Calorimetric study of rubber elasticity

Yu. K. Godovsky
Karpov Institute of Physical Chemistry, Moscow, USSR
(*Received* 21 *August* 1980; *revised* 6 *March* 1980)

The thermodynamics of simple elongation of a large number of rubberlike materials has been studied by deformation calorimetry with particular reference to the energy contributions to rubber elasticity. Expressions for mechanical work, heat and change of internal energy on deformation have been derived from the elastic equation of state. New equations for determination of the relative intramolecular energy contribution based on the analysis of elastic inversions of heat and internal energy are proposed. For the majority of polymers studied the free energy of deformation contains a significant intramolecular energy contribution. The temperature coefficients $d\ln\langle r^2\rangle_0/dT$ of the unperturbed dimensions of chains obtained by calorimetry are compared with literature data. Calorimetric results for four networks in the region of $1.02 < \lambda < 2$ have shown that the relative intramolecular energy contribution is independent of deformation and that strain-induced volume dilation and intermolecular energy and entropy changes resulting from this dilation follow the statistical theory only up to $\lambda < 1.3$ and at larger deformations the statistical theory underestimates the intermolecular changes. The data obtained for styrene-butadiene thermoplastic elastomers up to $\lambda = 10$ demonstrate that the intramolecular energy contribution is independent of deformation in the whole range of deformations. It is concluded that this is a consequence of the validity of the Gaussian statistics at large deformations.

INTRODUCTION

Theoretical and experimental investigations of thermoelastic properties of rubber-like networks during the past twenty years have demonstrated that rubber-like elasticity is not exclusively entropic as had been supposed earlier. It is well known now that deformation of polymer networks is accompanied by intramolecular energy changes which are closely related to the conformational energies of macromolecules[1-3]. The sign and value of these energy changes as has been demonstrated by the rotational isomeric state theory[1-4] are dependent on the chemical structure of the macromolecules. Reliable determination of these intramolecular energy changes and their interpretation by means of isomeric state theory provide a deeper insight into both thermodynamic and molecular aspects of rubber-like elasticity. Flory[3] has pointed out that thermoelastic measurements on rubber-like networks is the most effective method of determining the temperature coefficient $d\ln\langle r^2\rangle_0/dT$ of the unperturbed dimensions of the polymer chains making up the network. This molecular parameter is also closely related to conformational energies and can be calculated from the rotational isomeric state theory of chain configuration. Comparison of experimental and theoretical values of these quantities is extremely useful for interpretation of molecular mechanisms of rubber-like elasticity.

The main source of experimental information on thermoelasticity of rubber-like materials is stress–temperature measurement in uniaxial elongation by means of which one can resolve the total elastic force into energetic and entropic components[4-6]. Another experimental approach to the thermoelasticity of polymer networks is deformation calorimetry. Müller *et al.*[7-10] were the first to use deformation calorimetry for thermodynamic study of deformation of natural rubber and demonstrated that this approach is very useful for characterization of thermoelastic properties of rubber-like materials. We have also widely used this method in our research of thermoelastic properties of solid polymers[11-14]. Recently some new studies appeared in which deformation calorimetry was used for determination of energy changes during deformation of polymer networks[15-17] but most of these studies deal only with thermoelasticity of natural rubber.

In the present study deformation calorimetry has been used to characterize the thermoelastic properties of a wide class of polymer networks. The main purpose of our investigation has been to assess the role of internal energy in thermoelasticity of rubbers at different stages of deformation. New approaches for determining the energy contribution to rubber elasticity based on analysis of thermoelastic inversions of elastic heat and internal energy as well as on the heat effect resulting from instant unloading of the extended sample in the absence of external stresses will be presented. Finally, the data obtained with the calorimetric technique are compared with those literature data obtained by the classical method of stress–temperature relationship.

THEORETICAL

The classical equations of thermoelasticity for simple elongation resolving the total elastic force into energetic and entropic components cannot be used immediately for analysis of calorimetric results because in this case one needs equations for mechanical work W, heat Q and internal energy U*. These expressions can be obtained by means of an elastic equation of state for the Gaussian

* The change of internal energy ΔU during a deformation process under atmospheric pressure is practically identical to the change of enthalpy ΔH, because values of $P\Delta V$ (ΔV = volume change) are negligibly small in comparison with other values.

0032 3861/81/010075-12$02.00

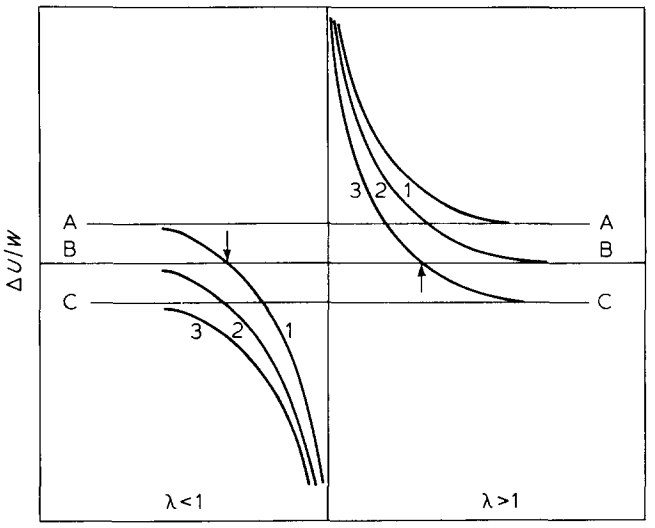

Figure 1 The relative internal energy contributions as a function of deformation. 1, 2, 3, $(\Delta U/W)_{P,T}$; A, B, C, $(\Delta U/W)_{V,T}$; A, $d\ln\langle r^2\rangle_0/dT > 0$; B, $d\ln\langle r^2\rangle_0/dT = 0$; C, $d\ln\langle r^2\rangle_0/dT < 0$. The arrows indicate inversion of internal energy (see text)

polymer network. For simple elongation or compression this equation may be written[18,19]:

$$f=\frac{\nu kT}{L_0}\cdot\frac{\langle r^2\rangle_i}{\langle r^2\rangle_0}\left(\lambda-\frac{V}{V_0\lambda^2}\right) \tag{1}$$

where L_0 and V_0 are length and volume of the network at zero force, zero pressure and temperature T; L and V are the corresponing quantities at force f, pressure P and temperature T; $\lambda=L/L_0$ is the elongation (or compression), ν is the number of chains in the network, k is the Boltzmann constant and $\langle r^2\rangle_i$ is the mean square end-to-end distance of the network chains in volume V_0 and $\langle r^2\rangle_0$ is that of the corresponding free chains.

Making use of this equation of state for rubber elasticity we have derived the following expressions which are necessary for treating calorimetric results[11,20]:

$$W=\frac{1}{2}C\frac{(\lambda-1)}{\lambda}(\lambda^2+\lambda-2) \tag{2}$$

$$Q_{P,T}=-\frac{1}{2}C\left[\left(1-T\frac{d\ln\langle r^2\rangle_0}{dT}\right)-\frac{2\alpha T}{\lambda^2+\lambda-2}\right]\frac{(\lambda-1}{\lambda}(\lambda^2+\lambda-2) \tag{3}$$

$$\Delta U_{P,T}=\frac{1}{2}C\left(T\frac{d\ln\langle r^2\rangle_0}{dT}+\frac{2\alpha T}{\lambda^2+\lambda-2}\right)\frac{(\lambda-1)}{\lambda}(\lambda^2+\lambda-2) \tag{4}$$

In these equations $C=kTL_0^{-1}$ $(\langle r^2\rangle_i/\langle r^2\rangle_0)$ and α is the thermal expansion coefficient of the undeformed sample.

For analysing the energy contribution to the elasticity of polymer networks it is more suitable to use them in the relative form:

$$\left(\frac{Q}{W}\right)_{P,T}=-1+T\frac{d\ln\langle r^2\rangle_0}{dT}+\frac{2\alpha T}{\lambda^2+\lambda-2} \tag{5}$$

$$(\Delta U/W)_{P,T}=T\frac{d\ln\langle r^2\rangle_0}{dT}+\frac{2\alpha T}{\lambda^2+\lambda-2} \tag{6}$$

These equations demonstrate that the change of entropy and internal energy on deformation of polymer networks under $P,T=$constant, is both inter- and intramolecular in origin. Intramolecular changes, which are independent of deformation, are characterized by the first term $T\,d\ln\langle r^2\rangle_0/dT$, i.e. the temperature coefficient of the unperturbed dimensions of the chains. Intermolecular changes, which are dependent upon deformation, are characterized by the last term.

