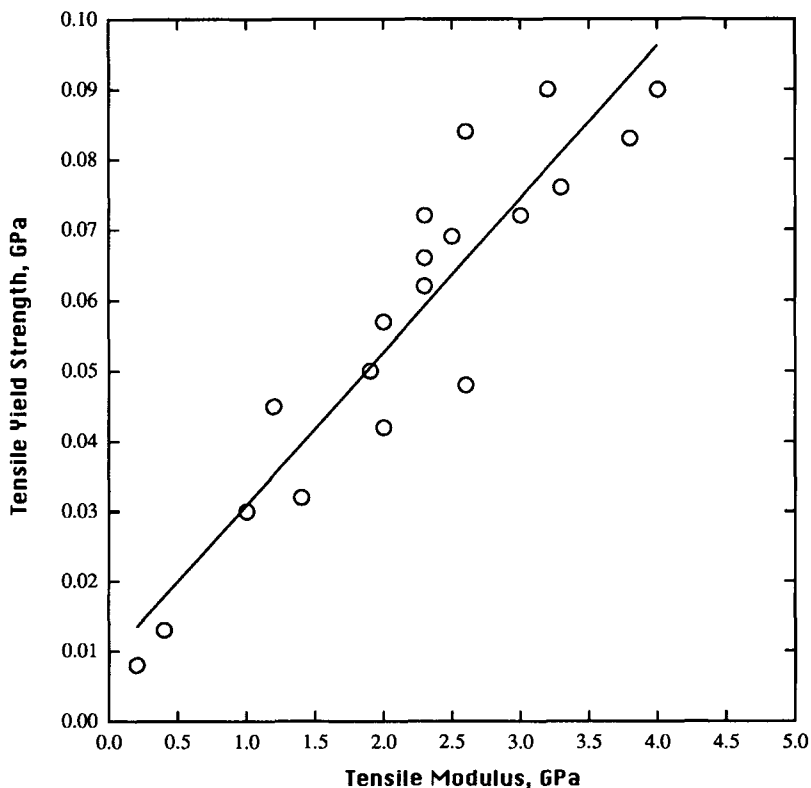


Figure 10 Tensile modulus vs. tensile yield strength.

process interferes before this limiting value is reached. However, it can be used as a base line to establish the maximum stress that a material can withstand. Therefore, if a shear yield stress is calculated that is higher than this value, brittle fracture can be expected to occur.

Vincent⁴⁰ attempted to quantify this number for a series of different polymeric materials and related the brittle stress to the number of backbone bonds per unit area. Data from Vincent as well as data from this laboratory along with pertinent molecular information are shown in Table IX. The number of bonds/cm² are calculated from the following expression:

$$n_B = \frac{Nl_m}{V} \quad (39)$$

where n_B is the number of bonds; N , Avogadro's number; l_m , the length of the repeat unit; and V , the molar volume. The theoretical brittle stress is then the number of bonds times the strength of an individual bond. The real strength of the material is much less because defects exist within the material that result in very highly stressed local areas. If we

plot n_B against the measured brittle strength, the result is a straight line. The slope of the line represents the strength per bond.

The results of a linear regression analysis of the data in Table IX is shown in Figure 11. The straight-line fit to the data has a standard deviation of regression of 16 MPa and a correlation index of 0.982.

The force to break a C—C bond is estimated to be $3-6 \times 10^{-9}N$.^{41,42} The slope of the brittle strength line is $0.038 \times 10^{-9}N$. Thus, only about 1% of the bonds are involved in the fracture process in amorphous materials or, in other terms, the stress concentration factor appears to be about 100 for a large number of materials. The brittle strength for amorphous polymers can be calculated from the following equation:

$$\sigma_b = 0.038 \times 10^{-9} \frac{N_A l_m}{V_m} \quad (40)$$

This approach can be used to estimate the theoretical strength of a fully oriented polymer as well as a thermoset. As an example using this correlation, we estimate the strength of a fully extended linear

