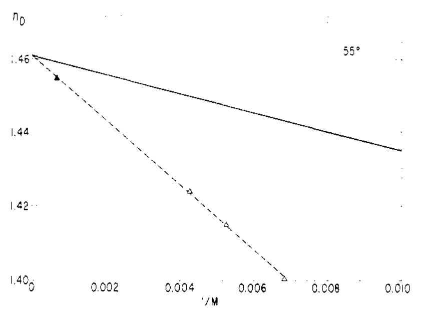

Figure 2. Refractive indices *vs.* $1/M$. Poly(ethylene oxide) diacetates at 55.5°. In Figures 1 and 2, solid lines represent poly(ethylene glycols) at the corresponding temperature, from data of Ingham and Lawson.[5]

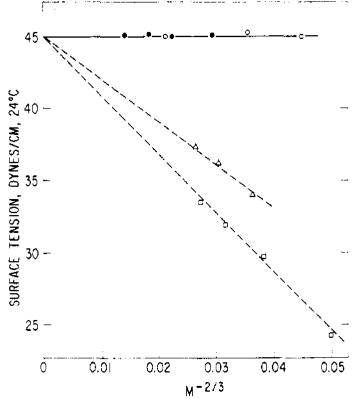

Figure 3. Surface tension of poly(ethylene oxide) derivatives at 24°: ○, ●, poly(ethylene glycols) (data of Gallaugher and Hibbert[1] and ring measurements in this laboratory); △, poly(ethylene oxide) diacetates; ◻, poly(ethylene oxide) dimethyl ethers (data of Gallaugher and Hibbert[1] and A. I. Vogel, [*J. Chem. Soc.*, 616 (1948)] for di- and tetraethylene oxide dimethyl ethers, respectively).

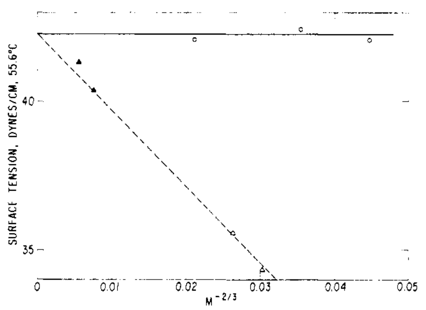

Figure 4. Surface tension of poly(ethylene oxide) diacetates at 55.6° (△, ▲). Data for poly(ethylene glycols) at 55.6° (○) from data of Gallaugher and Hibbert[1] included for comparison.

glycols) are also indicated. The dashed straight lines, drawn in each case to intercept the infinite molecular weight axis at the extrapolated poly(ethylene glycol) value, appear to represent the data adequately.

Some comment is needed concerning the first member of each series. The refractive indices of these materials appear to fit the molecular weight correlation shown in Figures 1 and 2. Their surface tensions, however, are anomalous. Ethylene glycol has a higher surface tension than the higher glycols over the temperature range 20–150°.[1] Ethylene glycol diacetate, which fits the $M^{-2/3}$ correlation at room temperature, has a lower surface tension at 55.6° than would be predicted. A cursory examination over the temperature range 6–70° shows $d\gamma/dT = -0.125$ dyn/cm/deg, about twice the value for the higher diacetates. The fit at room temperature, therefore, appears to be accidental. Consideration of the structure of ethylene glycol and its diacetate shows that they differ from the higher homologues in that they contain no $-CH_2OCH_2-$ segments and suggests that they should not be considered members of these homologous series.

We have already noted the relevance of free volume concepts to the molecular weight dependence of these properties. The coincidence of the extrapolated infinite molecular weight values indicated in the figures would appear to lend further credence to this (admittedly vague) interpretation. Measurements of glass transition temperatures for these derivatives would permit comparison with our earlier attempt[8] to provide a quantitative connection to free volume theory. Unfortunately, our attempts (by differential scanning calorimetry) to obtain such measurements on the poly(ethylene oxide) diacetates have not yielded meaningful results because of the strong tendency of the samples to crystallize. Hence we prefer not to attempt a more detailed discussion at the present time.