For direct determination of intramolecular changes of entropy and energy during deformation it is necessary to carry out experiments under $V,T=$const. Integration of equation (1) under these conditions yields:

$$Q_{V,T}=-\frac{1}{2}C\left(1-T\frac{d\ln\langle r^2\rangle_0}{dT}\right)\left(\frac{\lambda-1}{\lambda}\right)(\lambda^2+\lambda-2) \tag{7}$$

$$\Delta U_{V,T}=\frac{1}{2}CT\frac{d\ln\langle r^2\rangle_0}{dT}\left(\frac{\lambda-1}{\lambda}\right)(\lambda^2+\lambda-2) \tag{8}$$

Mechanical work is also represented in this case by equation (2). These equations may be written in relative form:

$$\left(\frac{Q}{W}\right)_{V,T}=-1+T\frac{d\ln\langle r^2\rangle_0}{dT} \tag{9}$$

$$\left(\frac{\Delta U}{W}\right)_{V,T}=T\frac{d\ln\langle r^2\rangle_0}{dT} \tag{10}$$

Comparing equations (5), (9) and (6), (10) one can obtain:

$$\left(\frac{Q}{W}\right)_{P,T}-\left(\frac{Q}{W}\right)_{V,T}=\left(\frac{\Delta U}{W}\right)_{P,T}-\left(\frac{\Delta U}{W}\right)_{V,T}=\frac{2\alpha T}{\lambda^2+\lambda-2} \tag{11}$$

Thus, equation (11) expresses the relative intermolecular changes of entropy and internal energy which arise as a result of a volume change in the course of deformation. This is, of course, the integral form of the corresponding term in the equation for energy contribution proposed by Flory *et al.*[19,21].

Figure 1 shows the theoretical energy contribution to rubber elasticity according to equations (6) and (10). The theoretical entropy contribution according to equations (5) and (9) is of the same character. As seen from this graph the difference between $(\Delta U/W)_{P,T}$ and $(\Delta U/W)_{V,T}$ strongly increases at small deformations because of very strong intermolecular energy changes with decrease of deformation. This behaviour of relative intermolecular changes of internal energy and entropy is quite consistent with the behaviour of solids. In fact,

$$\left(\frac{Q}{W}\right)_{\Delta V}=\frac{2\alpha T}{(1+\varepsilon)^2+(1+\varepsilon)-2}=\frac{2\beta T}{\varepsilon} \tag{12}$$

where ε is strain and β is thermal linear expansion coefficient in the direction of deformation. The same expression occurs for solids[11]. This demonstrates that the term $2\alpha \quad T/\lambda^2+\lambda-2$ is a good approximation for intermolecular changes at small deformations of rubber-like materials. One can see that as $\lambda\to1$

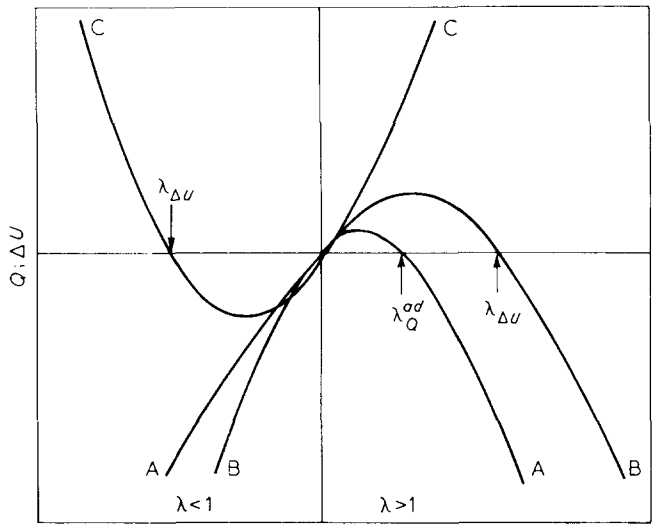

Figure 2 Internal energy and heat changes as a function of deformation according to equations (3) and (4). A, Heat; B, internal energy ($d\ln\langle r^2\rangle_0/dT < 0$); C, internal energy ($d\ln\langle r^2\rangle_0/dT > 0$). The arrows indicate inversion points (see text)

$(Q/W)_{\Delta V}=(\Delta U/W)_{\Delta V}\to\infty$ and at large λ it may be very small in comparison with the term $T\,d\ln\langle r^2\rangle_0/dT$.

Equations (3) and (4) predict the inversions of heat and internal energy at P,T=constant (conditions of calorimetric experiment) (*Figure* 2). For $dQ/d\lambda$ one can write an equation for isothermal inversion of heat:

$$\lambda_Q^{is}=\sqrt[3]{1+\frac{\alpha T}{1-T\frac{d\ln\langle r^2\rangle_0}{dT}}}\approx 1+\frac{1}{3}\frac{\alpha T}{\left(1-T\frac{d\ln\langle r^2\rangle_0}{dT}\right)} \tag{13}$$

and for $Q=0$ we obtain an equation for adiabatic inversion of heat:

$$\lambda_Q^{ad}=-\frac{1}{2}+\frac{3}{2}\sqrt{1+\frac{8}{9}\frac{\alpha T}{(1-T\frac{d\ln\langle r^2\rangle_0}{dT}}}\approx 1+\frac{2}{3}\frac{\alpha T}{\left(1-T\frac{d\ln\langle r^2\rangle_0}{dT}\right)} \tag{14}$$

Thus, one can see that for real polymer chains the inversion points are shifted to smaller deformations ($d\ln\langle r^2\rangle_0/dT<0$) or to larger deformations ($d\ln\langle r^2\rangle_0/dT>0$) in comparison with chains with free rotation. Inversions of heat are a result of competition between the increase of vibrational entropy, connected with the volume change at deformation and the decrease of conformational entropy resulting from change of shape. Because for undeformed polymer networks α is always positive and because $d\ln\langle r^2\rangle_0/dT$ seldom exceeds 1.5×10^{-3} K^{-1}, inversions of heat must occur only at elongation.

According to equation (4) the change of internal energy is zero not only at the obvious value $\lambda=1$ but also at the deformation:

$$\lambda_{\Delta U}=-\frac{1}{2}+\frac{3}{2}\sqrt{1-\frac{8}{9}\frac{\alpha T}{T\frac{d\ln\langle r^2\rangle_0}{dT}}}\approx 1-\frac{2}{3}\frac{\alpha T}{T\frac{d\ln\langle r^2\rangle_0}{dT}} \tag{15}$$

It is evident from this equation that for $d\ln\langle r^2\rangle_0/dT<0$ the inversion must occur at $\lambda>1$, i.e. at elongation, and *vice versa*. For values $\alpha=(7-9)\times10^{-4}$ K^{-1} and $d\ln\langle r^2\rangle_0/dT=(5-10)\times10^{-4}$ K^{-1}, which are typical for polymer networks, $\lambda_{\Delta U}=1.5$–2.0 for extension and $\lambda_{\Delta U}>0.5$ for compression. It must be emphasized that this thermoelastic inversion of internal energy is not connected with stress-induced crystallization and arises because of the different signs of inter- and intra-molecular components of the change of internal energy. It is also clear that both inversion of heat and internal energy disappear under the condition V,T=constant. Equations (13)–(15) yield the following expressions for the internal energy contribution or the temperature coefficient of unperturbed dimensions of polymer chains:

$$T\frac{d\ln\langle r^2\rangle_0}{dT}=\left(\frac{\Delta U}{W}\right)_{V,T}=1-\frac{1}{3}\cdot\frac{\alpha T}{(\lambda_Q^{is}-1)} \tag{16a}$$

$$T\frac{d\ln\langle r^2\rangle_0}{dT}=\left(\frac{\Delta U}{W}\right)_{V,T}=1-\frac{2}{3}\cdot\frac{\alpha T}{(\lambda_Q^{ad}-1)} \tag{16b}$$

$$T\frac{d\ln\langle r^2\rangle_0}{dT}=\left(\frac{\Delta U}{W}\right)_{V,T}=\frac{2}{3}\cdot\frac{\alpha T}{(1-\lambda_{\Delta U})} \tag{16c}$$

According to equations (3), (4) and (7), (8) the intermolecular change of internal energy and entropy associated with volume dilation may be written:

$$(\Delta U)_{\Delta V}=(T\Delta S)_{\Delta V}=C\alpha T\frac{(\lambda-1)}{\lambda} \tag{17}$$

It is seen that the increase of internal energy resulting from the expansion of a Gaussian network is exactly balanced by the equivalent change of entropy and thus this volume dilation gives no contribution to the free energy of deformation. Gee[22] also came to the same conclusion using another approach. Provided α and the isothermal compressibility x are independent of strain and using the well known thermodynamic equation[23]:

$$\left(\frac{\partial U}{\partial V}\right)_{P,T}=\frac{\alpha}{x}T \tag{18}$$

one can obtain the equation for volume dilation:

$$\frac{\Delta V}{V_0}=Cx\frac{(\lambda-1)}{\lambda} \tag{19}$$

which was first derived by Khazanovich[24] and Flory[19].