Table IX Brittle Strength of Polymers

Polymer	T_g (K)	T_B (K)	l_m (Å)	V_w (cc/mol)	No. Bonds $\times 10^{-14}$	Brittle Strength (MPa)
PE ^a	147	77	2.53	20.4	4.94	160
P4MP ^a	305	243	1.98	61.3	1.26	53
PVC ^a	358	193	2.55	28.6	3.56	142
PS ^b	373	298	2.21	62.8	1.34	41
PMMA ^a	387	333	2.11	56.1	1.46	68
PP ^a	264	153	2.17	36.6	2.83	98
PET ^a	345	173	10.77	90.8	4.78	155
PC ^a	423	133	10.75	136.2	3.24	145
<i>p</i> -CLST ^b	389	298	2.21	72.7	1.16	41
PTBS ^b	405	298	2.21	104.6	0.81	31
PVT ^b	353	298	2.21	74.0	1.14	46
PMO ^a	216	173	1.92	16.0	4.6	216
SAN ^b	380	298	2.00	53.7	1.42	62
PPE ^a	255	213	2.16	51.1	1.79	58
PB-1 ^a	200	173	2.17	40.9	2.02	81
PTFE ^a	113	77	2.6	30.7	3.22	117
PES ^a	503	93	10.4	107.2	3.70	148
NY ^a	324	173	17.3	141.2	4.67	179

^a Ref. 40.

^b Internal data of The Dow Chemical Co. All brittle strength data was obtained at room temperature using a crosshead speed of 0.2 in./min with a type B tensile specimen under conditions of ASTM D638.

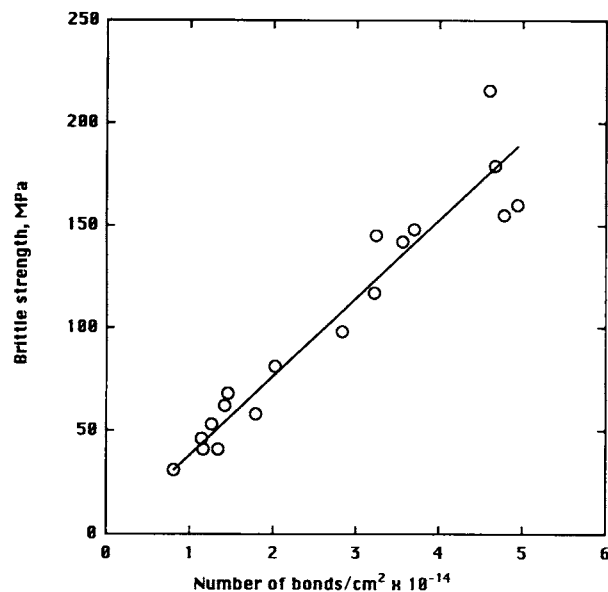


Figure 11 Brittle strength vs. number of backbone bonds.

polyethylene polymer to be 13.2 GPa. In practice, about 5 GPa has been achieved and the value of 13 GPa has been extrapolated from experimental data. This agreement points out the utility of this approach in estimating the strength of ordered polymers.

The effects of molecular weight on the strength of glassy polymers is to increase from near zero at very low molecular weights to a constant value at high molecular weights. Flory⁴³ showed that a plot of tensile strength vs. the reciprocal molecular weight gave a straight-line relationship for cellulose acetate. Gent and Thomas⁴⁴ derived the maximum value for the number-average molecular weight at zero flexural strength (M_f). Kinloch and Young⁴⁵ listed a few values for M_f and six have been plotted against the entanglement molecular weight (M_e).

As can be seen from Figure 12, the result is a fairly good straight-line relationship between M_f and M_e with a slope of 0.296. Assuming that the tensile strength and the flexural strength go to zero at the same molecular weight, a function of molecular weight can be written as follows:

$$\sigma_f = \sigma_b \left(1 - \frac{3.4 M_e}{M} \right) \quad (41)$$

where σ_f is the stress to fail; σ_b , the stress calculated from eq. (40); and M , the number-average molecular weight.

