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Effect of Side-Chain Structure on Thermoelasticity of Acrylic Polymers

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Effect of Side-Chain Structure on Thermoelasticity of Acrylic Polymers

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SUMMARY

The validity of the current statistical theory of rubber elasticity is verified by demonstrating the importance of intra- rather than intermolecular forces in the energy contribution to the elastic stress of polyacrylates.

According to the current statistical theory of rubber elasticity, the internal energy contribution must be wholly attributable to intra-, rather than intermolecular energies. In order to test the validity of the aforementioned assumption, a few reports have been published from this laboratory [1-3]. It was found that the relative energy contribution to the elastic force (f_e/f) remains invariant with diluent content [1, 4], cross-linking [2] and deformation [3]. In this note we shall report the results on our thermoelastic measurements for a number of acrylic polymers with different side-chain structures in order to examine the effect of intramolecular forces on f_e/f by changing the molecular constitution of polyacrylates.

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 [1, 5]:

$$\frac{f_e}{f} = 1 - \frac{d \ln G}{d \ln T} - \beta_L^0 T \tag{1}$$

Where f is the total force, f_e is the energetic component of the elastic force, T is absolute temperature, β_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:

$$f = GA_0(\lambda - V/V_0\lambda^2) \tag{2a}$$

and

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

In Eqs. (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, respectively; and L and V are the length and volume at force f, and pressure P, respectively; 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 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 [1, 4]. 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 Eqs. (1) and (2) to measure the temperature coefficient of the unperturbed chain dimensions [4]:

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

In addition, based on the folding chain model, the ϵ' folding energy can be deduced by the following expression [6, 7]:

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

Recently more refined calculations have become available for various polymer chains in predicting the temperature coefficient of the unperturbed chain dimensions from detailed molecular models [8].

Monomers were purchased from the Borden Chemical Co. Polymer samples were prepared by UV photopolymerization. Length-temperature measurements were carried out for strips of rubbers at a series of loads, the procedure of which has been previously described [1]. Due to the low extensibility of these samples, data were taken at $1.0 \leqslant \lambda \leqslant 1.10$. 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 the following equation [1]:

$$\beta_L = \beta_L^0 - [(\lambda^3 - 1)/(\lambda^3 + 2)] \ (d \ln G/dT + 2\beta_L^0) \tag{5}$$

where β_L is the linear thermal expansion coefficient of the strained rubber in the direction of stretch. From the intercept and the slope of a $(\beta_L - \beta_L^0)$ vs. $[(\lambda^3 - 1)/(\lambda^3 + 2)]$ plot, the desired quantities can be readily obtained. From Eqs. (1), (3), and (4), the relative energy contribution, temperature coefficient of the unperturbed chain dimension, and the folding energy were calculated.

Table 1 shows the summarized thermoelastic data of four butyl esters of polyacrylic acid and are compared with the data of previous work [10]. It is well known that glass transition temperature (T_g) of polymers containing butyl groups are usually fairly similar for the three isomers, but drastically higher for the tertiary isomers [9]. For instance, T_g's for poly-n-butyl acrylate (PnBA), poly-sec-butyl acrylate (PsBA), and poly-tert-butyl acrylate (PtBA) are, respectively, -56, -22, and 43°C. The effect is generally believed to be attributable to the increased chain stiffness due to the relatively rigid t-butyl group, i.e., greater intramolecular interaction. In Table 1 it is seen that the value of f_e/f for PnBA is lowest since PnBA

Table 1. Thermoelastic Data of Acrylic Polymers[a]

	d ln G/dt × 10^3 (°C^{-1})	$\beta_L^0 \times 10^4$ (°C^{-1})	f_e/f	d ln $\overline{r_f^2}$/dT × 10^3 (°C^{-1})	ϵ' (cal/mole)
Poly-n-butyl acrylate (PnBA)	4.2	2.7	-0.68	-1.73	535
Poly-iso-butyl acrylate (PiBA)	3.4	2.4	-0.42	-1.07	320
Poly-sec-butyl acrylate (PsBA)	3.5	2.3	-0.47	-1.20	369
Poly-tert-butyl acrylate (PtBA)	2.5	2.4	-0.09	-0.23	71
Poly-iso-butyl methacrylate (PiBMA)[b]	2.3	2.2	0.02	0.05	-20
Poly-2-hydroxypropyl acrylate (PHPA)[b]	3.6	2.8	-0.53	-1.35	420

[a] Reference temperature: 120°C.

[b] Ref. 10.

has the highest flexibility among the isomers. Values of f_e/f for PsBA and poly-iso-butyl acrylate (PiBA) are almost identical since their molecular constitutions are very similar. On the other hand, PtBA is very different from the former three isomers. Now when we compare the value of f_e/f for PiBA with that of poly-2-hydroxypropyl acrylate which has higher intermolecular forces due to hydroxyl group [10], there is very little alternation in f_e/f, but poly-iso-butyl methacrylate has a value of f_e/f that is not only distinctly different from PiBA but has even greater value of f_e/f than that of PtBA. Thus the importance of intra- rather than intermolecular effects in rubber elasticity is demonstrated.

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