Finally, let us consider a special method of determining the energy contribution by deformation calorimetry in which an extended sample is unloaded instantly without external stresses, i.e. without mechanical work. It is clear that in this case:

$$\Delta U_{P,T}=-Q/W \tag{20}$$

$$\left(\frac{\Delta U}{W}\right)_{P,T}=\frac{Q^*}{Q^*+Q} \tag{21}$$

where Q^* is the heat effect resulting from instant unloading of a stretched sample. There may be three cases: Q^*

Table 1 Materials used in the investigation

Polymer	Abbreviation	Characteristics
Natural rubber		
Sample I	NR–1	100% natural rubber, 3% sulphur, 5% ZnO and 0.5% stearic acid were mixed and sheet were cured at 143°C for 45 min
Sample II	NR–2	Rubber was compounded with 3% dicumyl peroxide and cured at 145°C for 45 min
Poly(*cis*-1,4-isoprene)	PIR	High molecular weight polymer of approximately 98% *cis*-1,4-content was compounded with 3% dicumyl peroxide, 5% ZnO and 0.5% stearic acid and cured at 145°C for 45 min
Polydimethylsiloxane		
Sample I	PDMS–1	Sheet of polymer of molecular weight ~4 x 10^5 were cross-linked at room temperature by high-energy electrons. The total dose was ~10 Mrad
Sample II	PDMS–2	Filled polydimethylsiloxane rubber Sil-4600 (Dow Corning)
Ethylene–propylene copolymer	EPR	45% propylene; cured with 3% dicumyl peroxide at 160°C for 50 min
Buradiene–acrylonitrile copolymer	ABR	26% acrylonitrile (SCN-26). Cured at 150°C for 35 min with dicumyl peroxide
Butadiene–styrene copolymer	SBR	30% styrene (SCS-30). Cured at 150°C for 30 min with dicumylperoxide
Polychloroprene	PCR	Cured at 120°C for 40 min with mixture ZnO and MgO
Polyurethane	PUR	Poly(ester-2,4-tolylene diisocyanate)polyurethane (SCU-9)
SBS thermoplastic elastomers		
Sample I	DST–30	Linear block copolymer. Styrene content = 33.7%; $[\eta]$ = 0.86
Sample II	Solprene-406	4-armed star block copolymer (Phillips Petroleum Co). Styrene content = 39.4%; $[\eta]$ = 1.25

$=0$, if $\Delta U=0$; $Q^*>0$, if $\Delta U<0$; and $Q^*<0$, if $\Delta U>0$. Thus, the heat effect resulting from instant contraction directly shows the sign and value of energy changes during deformation.

All these equations for thermoelasticity of Gaussian polymer networks were used for analysis of the calorimetric results.

EXPERIMENTAL

Deformation calorimetry

Thermal effects accompanying simple elongation of natural rubber were first studied quantitatively by Müller *et al.*[9,10], who used a gas calorimeter in their investigations. Having analysed the possibilities of this instrument we came to the conclusion that for registration of very small thermal effects the Tian–Calvet[25] method would be more suitable, especially as we had already successfully used it for investigating heat capacity and crystallization kinetics of polymers[26–30]. Starting from this conclusion we developed an automatic microcalorimetric system based on this principle for simultaneous registration of thermal effects and mechanical characteristics (stress and strain) at uniaxial deformation. Later Tian–Calvet type calorimeters were used for this purpose by other workers[15–17,32], including Müller and his collaborators[33].

The construction of our instrument has been described in detail elsewhere[11,26] and therefore we will only briefly describe its main characteristics and experimental procedure. The device consists of two parts: microcalorimeter and mechanical loading system with dynamometric assembly. The temperature differences between working and reference cells are measured by means of two thermobatteries, each of them including 810 copper–constantan thermojunctions made electrochemically. The working dimensions of the calorimetric cells are as follows: diameter, 10 mm; length 125 mm. For registration of temperature differences a highly sensitive amplifier and electronic recorder were used. Joule heating was used for the calibration procedure according to the method of Calvet[25]. The maximum sensitivity of our calorimeter at room temperature was $\sim 2\times10^{-7}$ J/s. The time constant of the empty calorimetric cells was ~30 s.

For recording force and strain an automatic tensometric bridge was used. The sensitivity of this tensometer was 0.5 g/mm.

The experimental procedure was as follows. The clamped sample was placed in the working cell of the calorimeter and after stabilization of the base line it was stretched 4–5 times to the highest extensions and only after this were the chief measurements conducted. They consisted of extension of the sample at constant rate to the desired deformation. Then the extension was stopped and after a certain time needed for relaxation of heat flux (usually ~10 min) the sample was contracted at the same rate. The rates of deformation were 10 and 20%/min.

The thermoelastic properties of large deformations (more than 200%) were studied by means of two methods: the integral method, in which the whole deformation was achieved in non-stop regime, and the differential method, in which large deformations were achieved step by step (20–30% in each step) with stops after each step.

A series of experiments was made in the instant unloading regime. In these experiments the upper end of the sample was joined with a very thin wire. The first stage of the run was as usual — a sample was extended to the desired elongation and after the recorded traces had returned to the base line the wire was cut and the sample contracted instantly to its initial length.

All the measurements were made at temperature of 21°C. These measurements allowed us to obtain heat effects resulting from extension and contraction as well as mechanical work as a function of elongation with ~3% accuracy.

Materials and samples

Measurements were made on typical polymer networks some of whose characteristics are listed in *Table* 1. Cross-sections of samples used were 1 or 2×3.5 mm^2. The lengths of the samples were chosen according to ma-

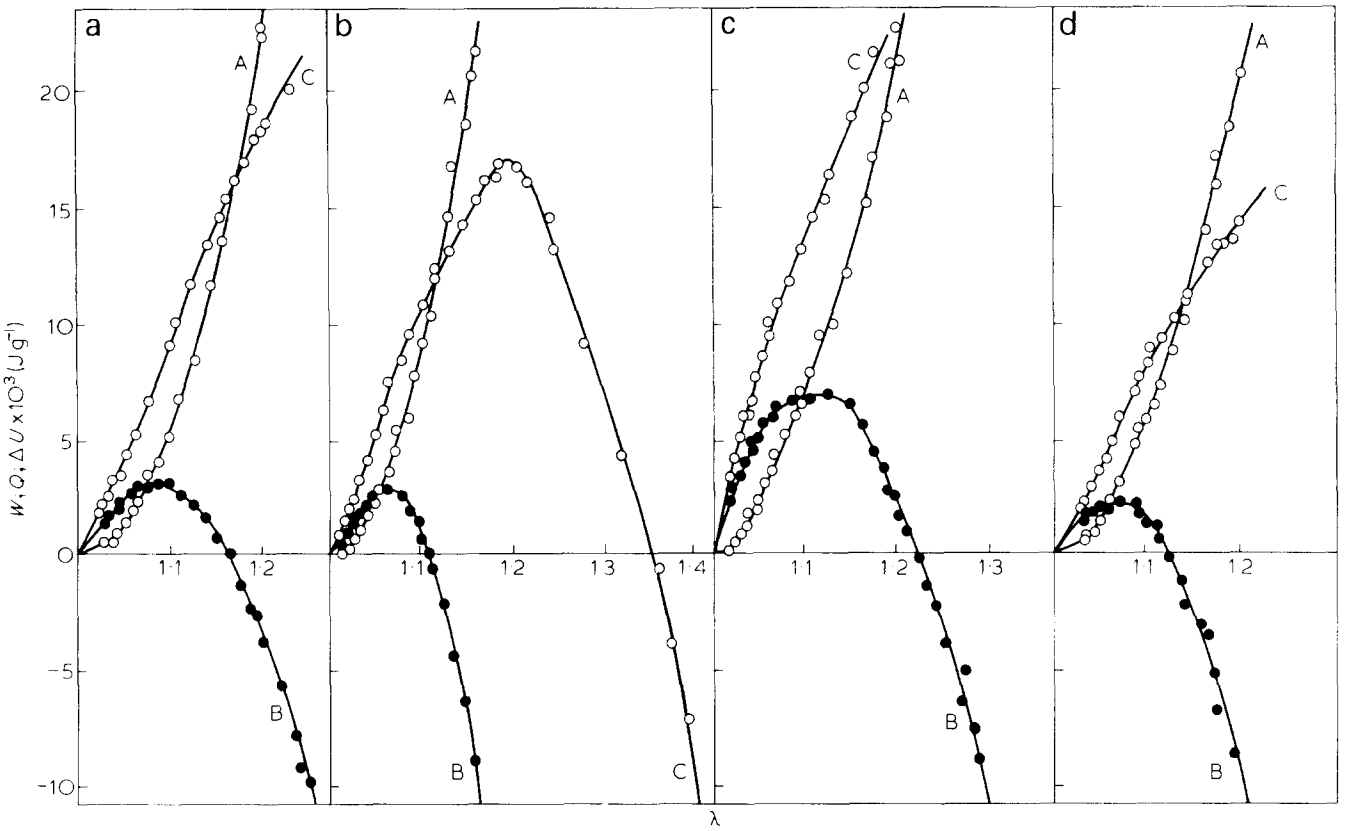

Figure 3 Mechanical work (A), heat (B) and internal energy (C) on stretching samples from the unstrained state to λ. (a) NR–1; (b) EPR; (c) PDMS–2; (d) PCR