C. Entanglements and Mechanical Properties

We have already noted the dependence of crazing on the entanglement length. Many other properties also depend on the entanglement spacing such as the modulus in the plateau region above the glass transition, the viscosity, the fracture strength, and the glass transition.

Calculating shear and tensile properties above the glass transition is more difficult because polymers are viscoelastic and therefore very time-dependent. Our models are static models and therefore no information about time dependency can be obtained from them. However, we can estimate the shear modulus in the plateau zone from the analogy with rubber elasticity, where G_e is the equilibrium modulus; r , the density; R , the gas constant, and T , the absolute temperature:

$$G_e = \frac{\rho RT}{M_e} \quad (42)$$

This, of course, can only be obtained if the plateau zone were constant. In real polymers, there is almost always a slope, so that it is difficult to determine at what point to take the data. Since we are dealing with a viscoelastic material, the true equilibrium modulus cannot be obtained. The general approach is to use the viscoelastic equivalent called the pseudo-equilibrium modulus, G_N^0 , which can be obtained from dynamic data by integrating the loss modulus, G'' , from dynamic mechanical data. The author has found that the value of the storage modulus G' ob-

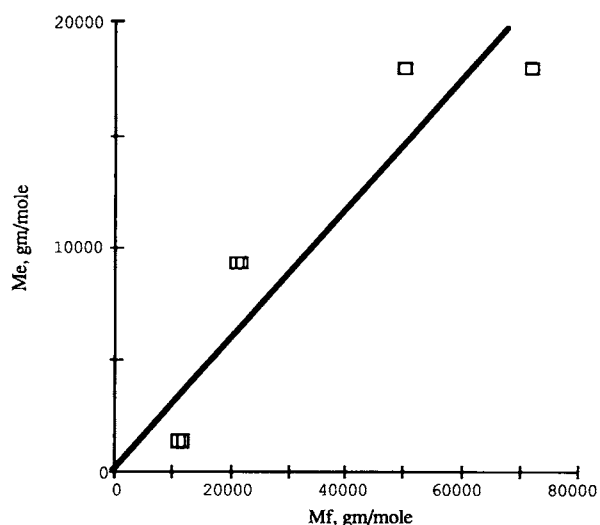


Figure 12 Molecular weight at zero flexural strength (M_f) vs. entanglement molecular weight.