Thermoelastic Behavior of Some Acrylic Polymers

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In previous publications from this laboratory, we have proposed a new equation for the calculation of the relative energy contribution to the elasticity of polymers in the rubbery state[2]

$$f_e/f = 1 - \frac{d \ln G}{d \ln T} - \beta_L{}^0 T \qquad (1)$$

where f is the total force, f_e is the energetic component of the elastic force, T is absolute temperature, $\beta_L{}^0$ is the linear thermal expansion coefficient of unstrained rubber, and G is the shear modulus. The latter is defined by the equation of state for rubber elasticity

$$f = GA_0(\lambda - V/V_0\lambda^2) \qquad (2a)$$

and

$$G = (NRT/V_0)(\overline{r_i^2}/\overline{r_f^2}) \qquad (2b)$$

In eq 2, λ is the extension ratio, L/L_0; L_0, A_0, and V_0 are the length, cross-sectional area, and volume of the rubber at zero pressure, zero force; and L and V are the length and volume at force f, and pressure P; N is the number of moles of network chains in the sample; R is the gas constant; $\overline{r_i^2}$ is the mean square

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(2)(a) M. Shen and P. J. Blatz, *J. Appl. Phys.*, 39, 4937 (1968); (b) M. Shen, *Macromolecules*, 2, 358 (1969).

end-to-end distance of the network chain and $\overline{r_f^2}$ is that of the corresponding free chain. By means of eq 1, it was shown that the energy contribution to rubber elasticity is independent of the applied strain in the range for which the statistical theory of rubber elasticity is valid.[2] This conclusion is important in that it is consistent with the free energy additivity principle of the statistical theory.

According to the statistical theory, the internal energy contribution to the elastic stress must be wholly attributable to the intramolecular energies. Thus f_e/f can be shown by combining eq 1 and 2 to measure the temperature coefficient of the unperturbed chain dimensions[3]

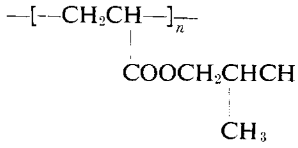
$$\frac{\mathrm{d}\ln \overline{r_f^2}}{\mathrm{d}T} = \frac{f_e}{fT} \tag{3}$$

In addition, based on the folding chain model, the ϵ' folding energy was shown to be[4,5]

$$\epsilon' = -RT(f_e/f) \tag{4}$$

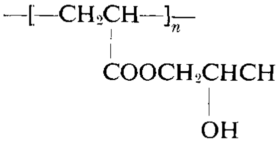
Recently more refined calculations are available for various polymer chains in predicting the temperature coefficient of the unperturbed chain dimensions from detailed molecular models.[6]

An important test of the validity of neglecting intermolecular energies in the statistical theory is to determine the effect of changing the intermolecular forces in the rubber on f_e/f. One such method is to introduce diluents into the rubber network.[2b,7] It was found that f_e/f remains invarient with diluent content in the sample. Another method is to change the molecular constitution of the polymer chains themselves. For instance, we can increase the intermolecular interactions of poly(isobutyl acrylate) (PiBA)



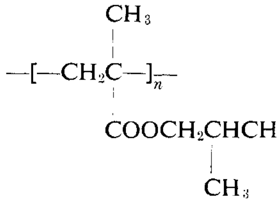
$$-[-CH_2\underset{\underset{\underset{CH_3}{|}}{COOCH_2CHCH_3}}{\underset{|}{CH}}-]_n-$$

by replacing one of the methyl groups with a hydroxyl group. The hydrogen bonds due to the -OH groups in poly(2-hydroxypropyl acrylate) (PHPA)



$$-[-CH_2\underset{\underset{\underset{OH}{|}}{COOCH_2CHCH_3}}{\underset{|}{CH}}-]_n-$$

can be expected to provide increased intermolecular interactions, but with a minimum change in other molecular parameters such as steric hindrance, side-chain geometry, etc. Again one would expect only minor alterations in f_e/f if intermolecular forces were indeed negligible. By contrast, we can keep the intermolecular interactions relatively unaffected but increase the intramolecular interactions by adding an α-methyl group to



$$-[-CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{CH_3}{|}}{COOCH_2CHCH_3}}{\underset{|}{C}}}-]_n-$$

PiBA; which is just poly(isobutyl methacrylate) (PiBMA). In this instance, f_e/f should be significantly altered in comparison with that of PiBA due to the steric hindrance provided by the α-methyl group.