Table 2 Parameters of inversions of heat and internal energy and values of $(\Delta U/W)_{V,T}$ and $d\ln\langle r^2\rangle_0/dT$ computed on this basis[a]

	Heat inversion			Internal energy inversion		
Polymer	λ_Q^{ad}	$(\Delta U/W)_{V,T}$	$d\ln\langle r^2\rangle_0/dT \times 10^3$ (K^{-1})	$\lambda_{\Delta U}$	$(\Delta U/W)_{V,T}$	$d\ln\langle r^2\rangle_0/dT \times 10^3$ (K^{-1})
NR–1	1.165 (±0.005)	0.22 (±0.03)	0.82 (±0.10)	–	–	–
PDMS–2	1.235 (±0.005)	0.25 (±0.03)	0.96 (±0.12)	–	–	–
EPR	1.105 (±0.005)	−0.40 (±0.03)	−1.36 (±0.10)	1.35 (±0.01)	−0.42 (±0.02)	−1.43 (±0.10)
PCR	1.130 (±0.005)	−0.08 (±0.03)	−0.28 (±0.10)	2.37 (±0.03)	−0.10 (±0.02)	−0.35 (±0.10)

[a] For α used in computations see *Table 4*

ximum deformation in every experiment. The length of the samples used to study thermoelastic behaviour at small deformations ($1 < \lambda < 2$) was 50–70 mm. In other cases it was 20–40 mm.

RESULTS

Small deformations

Inversions. *Figure* 3 shows the plots of mechanical work, heat and change of internal energy as a function of λ for four networks. These data demonstrate that heat inversion points are dependent on the chemical nature of macromolecules in full accord with equations (13) and (14). Parameters of adiabatic inversion of heat are collected in *Table* 2*).

* We will analyse only adiabatic inversion points of heat, because it is more suitable for characterization in calorimetric experiment.

In EPR elastic inversion of internal energy occurs on extension and according to equation (15) the energy contribution must be negative. Experimental parameters of this inversion are also given in *Table* 2. The energy contribution in PCR is also negative but its value is much smaller than in EPR and because of this internal energy inversion must occur at larger deformations ($\lambda_{\Delta U} \sim 2.4$). However, it is difficult to obtain exact values of parameters of inversion of internal energy in PCR with good accuracy because of stress-induced crystallization at these deformations.

Instant unloading. To demonstrate the possibilities of this approach for energy contribution characterization and to cover all three cases mentioned above, samples of EPR and NR-1 were chosen for experiments. The experimental results are summarized in *Table* 3. These results definitely demonstrate the advantage of this new approach for quick determination of the sign and value of

Table 3 Energy characteristics of instant unloading processes[a]

Polymer	λ	Q (J/g)	Q^* (J/g)	$Q^*/(Q^*+Q)$	$2\alpha T/(\lambda^2+\lambda-2)$	$(\Delta U/W)_{V,T}$	$d\ln\langle r^2\rangle/dT \times 10^3$ (K^{-1})
EPR	1.23	−0.035	−0.0092	0.208	0.598	−0.39	−1.32
	1.37	−0.115	0.0082	−0.077	0.353	−0.43	−1.46
	1.78	−0.583	0.117	−0.251	0.149	−0.40	−1.36
NR−1	1.45	−0.055	−0.060	0.521	0.251	0.27	0.92
	1.97	−0.260	−0.123	0.320	0.101	0.22	0.82

[a] For α used in computations see *Table 4*

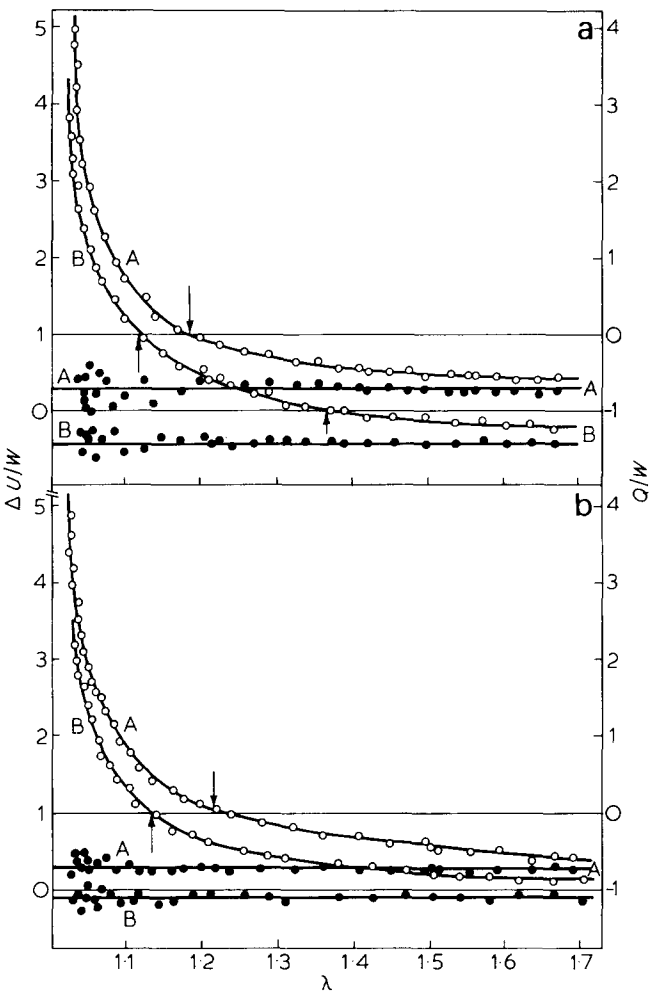

Figure 4 The relative entropy and internal energy contributions as a function of extension ratio λ. ○, $(Q/W)_{P,T}$ and $(\Delta U/W)_{P,T}$; ●, $(Q/W)_{V,T}$ and $(\Delta U/W)_{V,T}$. (a), NR−1 (A); EPR (B). (b) PDMS−2 (A); PCR (B)

the energy contribution during the deformation process of rubber-like materials. It is especially important to emphasize that these results clearly show that the energy contribution obtained by deformation calorimetry is practically insensitive to deformation rate.

Inter- and intra-molecular changes of entropy and internal energy. *Figure* 4 demonstrates the analysis of experimental results according to equations (5), (6) and (9), (10). The most important conclusion from this analysis is that intramolecular changes of entropy and internal energy are practically independent of strain at small deformations. In this region of deformations there is a large scatter of experimental points but this is a consequence of the fact that here intramolecular changes are the differences of two large values.

Now making use of equations (3)–(11) one can resolve the total entropy and energy changes into inter- and intramolecular components. The results of this treatment are shown in *Figure* 5. Although intermolecular changes of internal energy and entropy are qualitatively similar for all polymers those for EPR are somewhat higher. On the other hand, one may recall that in PDMS-2 there is about 25% fillers and therefore the real value of intermolecular changes is higher than that shown in *Figure* 5. Good coincidence between experimental values of $(\Delta U)_{\Delta V}$ and those predicted by equation (17) is noticeable only for PDMS-2. For the other three polymers this equation predicts $(\Delta U)_{\Delta V}$ well only for λ rather close to unity ($\lambda < 1.3$). At higher extensions, experimental results are higher and the difference between experiment and theory increases with increasing extension.

An empirical equation was found which describes the dependence of intermolecular energy components on strain. This equation has the form:

$$(\Delta U)_{\Delta V} = C\alpha T \frac{(\lambda-1)}{\lambda}[1+\gamma(\lambda^2+\lambda-2)] \qquad (22)$$

In this equation $\gamma = 0.1$ for EPR, 0.15 for NR-1 and 0.07 for PCR. If $\gamma = 0$ equation (22) is reduced to equation (17).

Strain-induced volume dilation. The results on $(\Delta U)_{\Delta V}$ presented above open the possibility to determine strain induced volume dilation by means of equation (19). Corresponding results are shown in *Figure* 6. In calculations the following compressibilities x (in cm^2/kg) were used: $x = 1.5 \times 10^{-5}$ for NR[34], 5.95×10^{-5} for EPR[35], 9.3×10^{-5} for PDMS[35] and 4.35×10^{-5} for PCR[36]. Taking into account the availability of fillers in PDMS-2 one may conclude that the largest increase of volume on deformation occurs for this sample, being probably connected with weak intermolecular interaction in this network and also the presence of fillers. The data for direct dilatometric determination of strain-induced volume dilation for a similar sample of NR[37] agree fairly well with our results. The dependences of strain-induced volume dilation on strain are similar to those for $(\Delta U)_{\Delta V}$ and may be expressed as follows:

$$\frac{\Delta V}{V_0} = Cx\frac{(\lambda-1)}{\lambda}[1+\gamma(\lambda^2+\lambda-2)] \qquad (23)$$

with $\gamma = 0$ for PDMS-2, 0.1 for EPR, 0.15 for NR-1 and 0.07 for PCR.

