THERMODYNAMIC EXAMINATION

OF THE POLYMORPHOUS

TRANSITION OF TRANS-1,4

POLYBUTADIENE

By: G. Natta, M. Pegoraro, and L. Szilagyi,
Istituto di Chimica Industriale del Politecnico,
Milano, Italy.

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Istituto di Chimica Industriale del Politecnico, Milano, Italy

HIGH purity trans-1,4 polybutadiene (steric purity > 99 per cent) was synthesised for the first time[1] at this Institute. Being crystalline, it differs from cis-1,4 polybutadiene, which was also synthesised for the first time[2] with very high purity (> 99 per cent) at this Institute: in fact the cis-1,4 polymer behaves as an elastomeric substance at temperatures above 2°C (melting point). Trans-1,4 polybutadiene shows a solid-solid transition of the first order: if the material is not subjected to mechanical stress at atmospheric pressure, the transition temperature is 76°C[3].

The crystalline form, denominated form I, is stable below 76°C, while the other crystalline form, called form II, is stable above 76°C and up to the melting temperature (145°C).

Transformation from one to the other form is reversible and is caused by a particular variation in the conformation of the main chain: the identity period of the macromolecule in form II (4·68 Å) is lower than that of the same chain in form I (4·92 Å)[4], while its cross section is 15·6 per cent higher. Consequently, in oriented fibres, the transition phase I→II causes the contraction of the sample and an increase in cross section. The transition [3] is accompanied by an increase in volume. We have thought to utilise this transition in oriented fibres to turn thermal energy into mechanical work: to this end, we realised a particular thermodynamic cycle that utilises an oriented fibre of trans-1,4 polybutadiene as evolving medium.

Description of the Cycle

(1) Ideal Case. Let us consider a phase transition[5] of a system consisting of an ideal fibre, completely oriented and crystalline, constituted by only one component, subjected at constant pressure to a force f (temperature T and force f being the physical variables). When two phases are present (during the transition) the system presents a unitary degree of variance. It follows that the temperature of the phase transition is a univocal function of the applied force. By increasing the force (Le Chatelier) the transition temperature increases, if the transition in the sense of increasing temperatures is accompanied, as in the case considered, by fibre contraction.

Fig. 1 shows the variation of the temperature of the phase transition with varying the tensile force (and stress) applied to the fibre, calculated by us[5] for an ideal single crystal with axial orientation having length = 100 cm, section 0·54 cm², transition temperature = 70°C and ΔH of transition 1,000 cal.

It is possible to calculate [6] quantitatively the mechanical work that can be obtained, in the case of an ideal fibre, by applying an axial force f_2 and going through the transition that happens at the corresponding equilibrium temperature and coming back through the inverse transformation (accompanied by elongation) at lower force f_1 or at zero force (and therefore at a lower temperature). The increasing $f_1 \rightarrow f_2$ and the decreasing $f_2 \rightarrow f_1$ of the loads is supposed to be made at constant temperature, out of the field of the transition temperatures. In Fig. 2 it is possible to follow the length of a fibre with increasing temperature (from T_a to T_e) when loaded with a force f_2 (run b c d e) and with decreasing temperatures (from T_e to T_a) when loaded with the force f_1 (run f g h a).

The direct phase transition with contraction happens at T_c under force f_2, and the reverse phase transition with elongation at T_g. Both T_c and T_g are greater than T_0, which is the unloaded fibre transition temperature. The dotted line indicates the phase transition of an unloaded sample.

The cycle may be effected also by suppressing the thermal variation T_c–T_e and T_g–T_a: in this case, the other conditions being constant, the resultant mechanical work is higher.

Left:

Fig. I. Equilibrium curve force (f)-temperature (T) for an ideal fibre, having transition temperature $T_0 = 70°C$, ΔH 1,000 cal, weight 54·1 g, length 100 cm, cross section 0·543 cm². a—calculated [5] for ΔH = cost and ΔL function of force; b—for ΔH/ΔL = constant

Below:

Fig. 2. Ideal cycle, possible for an ideal fibre of trans-1,4 polybutadiene, in the coordinates length L, temperature T
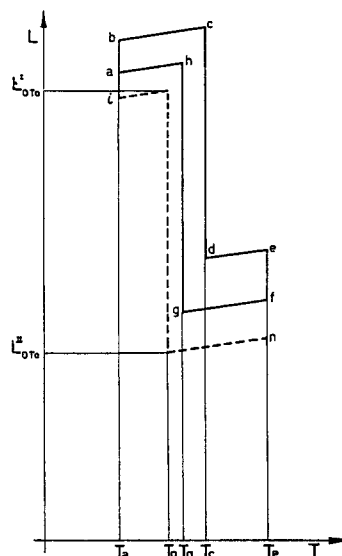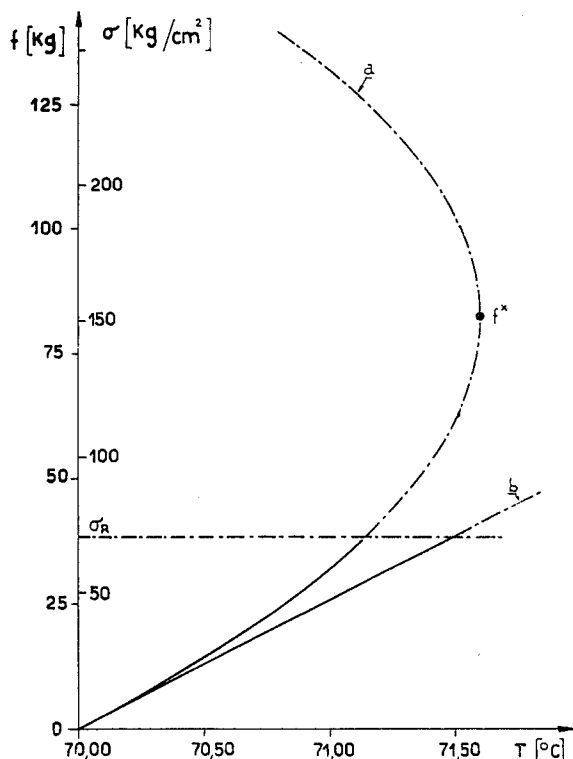
(2) Real Case. Let us now consider a real case and precisely that corresponding to the use of oriented trans-1,4 polybutadiene.

A trans-1,4 polybutadiene fibre differs from the ideal model in that, in spite of the high steric purity, it shows at constant force and pressure a transition interval of about 15°C, probably due to the different crystallinity of its crystals, caused both by the dispersion of the molecular weights and by the co-existence of amorphous and crystalline parts in the same molecule. For instance, a typical curve length temperature $L = L(T)$ is shown in Fig. 3a where $f > 0$ (atmospheric pressure). A slight shift of curve $L = L(T)$ toward higher temperatures is observed experimentally when increasing the value of the applied force; this was described by us in a previous paper[5] and is in agreement with the Le Chatelier principle. The low entity of the shift depends on the very steep slope of the equilibrium curve $f = f(T)$, which is proportional[5], to a first approximation, to $\dfrac{\Delta H}{\Delta L} \dfrac{1}{T_0}$, and also on the fact that only slight increases in stress consistent with the mechanical resistance of the test piece are possible.

An interesting aspect of the real phenomenon is given by the thermal hysteresis of the transition. Curves $L = L(T)$ at constant force and pressure show that on cooling (see, e.g. Fig. 3b) the transition phase II→phase I is shifted by about 20° below that of the direct transition. Moreover, the initial length is totally recovered, at least for the cycles successive to the first cycle, only if, when passing from high to low temperatures, the test-piece is not unloaded, but subjected to a sufficient load to maintain a good orientation.

A cycle like that of Fig. 3, carried out at constant force, becomes reversible from a mechanical point of view, while it is not so from a thermodynamic standpoint, because the Clausius integral $\displaystyle\int \dfrac{dq}{T} < 0$. In fact, for its evaluation, it is enough in a first approximation to take into account the direct and inverse state passages, being small by comparison, the contributions associated with the transformations of simple heating and cooling that are not accompanied by phase transitions. Since the amount of heat exchanges with the environment during the direct and inverse passages of state is practically the same (at constant force) in absolute value[3], and since the temperature of the reverse state passage is lower than that of the direct one, it follows that the Clausius integral is less than zero. Although the system is not reversible from a thermodynamic point of view, it can still be used for the cyclic production of work: as evidenced by experience, in fact, the fibre can practically regain its initial state after a set of suitable physical transformations that produce work at expense of thermal energy.

In the real case, we could practically perform the experimental cycle of Fig. 4, similar to the ideal one (Fig. 2), consisting of two isodynes (constant force) at variable temperature, that is b, c, d, e (up) with force f_2 and f, g, h, a with force$_1$ (back), and of two isotherms at variable force (ab, ef). The dotted parts of the cycle in Fig. 4 only comprise the physical transfers that are not accompanied by state exchange.

In order to obtain work, the f_2 force, applied during the transition of shortening, must necessarily be higher than force f_1, applied during the transition of elongation occurring at lower temperature,
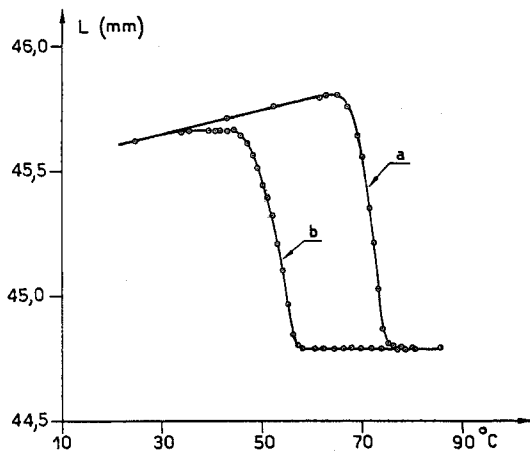
and the cycle must be run across in the sense abcdefgh, a. This may be well understood by observing Fig. 5, which represents the same cycle in the fL plane.