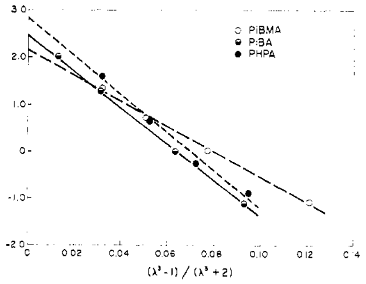


Figure 1. Linear thermal expansion coefficient of strained rubber *vs.* $(\lambda^3 - 1)/(\lambda^3 + 2)$ for poly(isobutyl acrylate) (PiBA), poly(isobutyl methacrylate) (PiBMA), and poly(2-hydroxypropyl acrylate) (PHPA).

Monomers of iBA, HPA, and iBMA were purchased from the Borden Chemical Co. Polymer samples were prepared by uv photopolymerization.[8] Length-temperature measurements were carried out for strips of rubbers at a series of loads, the procedure of which has been previously described.[2b] Owing to the low extensibility of these samples, data were taken at $\lambda < 1.0$. Magnitudes of length changes are consequently smaller, producing greater experimental errors. The temperature coefficient of shear modulus as well as the linear thermal expansion coefficient of the unstrained rubber were determined by means of eq 6,[2b]

$$\beta_L = \beta_L^0 - [(\lambda^3 - 1)/(\lambda^3 + 2)](\mathrm{d}\ln G/\mathrm{d}T + 2\beta_L^0) \tag{6}$$

where β_L is the linear thermal expansion coefficient of the strained rubber in the direction of stretch. Data are given in Figure 1. From the intercept and the slope of this plot, the desired quantities can be readily obtained. From eq 1, 3, and 4, the relative energy contribution, temperature coefficient of the unperturbed chain dimension, and the folding energy were calculated. Results are summarized in Table I. Two reference temperatures were chosen (60 and 120°). No data were given for PiBMA at 60°, at which the sample is glassy.

It is clear from Table I that changes in f_e/f and related quantities are small between PHPA and PiBA, but quite large between PiBMA and PiBA. Thus

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(3) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience Publishers, New York, N. Y., 1963.

(4) K. W. Scott and A. V. Tobolsky, *J. Colloid Sci.*, **8**, 465 (1953).

(5) A. V. Tobolsky, D. W. Carlson, and N. Indictor, *J. Polym. Sci.*, **54**, 175 (1961).

(6) P. J. Flory, J. E. Mark, and A. Abe, *J. Amer. Chem. Soc.*, **88**, 639 (1966).

(7) A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *ibid.*, **83**, 1015 (1961).

(8) M. Shen, J. D. Strong, and F. J. Matusik, *J. Macromol. Sci.*, **B1**, 15 (1967).

Table I
Thermoelastic Data of Acrylic Polymers

Sample	d ln G/dT × 10^3, deg^{-1}	β_L^0 × 10^4, deg^{-1}	f_e/f		d ln r_f^2/dT × 10^3, deg^{-1}		$-\epsilon'$, cal/mol	
			60°	120°	60°	120°	60°	120°
Poly(2-hydroxypropyl acrylate)	3.6	2.8	−0.30	−0.53	−0.90	−1.35	200	420
Poly(isobutyl acrylate)	3.4	2.4	−0.20	−0.42	−0.60	−1.07	130	320
Poly(isobutyl methacrylate)	2.3	2.2		0.02		0.05		−20

the importance of intra- rather than intermolecular effects in rubber elasticity is again demonstrated. There is little reason to expect that values of f_e/f should be identical for PiBA and PHPA, since they are different in molecular constitution. In addition, the hydrogen bonds furnished by the -OH groups of PHPA probably also effect intramolecular interactions to some extent.

Table I also shows that d ln r_f^2/dT for the polyacrylates are negative, while that for the polymethacrylate is positive. These are in general agreement with the results of Tobolsky.[5] Theoretically, Ptitsyn[9] has predicted the unperturbed chain dimensions to decrease with temperature for vinyl polymers, while Flory[6] arrived at the opposite conclusion. Present data indicate only that they are both possible, depending on the molecular structure of the polymer chains.