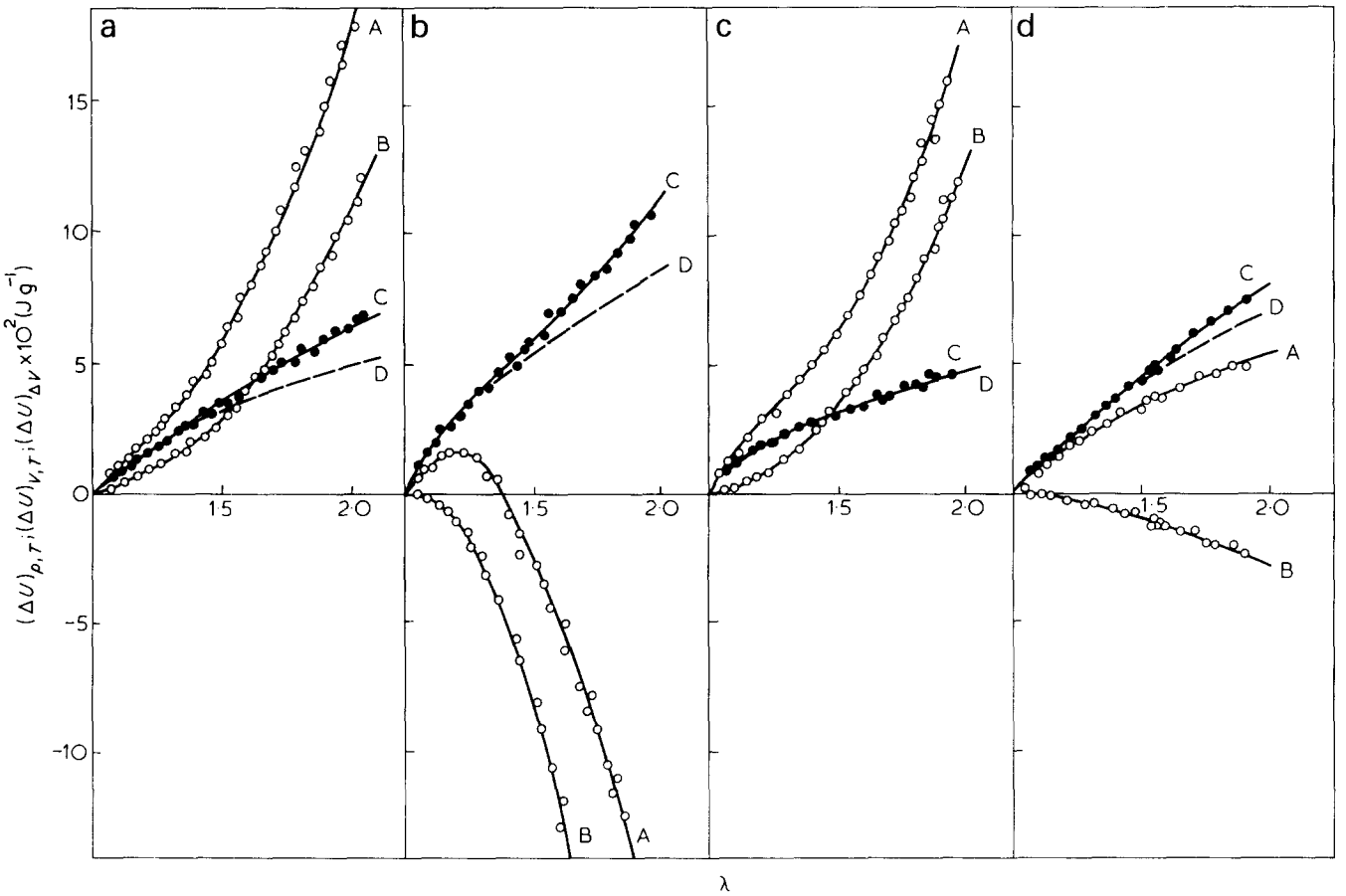

Figure 5 Intra- and inter-molecular energy changes on stretching samples from the unstrained state to λ. A, $(\Delta U)_{p,T}$; B, $(\Delta U)_{V,T}$; C, $(\Delta U)_{\Delta V}$; D, $(\Delta U)_{\Delta V}$ according to equation (17). (a) NR–1; (b) EPR; (c) PDMS–2; (d) PCR

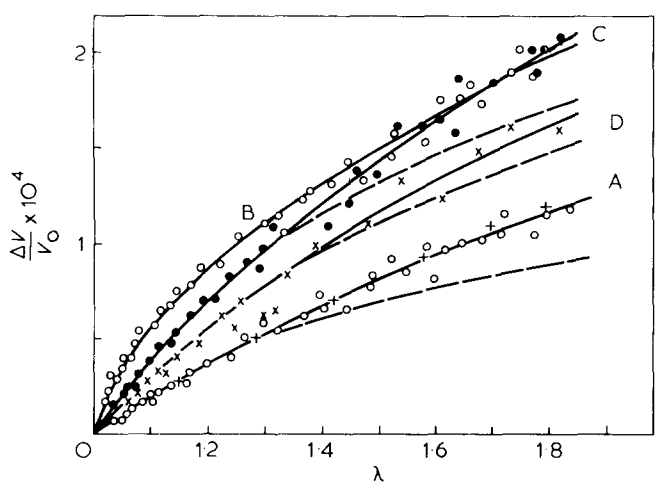

Figure 6 Strain-induced volume dilation of polymer networks plotted as a function of λ. A, NR–1 (○ = our results, + = data of Christensen and Hoeve[37]); B, PDMS–2 (○); C, EPR (●); D, PCR (X); – – – –, according to equation (19)

Moderate deformations. The dependences of heat and mechanical work as a function of extension ratio λ for all polymers studied are shown in *Figure* 7. On the basis of these results entropy and energy contributions were determined by means of equations (6) and (11) and the results obtained were collected in *Table* 4. The literature data concerning the energy contribution obtained from the temperature dependence of the elastic force are also listed in *Table* 4 and were taken from Mark's review[4]. The majority of the networks studied are not capable of crystallizing on deformation, but four of them namely NR, PIR, PCR and PUR crystallize on extension. In this case irrespective of the sign of the energy contribution, heat liberation begins to increase and consequently the internal energy begins to decrease. Crystallization of NR during the deformation process was studied by Müller *et al.*[9,10,38] in considerable detail by deformation calorimetry and we will not discuss this problem in our paper.

Large deformations

There are no experimental results concerning the energy contribution to the elasticity of rubber-like materials at large deformations. This is a consequence of either extensive crystallization at large deformations as in the case of NR or rupture of samples because of their poor strength. New possibilities have been opened in this field after synthesis of thermoplastic elastomers, which possess a very high strength and are capable of deformations up to 1000% and more. To elucidate the energy changes at large deformations we recently studied the thermoelastic properties of butadiene–styrene and isoprene–styrene triblock copolymers[39]. Here we will consider only the results dealing with energy contributions obtained for two samples — styrene–butadiene–styrene block copolymer with linear (DST-30) and with star-like (Solprene-406) structure of macromolecules.

Because the ability to crystallize is extremely important for the conclusion concerning energy changes at large deformations we studied thoroughly the conformational composition of the elastomeric phase by i.r.-spectroscopy[40]. This study led to the following results