Table X Entanglement Data

Polymer	M_0 (g/mol)	V_w (cc/mol)	l_m (Å)	n_b	M_e (g/mol)	$\frac{n_b M_0 V_w}{N_a l_m^3}$
PE ^a	28.0	20.5	2.56	2	1422	113.7
PET ^b	192.0	90.9	11.80	6	1450	105.8
HPIP ^a	69.0	47.7	5.08	4	1833	166.7
PBD 51/37/12 ^c	54.0	37.4	4.42	2	1844	77.7
NY66 ^b	226.0	141.9	20.40	12	2000	75.3
APA ^b	246.0	140.7	16.20	10	2040	135.1
POE ^a	44.0	24.1	4.00	3	2200	82.5
PSF ^c	442.0	221.6	18.32	5	2250	132.2
PVF2 ^b	64.0	26.2	2.30	2	2400	356.2
PEC 1 : 1 ^c	596.0	194.7	25.06	8	2402	97.9
PEC 1 : 2 ^c	938.0	253.2	39.38	12	2429	77.5
NY ^b	113.0	70.9	10.20	6	2490	75.2
PC ^c	254.0	136.2	10.70	4	2495	187.5
POM ^b	30.0	13.9	2.80	2	2540	63.1
PHEN ^b	288.0	167.6	14.2	5	2670	139.9
PETG ^b	684.0	348.3	35.9	14	2880	119.7
PBD _{cis} ^a	54.0	49.2	4.40	2	2936	103.6
PBD _{vinyl} ^a	54.0	37.4	2.56	2	3529	399.9
PPO ^a	120.0	68.8	4.60	2	3620	281.6
SAN 50/50 ^c	70.2	42.2	2.56	2	5030	586.6
PTFE ^b	50.0	16.0	2.56	1	5580	79.2
SAN 63/37 ^c	76.7	59.5	2.56	2	7005	903.7
S/MMA 35/65 ^c	101.4	58.1	2.56	2	7624	1166.6
PDMS ^b	74.1	39.3	2.56	2	8160	576.7
PEMA ^b	114.0	66.3	2.56	2	8590	1496.7
PVAC ^a	86.0	46.2	2.56	2	8667.	786.8
SAN 76/24 ^c	84.5	50.9	2.56	2	8716	851.7
PIB ^a	56.0	40.9	2.56	2	8818	453.5
PMA ^b	86.0	47.2	2.56	2	9070	803.8
SAN 71/29 ^c	81.3	49.0	2.56	2	9154	788.9
PMMA ^c	100.0	37.4	2.56	2	9200	740.6
SAN 78/22 ^c	85.9	51.7	2.56	2	9536	879.4
PAMS ^a	111.0	68.5	2.56	2	12800	1505.7
SMA 67/23 ^c	101.9	55.1	2.56	2	14522	1111.8
SAA 92/8 ^c	100.5	59.9	2.56	2	14916	1198.0
SMA 91/9 ^c	103.5	61.3	2.56	2	16462	1256.4
SAA 87/13 ^c	98.3	58.1	2.56	2	16680	1130.9
SMA 79/21 ^c	102.7	58.0	2.56	2	17750	1179.5
PS ^c	104.0	62.9	2.56	2	17851	1295.4
P2EBMA ^a	142.0	90.1	2.56	2	22026	2533.5
P-PVT ^c	118.0	74.0	2.56	2	24714	1729.1
P-BRS ^c	184.0	74.5	2.56	2	29845	2714.5
PHMA ^a	156.0	100.4	2.56	2	33800	3101.5
TBS ^c	160.0	104.7	2.56	2	37669	3317.3

^a Ref. 46.^b Ref. 47.^c Internal data of The Dow Chemical Co. obtained from dynamic mechanical data by calculating entanglement molecular weight from the elastic portion of the modulus at the minimum in the loss tangent curve and using the theory of rubber elasticity.

tained from the point where $\tan \delta$ is a minimum in the dynamic mechanical data to a very close approximation is equivalent to G_N^0 .

Graessly and Edwards⁴⁶ developed a model that relates the plateau modulus to the entanglement length in the following manner:

$$\frac{G_N^0 l^3}{kT} \propto (\nu_c L l^2)^a \quad (43)$$

where G_N^0 is the plateau modulus; l , the Kuhn step length; L , the contour length of an entanglement; ν_c , the number of chains per unit volume; and a , a constant between 2 and 2.3. In fact, it did not seem to make much difference, using Graessly and Edwards data, which of the two numbers were used, so we have chosen 2 to simplify the calculations.

Based on the assumption that there is an equivalence between the entanglement and a chemical cross-link, the entanglement molecular weight is calculated from the plateau modulus using the theory of rubber elasticity:

$$M_e = \frac{\rho RT}{G_N^0} \quad (44)$$

where ρ is the density. Substituting eq. (44) into eq. (43) and solving for M_e ,

$$M_e \propto \frac{\rho N_A}{\nu_c^2 L^2 l} \quad (45)$$

With the use of the following relationships:

$$L = \frac{M_e}{M_0} l_m \quad (46)$$

$$n = \frac{Nr}{M_e} \quad (47)$$

$$\rho = \frac{M_0}{V} \quad (48)$$

where M_0 is the molecular weight of the mer; l_m , the length of the mer; and V , the molar volume based on the mer. Substituting into eq. (45) and solving for the entanglement molecular weight, we obtain