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(9) O. B. Ptitsyn, *Vysokomol. Soedin.*, **4**, 1445 (1962).

Communications to the Editor

Quantitative Aspects of the Stereoselectivity in the Stereoregulated Polymerization of Racemic α-Olefins by Ziegler–Natta Catalysts

In previous papers[1–4] we reported the separation of polymers from racemic vinyl monomers into fractions having optical activity of opposite sign and containing macromolecules made up predominantly of *R* or *S* units.[3,5]

The degree of separation *F* was calculated[2] on the basis of the weight per cent and the optical rotation of the collected fractions by the empirical relationship between polymer rotatory power and optical purity[4,6] of polymerized monomer.

The presence of macromolecules made up predominantly of *R* or *S* units may be foreseen also in a statistical copolymer of the two antipodes; in this case the average prevalence of units of one type becomes vanishingly small at high DP.[7]

The polymerization of a racemic monomer will be considered stereoselective[8] if the actual separability *D* of the polymer obtained is higher than the theoretical separability D_0 of a statistical copolymer of the two antipodes with the same molecular weight; D_0 has been taken equal to the average prevalence[7] of *R* (or *S*) units in half-weight[9] of the statistical copolymer.

D is not in general equal to *F* as the *F*/*D* ratio or efficiency *E* of the method of separation[2] is expected to be lower than unity. Furthermore, under the present experimental conditions, the polymers of racemic α-olefins are separated not only with respect to prevalence of *R* or *S* units, as shown by the sign of optical activity of the fractions, but also with respect to molecular weight and stereoregularity.[2]

In the case of polymers from racemic α-olefins having the asymmetric carbon atom in the 3 position, like 3-methyl-1-pentene and 3,7-dimethyl-1-octene, the value of *F*, which is a minimum value of *D*, suffices[3] for a qualitative demonstration of the occurrence of stereoselectivity. By contrast a knowledge of *E* appeared to be necessary[3] for polymers of racemic 4-methyl-1-hexene, in which the asymmetric carbon atom is in the 4 position. Furthermore a quantitative evaluation of the stereoselectivity might give interesting information on the mechanism not only of the stereoselection, but also of the steroregulation by Ziegler–Natta catalysts.

In order to evaluate *E* we have synthesized polymers of *R* and *S* antipodes of the above α-olefins and we have investigated the separation of their mixture by elution chromatography on an optically active support.

(*S*)-3,7-Dimethyl-1-octene ([α]^{25}D +13.81 (neat),

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(1) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Natta, *J. Amer. Chem. Soc.*, **84**, 1487 (1962).

(2) P. Pino, G. Montagnoli, F. Ciardelli, and E. Benedetti, *Makromol. Chem.*, **93**, 158 (1966).

(3) P. Pino, F. Ciardelli, and G. Montagnoli, *J. Polym. Sci., Part C*, **16**, 3265 (1968).

(4) E. Chiellini, G. Montagnoli, and P. Pino, *ibid., Part B*, **7**, 121 (1969).

(5) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Montagnoli, *Makromol. Chem.*, **61**, 207 (1963).

(6) P. Pino, F. Ciardelli, G. Montagnoli, and O. Pieroni, *J. Polym. Sci., Part B*, **5**, 307 (1967).

(7) P. L. Luisi, G. Montagnoli, and M. Zandomeneghi, *Gazz. Chim. Ital.*, **97**, 222 (1967).

(8) As is known a process is called stereoselective when produces one diastereoisomer of a given structure in considerable predominance over all the other possible diastereoisomers [E. L. Eliel, "Stereochemistry or Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 434]. Considering the units from a racemic monomer as *R* or *S*, independently of the main chain asymmetric carbon atom absolute configuration, we think that the above definition can be extended to an oligomerization or polymerization process which gives one type of copolymer of the two antipodes in larger amount over the other possible types.

(9) The half-weight to be considered is that containing all the macromolecules in which *R* (or *S*) units prevail and 50% of the macromolecules having the same content of *R* and *S* units. For the calculation of the prevalence the formulas reported in ref 7 have been used and the values averaged to give D_0.