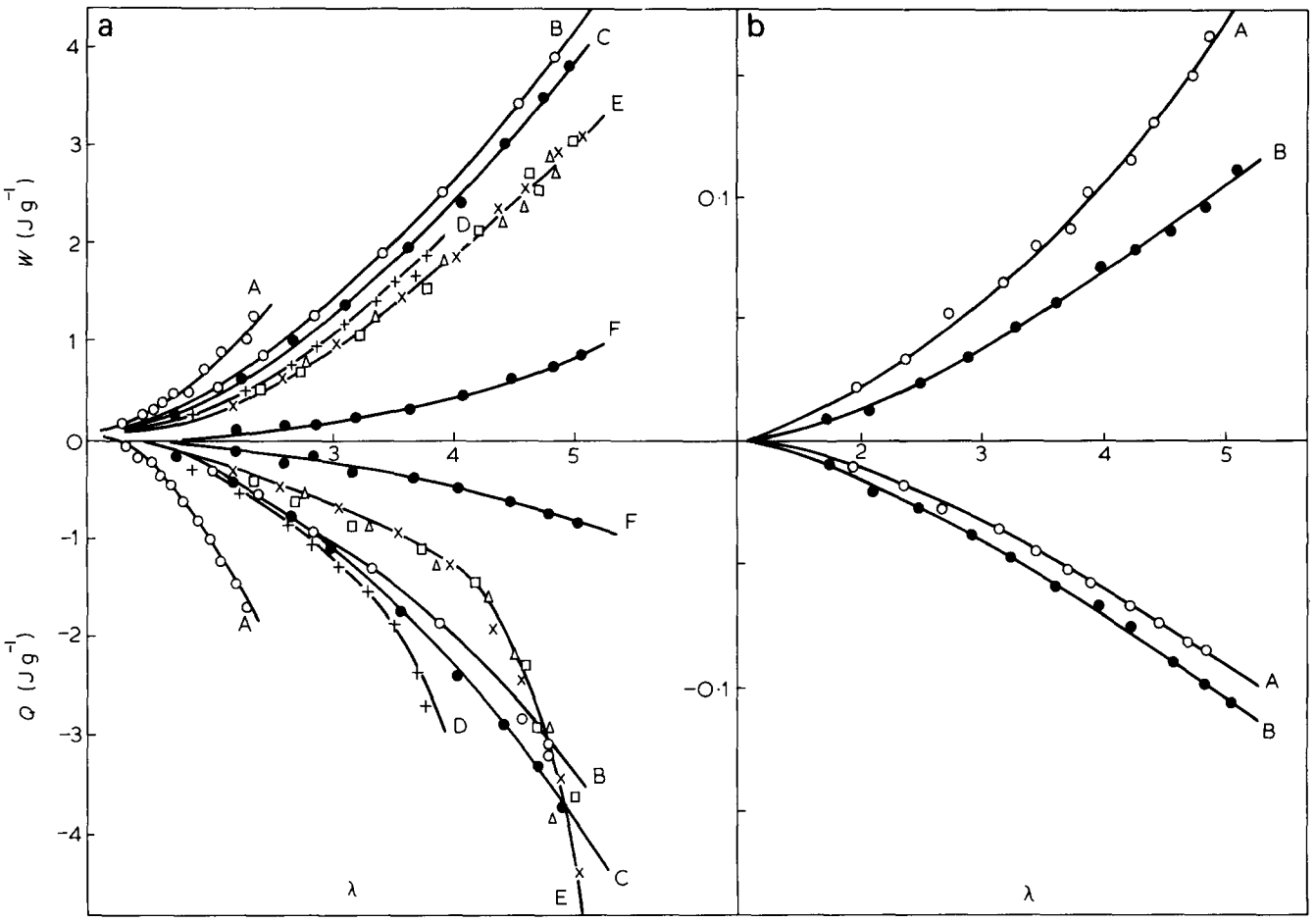

Figure 7 Mechanical work and heat plotted as a function of λ. (a) EPR (A); PDMS–2 (B); ABR (C); PCR (D); PIR (□), NR–1 (△) and NR–2 (X) (E); SBR (F). (b) PDMS–1 (A); PUR (B)

Table 4 The relative intramolecular entropy and internal energy contributions and temperature coefficients of unperturbed dimensions of chains

Polymer	$\alpha \times 10^4$ (K^{-1})	λ	$-(Q/W)_{V,T}$	$(\Delta U/W)_{V,T}$	$d\ln\langle r^2\rangle_0/dT \times 10^3$ (K^{-1})	f_u/f [a]
NR–1	6.6	1.02–3.5	0.72 (±0.03)	0.28 (±0.03)	0.96 (±0.10)	0.12–0.24
NR–2	6.6	1.5–3.5	0.72 (±0.03)	0.28 (±0.03)	0.96 (±0.10)	0.12–0.17
PIR	6.6	1.02–3.5	0.73 (±0.03)	0.27 (±0.03)	0.92 (±0.10)	
PDMS–1	9.0	1.5–2.8	0.70 (±0.05)	0.30 (±0.05)	1.00 (±0.17)	0.15–0.27
PDMS–2	9.0	1.02–4.5	0.70 (±0.05)	0.30 (±0.05)	1.00 (0.17)	
EPR	7.5	1.03–2.5	1.42 (±0.05)	−0.42 (±0.05)	−1.43 (±0.17)	−(0.3–0.52)
ABR	7.6	1.8–5.0	0.94 (±0.03)	0.06 (±0.03)	0.20 (±0.10)	0.03
SBR	8.4	2.0–5.0	1.0 (±0.05)	0 (±0.05)	0 (±0.17)	−0.13(±0.06)
PCR	7.2	1.05–3.5	1.10 (±0.05)	−0.10 (±0.05)	−0.34 (±0.17)	−0.10
PUR	–	1.3–3.5	1.0 (±0.05)	0 (±0.05)	0 (±0.17)	–

[a] Literature values from table compiled by Mark[4]

for both polymers: 1,4-*cis*-structure, 40.2%; 1,4-*trans*-structure, 50.3%; and 1,2-structure, 9.5%. Polybutadiene of such composition is not capable of crystallization.

Because for thermoplastic elastomers stress softening effects are usually present, samples were stretched many times to the highest tension ratios before calorimetric measurements. The dependence of work done and heat evolved as a function of extension λ is shown in *Figure* 8*a*. Thermoelastic properties of thermoplastic elastomers may be treated in a manner analogous to that of rubbers filled with spherical particles[41,42]. According to this treatment both W and Q depend upon amount of fillers but heat to work ratio (entropic component) and consequently energy component should not be dependent

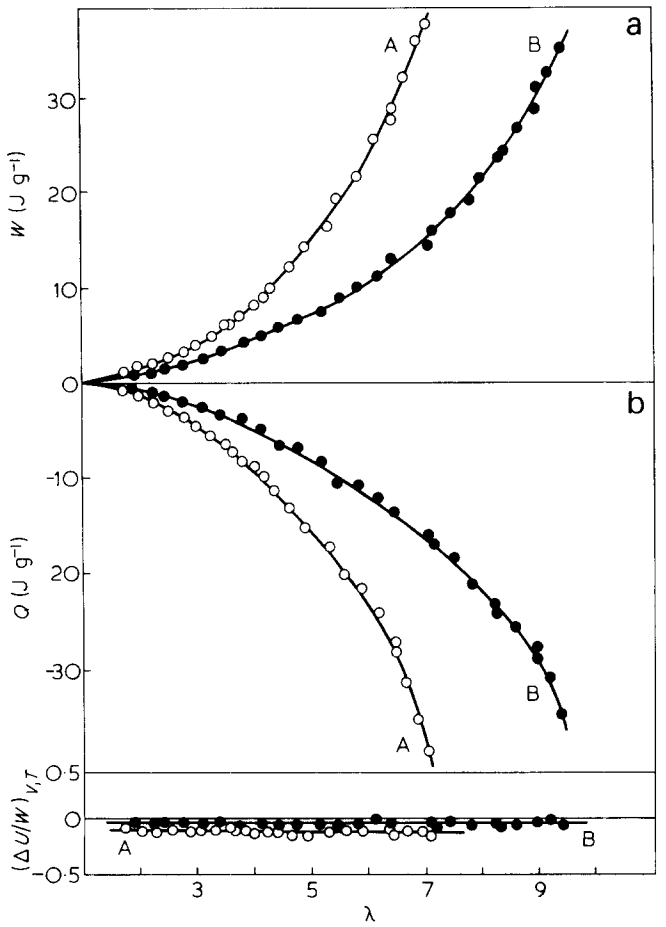

Figure 8 (a) Mechanical work and heat on stretching the thermoplastic elastomers from the unstrained state to λ. A, Solprene 406; B, DST–30. (b) The relative intramolecular energy contribution as a function of extension ratio λ

either on amount or properties of filler. Plot of energy component as a function of extension ratio λ is shown in *Figure 8b*. The most important feature of these results is the fact that the energy contribution is practically independent of extension ratio. This result has also confirmed that the polybutadiene phase does not crystallize at large deformations.

Using the *cis–trans* content of the butadiene phase and the energy contribution for the particular structures presented in Mark's review[4] we calculated the energy component for the polybutadiene phase of the thermoplastic elastomers studied. It happens to be $(\Delta U/W)_{V,T} = -0.08$. The values $(\Delta U/W)_{V,T} = -0.03 \pm 0.05$ and -0.13 ± 0.05 which obtained for DST-30 and Solprene-406 respectively, are close to the theoretical value. The reason for the small difference in the energy contribution for linear and star macromolecules is not clear so far.

DISCUSSION

Intramolecular changes

Comparison of the values of $(\Delta U/W)_{V,T}$ and $d \ln \langle r^2 \rangle_0 / dT$ obtained in our study by deformation calorimetry with the literature data obtained by other methods leads to the conclusion that in general the calorimetric results are in good agreement with results by other methods. For example, our mean calorimetric value of $(\Delta U/W)_{V,T}$ for the most widely studied NR is equal to 0.25 ± 0.03 which is rather close to the mean value of f_u/f summarised in a previous review[4]. For other polymers the agreement is even better. It is very important to note that the deformation rate in calorimetric experiments does not crucially influence the value of the energy contribution. This in turn means that although both work and heat of elastic deformation depend on deformation rate their dependence is similar; therefore the heat to work ratio and consequently the energy contribution is independent of deformation rate.

All methods used for determining energy contribution, i.e. $(U/W)_{P,T}$–λ dependence, inversions of heat and internal energy, instant unloading, lead to self-consistent results. The most general is the method of determination of $(\Delta U/W)_{P,T}$ in a wide range of deformations and transformations of these values to $(\Delta U/W)_{V,T}$. It gives the values of the energy contributions in a whole range of deformations. On the other hand, the inversion point methods give the values of energy contribution only at the deformation at which the inversion occurs, i.e. at a definite point.