$$M_e \propto \frac{M_0 V}{N_A l_m^2 l} \quad (49)$$

since to a first approximation V is proportional to V_w at the temperature of measurement, and l can be related to l_m by the characteristic ratio and the number of rotatable bonds n_b . (A rotatable bond is considered to be one that can rotate around its own axis.) Thus, $l = (C_\infty l_m)/n_b$. Upon making the substitution into eq. (49), it results in the following equation:

$$M_e \propto \frac{n_b M_0 V_w}{C_\infty N_A l_m^3} \quad (50)$$

Theoretically, C_∞ can be calculated from the rotational isomeric calculations of Flory.⁴⁸ However, the calculations are not easy and a computer is needed to obtain accurate results. To circumvent the problem and to approximate from group contributions the entanglement molecular weight, we have made the assumption to treat C_∞ as a constant, since the greatest variation over a wide range of vinyl polymers introduces a maximum error of about 40%. In condensation polymers, the relationship becomes more tenuous since it is difficult to determine what fundamental rotational unit to use.

Figure 13 shows the fit of eq. (50) to the data using linear regression. The results of the fit are shown in eq. (51). The mean error was 26%, while the correlation index is 0.960. This large error probability is related to the assumption that C_∞ is a constant. However, the high correlation index certainly indicates that it represents the trend rather well:

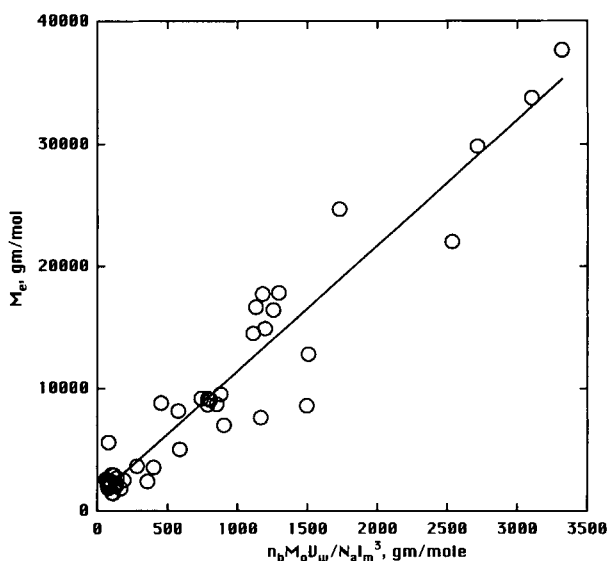


Figure 13 Entanglement molecular weight.

$$M_e = 10.3 \frac{n_b M_0 V_w}{N_A l_m^3} + 1120 \quad (51)$$

Since the fit to a number of polymers is better than one would expect and certainly gives a good first approximation to the entanglement molecular weight, one might expect it to give a reasonable estimation to shear yield or crazing criterion based on the previous discussion of these phenomena.

The molecular weight dependence of a polymer is strongly related to the entanglement molecular weight. Above $2M_e$, the viscosity of the melt increases as the 3.4 power of the molecular weight. In the glass, the mechanical strength is dependent on M_e , as shown by eq. (50) and discussed in the section on brittle strength. A useful approximation for determining the molecular weight of a new polymeric material is that it should be between 10 and 15 times the entanglement molecular weight. Polymers having molecular weights less than $10M_e$ will have poor strength, whereas polymers with molecular weights above $15M_e$ are difficult to process.

IV. DISCUSSION

The preceding approach to estimating various mechanical properties can be very useful in any approach to the design of new polymeric materials. All that the chemist really needs to know are the glass transition temperature, the van der Waals volume of the repeat unit, the cohesive energy of the repeat unit, and the bond angles and lengths in repeat unit. The glass transition temperature can be estimated by several group contribution methods.⁴⁹⁻⁵² The rest of the information can be obtained from sources already cited.

In many cases, the quantitative results obtained from these techniques can be greatly improved if the data for similar or homologous materials are already known or some properties, specifically the T_g and density, have already been obtained from a small amount of material in question. The results can be obtained almost instantaneously from small computers such as PCs and can be easily applied to real-world problems. The accuracy of the calculations is at least as good as any atomistic method. In terms of speed of results, its answers are obtained almost instantaneously, whereas atomistic methods take days to months to arrive at the same results. Although not providing the same level of scientific understanding as that of the atomistic approach, these

methods are able to extend to the bench chemist greater insight into property molecular structure relationships. The technique has been incorporated in to the Biosym Technologies Polymer Project Program, where it has been used by the chemists of the member companies.

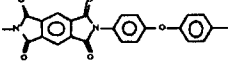
V. CONCLUSIONS

Based on the molecular structure of the repeat unit, a method has been developed for calculating mechanical properties from universal material constants. This technique has the following advantages:

1. Properties can be calculated from only four basic molecular properties. These are the molecular weight, van der Waals volume, length of the repeat unit, and the T_g of the polymer.
2. Since these properties are based on fundamental molecular properties, they can be obtained from either purely theoretical calculations or from group contributions. This allows unknown contributions to be calculated.
3. As a quantitative property structure relationship (QSPR) technique, it reduces the number of group contributions that are necessary to calculate the properties.

VII. ABBREVIATIONS OF POLYMER NAMES

APA	amorphous polyamide
ARYL	Copolyester of isophthalic, terephthalic acids with bisphenol A (1 : 1 : 2)
CHDMT	poly(cyclohexene dimethylene terephthalate)
NY	poly(hexamethylene adipamide)
<i>o</i> -CLST	poly(<i>o</i> -chlorostyrene)
POMA	poly(octyl methacrylate)
P4MP	poly(4-methyl pentene)
PaMS	poly(α -methylstyrene)
PBA	poly(butyl acrylate)
PBD	polybutadiene
PBE	poly(1-butene)
PBMA	poly(butyl methacrylate)
PBRs	poly(<i>p</i> -bromostyrene)
PC	poly(bisphenol A carbonate)
PCLST	poly(<i>p</i> -chlorostyrene)
PDMPO	poly(2,5-dimethyl phenylene oxide) (PPO)

PE	polyethylene
PEA	poly(ethyl acrylate)
PEC	polyestercarbonate
PEIS	poly(ethylene isophthalate)
PEMA	poly(ethyl methacrylate)
PES	polyethersulfone
PET	poly(ethylene terephthalate)
PETG	poly(1,4-cyclohexylenedimethylene terephthalate-co-isophthalate)(1:1)
PHEN	phenoxy resin
PHMA	poly(hexyl methacrylate)
PI	polyimide 
PIB	polyisobutylene
PMA	poly(methyl acrylate)
PMMA	poly(methyl methacrylate)
POM	polyoxymethylene
POMS	poly(o-methylstyrene)
PP	polypropylene
PPE	poly(1-pentene)
PPMA	poly(propyl methacrylate)
PS	polystyrene
PSF	polysulfone
PTBS	poly(p-t-butylstyrene)
PTFE	poly(tetra-fluoroethylene)
PVA	poly(vinyl acetate)
PVBE	poly(vinyl butyl ether)
PVC	poly(vinyl chloride)
PVEE	poly(vinyl ethyl ether)
PVHE	poly(vinyl hexyl ether)
PVME	poly(vinyl methyl ether)
PVT	poly(p-vinyl toluene)
SAA	poly(styrene-co-acrylic acid)*
SAN	poly(styrene-co-acrylonitrile)*
SMA	poly(styrene-co-maleic anhydride)
ST/AMS	poly(styrene-co- α -methyl)*
ST/MMA	poly(styrene-co-methyl methacrylate)*

* The comonomer concentrations are reported in wt %.

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