Our measurements on a large number of rubber-like materials lead to the conclusion that $(\Delta U/W)_{V,T}$ is independent of deformation in a wide range of deformations. For four polymer networks it is constant also at very small deformations, which is consistent with the statistical theory. Although in some investigations[6,15], it has been found that for some polymers including NR and EPR, f_u/f begins to increase at small deformations, Shen *et al.*[43–45] have convincingly shown that in fact this dependence is fictitious.

It is particularly worth mentioning the discrepancy between three sets of calorimetric results for NR. Göritz and Müller[10] in their comprehensive calorimetric study of energy contribution to the elasticity of NR have found that for $\lambda = 2$–4 $f_u/f = 0.35$, but when $\lambda < 1.8$ f_u/f begins to increase sharply (see Figure 1 in ref. 10). These authors concluded that the dependence of f_u/f on deformation was the result of an additional intermolecular contribution. On the other hand, Price *et al.*[15] have also studied energy changes in NR by deformation calorimetry and have shown that $f_u/f = 0.16 \pm 0.01$ for $1.4 < \lambda < 1.8$, i.e. is independent of λ. From this point of view our results for NR quite agree with the results of Price *et al.*, although the absolute value of $(\Delta U/W)_{V,T}$, equivalent to the f_u/f, is slightly higher.

An attempt was made to resolve this contradiction. Göritz and Müller used the following expression to obtain f_u/f (see equation (3) in ref. 10)

$$f_u/f = 1 + \frac{Q_{P,T}}{W} - \frac{\alpha T}{\lambda^3 - 1} \qquad (24)$$

(we use our notation). We feel that this is an incorrect form for the treatment of calorimetric results because in this equation instead of the ratio Q/W the ratio $(dQ/d\lambda)/(dW/d\lambda)$ should be used. Comparing equation (24) with equations (5) and (9) in which the ratio Q/W is incorporated we see that they differ only by the form of the term which reflects the intermolecular interaction. Although at large deformations the difference between these two terms is insignificant at small deformations ($1 < \lambda < 2$) however it becomes important. Using equations (5) and (11) we reconsidered the data of Göritz and Müller and concluded that their f_u/f is also practically independent of strain in the low strain region ($1.4 < \lambda < 1.8$). Thus, summing up the data of three sets of calorimetric results concerning the relative intra-

molecular energy contribution in NR we may conclude that at small deformations $(\Delta U/W)_{V,T}$ or f_u/f id independent of deformation.

It is generally accepted that at large deformations because of the limited extensibility of polymer chains the Gaussian statistics should not be valid and, therefore, the energy contribution should be changed[5,6,43]. Because stress–strain isotherms for some elastomers, first of all for NR, possess a definite upturn at large deformations this anomalous behaviour has almost invariably been attributed to the limited extensibility of the network chains. In a recent series of papers Mark *et al.*[46–48] have experimentally analysed in great detail the role of strain-induced crystallization and the limited extensibility of chains at large deformations. They concluded that in all cases studied so far the origin of the marked upturn on the stress–strain isotherms was crystallization of rubber on elongation and that the limited extensibility of chains was not revealed at all. Then Flory[49] came to a very important conclusion that 'the Gaussian approximation should be generally adequate and appropriate for the treatment of the elasticity of a network of random (i.e. non-crystalline) chains averaging 100 and more bonds in length, without qualifications on the range of deformation'. From the thermodynamic point of view it means that the intramolecular contribution at large deformations should not differ from that at small and moderate deformations. Unfortunately, so far there have been no experimental results concerning the energy changes in rubbers at large deformations in the absence of crystallization. It seems to us that our results on thermomechanical behaviour of thermoplastic elastomers, which demonstrate independence of the intramolecular energy changes of deformation even at deformations up to $\lambda = 10$, support the conclusion about the validity of the Gaussian statistics for the treatment of elasticity of rubber-like materials in the region of large deformations.

Intermolecular changes

All the results discussed above concern the intramolecular changes arising as a result of an energy difference between isomeric states. Because these differences are determined by internal rotation potentials of chains, the values of $(\Delta U/W)_{V,T}$ and $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ are practically insensitive to intermolecular interaction. This is the reason for the insensitivity of these characteristics to experimental conditions, type of deformation and conditions of sample preparation[4].

Let us now consider energy contribution resulting from intermolecular changes. For three unfilled networks studied at small deformations our calorimetric results demonstrate that the statistical theory predicts the volume dilation and related intermolecular entropy and energy changes only for $\lambda \sim 1.3$. At large deformations experimental results show a significant departure from statistical theory, i.e. this theory underestimates intermolecular changes on deformation. For NR this conclusion agrees with the results of other studies[37,43,50–52]. For filled PDMS the data follow the theoretical prediction but this behaviour, however, may be fortuitous because of the presence of a large amount of fillers.

The fact that the statistical theory cannot predict intermolecular changes in polymer networks at $\lambda > 1.3$ should probably not be surprising, because the liquid-like properties of networks are taken into account in this theory only by two ordinary parameters — α and x. At small deformations it is enough for characterization of intermolecular changes. But at moderate deformations there probably may be an additional intermolecular contribution arising from specific structure of networks, first of all their topology and their rearrangement in the course of deformation.

Empirical expressions obtained for volume dilation and intermolecular energy and entropy changes (see equations (22) and (23)) are closely related to the one proposed by Tobolsky and Shen[43,44,53] on the basis of their semi-empirical equation of state, which postulates a volume dependence of the front factor due to intermolecular interactions. Our experimental values of γ (which according to Tobolsky and Shen reflects this dependence) are in good agreement with independent results[43]. Tobolsky and Shen have emphasized that if γ is not equal to zero then the relative intramolecular energy contribution should be reconsidered. Using our empirical expression for $(\Delta U/W)_{\Delta V}$ we can now express $(\Delta U/W)_{V,T}$ as follows:

$$(\Delta U)_{V,T} = \frac{1}{2} C \left(T \frac{\mathrm{d}\ln\langle r^2\rangle_0}{\mathrm{d}T} - 2\gamma\alpha T \right) \frac{(\lambda - 1)}{\lambda} (\lambda^2 + \lambda - 2) \tag{25}$$

or in the relative form:

$$\left(\frac{\Delta U}{W}\right)_{V,T} = T \frac{\mathrm{d}\ln\langle r^2\rangle_0}{\mathrm{d}T} - 2\gamma\alpha T \tag{26}$$

It is evident that in this case the energy contribution is also independent of strain. Numerical calculations have shown that the last term in the right part of equation (26) is equal to 0.04 for EPR and to 0.06 for NR and thus it slightly increases $(\Delta U/W)_{V,T}$ for EPR and decreases it for NR. After this correction the energy contribution for NR becomes very close to that obtained by Allen *et al.*[50] in experiments under constant volume. Thus, it is seen that there is a strong experimental support for the suggestion that the front factor may really be dependent on volume.

CONCLUSIONS

Although the first quantitative investigation of thermodynamics of rubber elasticity by deformation calorimetry was carried out about 20 years ago the use of this approach so far has been limited mainly to studying thermoelastic properties of natural rubber. Besides, the sensitivity of calorimeters used was not high enough to study thermodynamics at small deformations including inversion regions. In this paper we have presented results on the thermodynamics of simple elongation of a wide class of rubber-like materials including not only classical elastomers such as natural rubber, polydimethylsiloxane, statistical copolymers, but also new elastomeric materials — rubber-like block copolymers. The results were obtained on a device developed by us, in which a Calvet-type microcalorimeter was coupled with an automatic dynamometer assembly. This device had such high sensitivity that it was possible to study very small thermal effects resulting from small deformations ($\lambda \sim 1.01$) when simple elongation of rubber, like elongation of ordinary solids, is accompanied by absorption of heat.

Relations between mechanical work, heat and change of internal energy for constant P and T, necessary for treatment of calorimetric results were obtained using the elastic equation of state for Gaussian networks. As a result of examination of inter- and intra-molecular changes of the internal energy and entropy, new expressions were derived for determining $(\Delta U/W)_{l,l}$ and $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ based on inversions of elastic heat and internal energy. Inversions of heat in calorimetric experiments occur as a result of a competition between an increase of vibrational entropy, associated with volume dilation during deformation, and a decrease of conformational entropy. On the other hand, internal energy inversion occurs for elongation of rubber-like materials with a negative intramolecular energy contribution and is a consequence of the competition between inter- and intra-molecular components of the change of internal energy.

The intramolecular energy contribution and the temperature coefficient of the chain dimension $\langle r^2\rangle_0$ were obtained for 9 polymer networks. Comparison of our results with literature data have demonstrated a rather good similarity. They also show that in general the free energy of deformation contains a significant intramolecular energetic contribution, the sign and value of which depend, in accord with the isomeric state theory, only on the chemical structure of macromolecules.

Particular attention was paid to the investigation of energetic changes at small deformations to check whether there is a dependence of the intramolecular energy contribution on the strain, as has been found in some experimental studies, though it is inconsistent with the statistical theory. With this aim the thermoelastic behaviour of four networks were studied at $1.02<\lambda<2$. Three independent methods were used for determining $(\Delta U/W)_{l,l}$ in NR and four in EPR. All methods used give self-consistent results and demonstrate independence of intramolecular relative energy changes at these deformations.

Elongation of rubber-like materials is accompanied not only by intramolecular changes of entropy and internal energy but also by intermolecular changes which arise as a result of the liquid-like interchain interaction. In calorimetric experiments they prevail at small deformations and diminish sharply with increase of deformation. Using deformation calorimetry it is possible to evaluate these intermolecular changes and hence to determine volume dilation the results of which they are. For networks of Gaussian chains these intermolecular changes do not contribute to the free energy of deformation. Analysis of the results obtained shows that the statistical theory of rubber elasticity predicts the intermolecular changes and the induced volume dilation only for $\lambda<1.3$, at least for three polymers studied at small deformations. At larger deformations experimental results exceed the values predicted by the theory and this discrepancy increases with increasing deformation. Empirical relations describing the strain-induced volume dilation and intermolecular energy changes resulting from this dilation are closely related to the equation proposed by Shen and Tobolsky on the basis of their semi-empirical equation of state for rubber elasticity, which postulates a volume dependence of the front factor due to intermolecular interactions.

It is generally accepted that at large deformations due to the limited extensibility of macromolecules the conformational statistics ought to change and the Gaussian approximation may become inadequate for the treatment of the elasticity of rubber-like materials. Hence, this should lead to a change of the intramolecular energy component. Reliable experimental checking of this prediction in the absence of strain-induced crystallization became possible on thermoplastic elastomers, which possess very high strength and are capable of reversible deformations up to $\lambda=10$. Using deformation calorimetry we studied the thermodynamics of simple elongation of a number of diene styrene block copolymers with different molecular architecture (linear and star) in particular detail. This study showed that the relative intramolecular energy changes are independent of deformation up to $\lambda=10$, in spite of the fact that there are sharp upturns in the vicinity of $\lambda\sim5$ on the Mooney Rivlin isotherms[39]. We have suggested that these upturns are connected with the presence of glassy polystyrene domains in the elastomeric matrix and are not the consequence of the limited extensibility of chains. Hence, we concluded that independence of intramolecular energy changes of deformations means that the Gaussian statistics are valid for the treatment of the elasticity of networks not only at small deformations but also at large deformations. This agrees with Flory's recent conclusion.

REFERENCES

1 Volkenshtein, M. V. 'Configurational Statistics of Polymeric Chains', Izd. AN SSSR, Moscow, 1959, Ch 8
2 Birshtein, T. M. and Ptitsyn, O. B. 'Conformations of Macromolecules', Izd. Nauka, Moscow, 1964, Ch 8
3 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1969, Ch 2
4 Mark, J. E. *Rubber Chem. Technol.* 1973, **46**, 593
5 Treloar, L. R. G. 'The Physics of Rubber Elasticity', Clarendon Press, Oxford, 1975, 3rd Edn, Ch 2
6 Krigbaum, W. R. and Roe, R.-J. *Rubber Chem. Technol.* 1965, **38**, 1039
7 Engelter, Ad. and Müller, F. H. *Kolloid-Z.* 1958, **157**, 89
8 Müller, R. H. 'Rheology', (Ed. Eirich), Wiley, New York, 1969, Vol 5, Ch 8
9 Dick, W. and Müller, F. H. *Kolloid-Z. Z. Polym.* 1962, **172**, 1
10 Göritz, D. and Müller, F. H. *Kolloid-Z Z. Polym.* 1973, **251**, 679
11 Godovsky, Yu. K. 'Thermophysical Methods of Polymers Characterization', Izd. Khimija, Moscow, 1976, Ch 6
12 Godovsky, Yu. K., Slonimsky, G. L., Papkov, V. S. and Dikareva, T. A. *Mechan. Polym.* 1970, (5), 785
13 Godovsky, Yu. K., Slonimsky, G. L., Papkov, V. S. and Dikareva, T. A. *IUPAC Symp. Macromolecules, Leiden* 1970, **2**, 669
14 Godovsky, Yu. K., Papkov, V. S., Slutzker, A. I., Tomashevsky, E. E. and Slonimsky, G. L. *Fiz. Tverdogo Tela* 1971, **13**, 2289
15 Price, C., Evans, K. A. and de Candia, F. *Polymer* 1973, **14**, 338
16 Price, C., Allen, G. and Yoshimura, N. *Polymer* 1975, **16**, 261
17 Allen, G., Price, C. and Yoshimura, N. *Trans. Faraday Soc.* 1975, **71**, 548
18 James, H. M. and Guth, E. *J. Chem. Phys.* 1943, **11**, 455; 1947, **15**, 669
19 Flory, P. J. *Trans. Faraday Soc.* 1961, **57**, 829
20 Godovsky, Yu. K. *Vysokomol. Soedin.* (A) 1977, **19**, 2359
21 Flory, P. J., Ciferri, A. and Hoeve, C. A. J. *J. Polym. Sci.* 1960, **45**, 235
22 Gee, G. *Trans. Faraday Soc.* 1946, **42**, 585
23 Prigogin, I. and Defay, T. 'Chemical Thermodynamics', Longmans, London, 1954, Ch 12
24 Khazanovich, T. N. *J. Appl. Phys.* 1959, **30**, 948
25 Calvet, E. and Prat, H. 'Microcalorimetrie', Masson, Paris, 1956
26 Godovsky, Yu. K., Slonimsky, G. L. and Alekseev, V. F. *Vysokomol. Soedin* (A) 1969, **11**, 1181
27 Godovsky, Yu. K. and Slonimsky, G. L. *Vysokomol. Soedin.* 1965, **7**, 621
28 Godovsky, Yu. K. and Barsky, Yu. P. *Vysokomol. Soedin.* 1966, **8**, 395
29 Godovsky, Yu. K., Slonimsky, G. L. and Garbar, N. M. *J. Polym. Sci.* (C) 1972, **38**, 1

30 Godovsky, Yu. K. and Slonimsky, G. L. *J. Polym. Sci. (Polym. Phys. Edn)*, 1974, **12**, 1053
31 Molchanov, Yu. M. and Molchanova, G. A. *Mechan. polym.* 1970, (5), 579
32 Andrianova, G. P., Arutunov, B. A. and Popov, Yu. V. *J. Polym. Sci. (Polym. Phys. Edn)*, 1978, **16**, 1139
33 Göritz, D. and Müller, F. H. *Kolloid-Z Z. Polym.* 1974, **252**, 862
34 Wood, L. A. and Martin, G. M. *J. Res. Nat. Bur. Stand.* 1964, **A68**, 259
35 Bianchi, U. and Pedemonte, E. *J. Polym. Sci. (A)* 1964, **2**, 5039
36 Van Krevelen, D. M. 'Properties of Polymers Correlations with Chemical Structure', Elsevier, Amsterdam, 1972, Ch 9
37 Christensen, R. C. and Hoeve, C. A. J. *J. Polym. Sci. (A-1)* 1970, **8**, 1503
38 Göritz, D. and Müller, F. H. *Kolloid-Z Z.Polym.* 1973, **251**, 892
39 Godovsky, Yu. K. and Tarasov, S. G. *Vysokomol. Soedin. (A)* 1980, **22**, 1613
40 Kozlova, N. V., Suchov, F. F. and Bazov, V. P. *Zavodsk. Labor.* 1965, (8), 968
41 Holden, J., Bishop, E. T. and Legge, N. R. *J. Polym. Sci. (C)* 1969, **26**, 37
42 Leonard, W. J. Jr. *J. Polym. Sci. (C)* 1976, **54**, 237
43 Shen, M. and Croucher, M. *J. Macromol. Sci. (C)* 1975, **12**(2), 287
44 Shen, M. and Blatz, P. *J. Appl. Phys.* 1968, **39**, 4937
45 Shen, M. *Macromolecules* 1969, **2**, 358
46 Mark, J. E., Kato, M. and Ko, J. H. *J. Polym. Sci. (C)* 1976, **54**, 217
47 Kato, M. and Mark, J. E. *Rubber Chem. Technol.* 1976, **49**, 85
48 Su, T.-K. and Mark, J. E. *Macromolecules* 1977, **10**, 120
49 Flory, P. J. *Proc. R. Soc.* 1976, **351**, 351
50 Allen, G., Kirkham, J. J., Pedget, J. and Price, C. *Trans. Faraday Soc.* 1971, **67**, 1278
51 Price, C. *Proc. R. Soc.* 1976, **351**, 331
52 Goebel, J. C. and Tobolsky, A. V. *Macromolecules* 1971, **4**, 208
53 Tobolsky, A. V. and Shen, M. *J. Appl. Phys.* 1966, **37**, 1952