Crystallites of the test-piece are in phase I during the run habc; in phase II during the run defg, while the two phases I and II are simultaneously present during transitions (cd; gh). The opportunity to apply a non null force f_1 during the isodyne f...a depends on the fact that, under these conditions, orientation is better preserved. Under these conditions, very many cycles can be performed keeping the shape of the cycle practically unaltered and the dimensions of the test-piece after each cycle constant.

The area inside the ab, be, ef, fa segments of Fig. 5 measures the mechanical work W that can be obtained in a cycle; being practically a trapezium, it is expressed by:

$$(1) \qquad W = \frac{f_2 - f_1}{2} \left[(L_b - L_e) + (L_a - L_f) \right]$$

where L with the suitable index represents the length of the test-piece in the corresponding point of the cycle. Such lengths at the limit points of the cycle depend on the applied forces f_1 and f_2 and on the temperatures of the tensile run ab (T_a) and of the unloading run ef (T_e).

Influence of the Limit Temperatures T_a and T_e and of Applied Forces (f_2 and f_1) on the Mechanical Work Obtained

By varying T_a and T_e, f_1 and f_2 remaining constant, the lengths at the limit points a, b, e, f vary both owing to the influence exerted by thermal expansion on the test-piece and to the decrease in elastic moduli of phase I and phase II with increasing temperature. Not to fall within the range of temperatures of the passage of state (Fig. 4), tensile run ab must be carried out at a temperature equal to or lower than T_h (point h), and unloading run ef at a temperature equal to or higher than T_d (point d). After examining Fig. 4 and on the basis of formula 1, we are led to conclude that, f_1 and f_2 being the same, the work developed in a cycle increases at a faster rate the more T_a approaches T_h and T_e approaches T_d, in that the differences L_b–L_e and L_a–L_f become greater.

In the case of the test-piece used for the run described in Figs. 4 and 5, which, at 23°C, has a section of 1.02 mm^2, useful length of 50 mm and mass of 51 mmg, we have found $T_h = 43°C$ and $T_d = 77.5°C$. For the sake of generality, we thought it better to use tensile and unloading temperatures different from those mentioned above: thus we chose $T_a = 35°C$ and $T_e = 82°C$. In expression (1) of the mechanical work, the applied forces exert an explicit and implicit influence, as the lengths of the test-piece in points ab ef of the cycle are a function, among other things, of the forces themselves in a hardly calculable manner, which could be done only in the case of the ideal fibre[6].

We have therefore developed experimental studies measuring the work that can be obtained by varying forces f_1 and f_2 separately, while the temperature limits of the cycle T_a and T_e were kept constant.

Fig. 4. Cycle in the L, T plane of an oriented fibre having at 23°C a section of 1.02 mm², length 50 mm, run bcde under force $f_2 = 100$ g; run fgha under force $f_1 = 50$ g
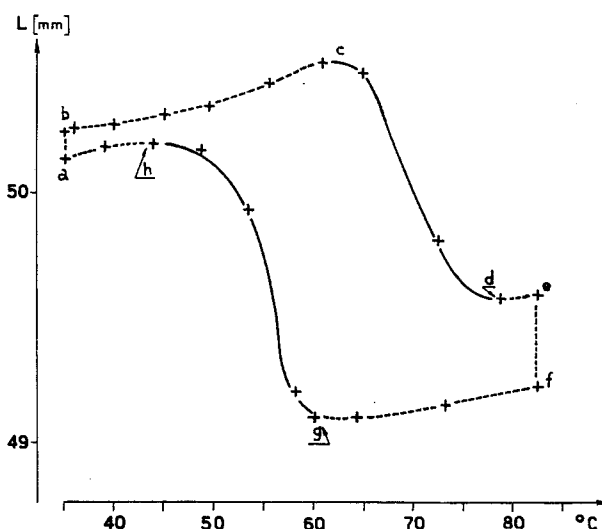
Fig. 3. Curve length (L) temperature (T) of an oriented fibre having section of 0.78 mm² at 23°C, loaded with a constant load of 83 g. a—increasing temperatures; b—decreasing temperatures

Fig. 6 shows the results obtained from measurements done on a test-piece that, at 23°C, has useful length of 50 mm, section of 1·02 mm², and mass of 51 mmg, by operating within the temperature limits $T_a = 35°C$ and $T_e = 82°C$, at constant force f_1 (50 g) and f_2 different from cycle to cycle (75, 100, 125 g respectively).

On the axis of the abscissae, the absolute value of the lengths is not reported, but the variations in length with respect to the length L_a of the test-piece which was practically constant for all cycles.

Fig. 7 reports instead the results of measurements done on the same test-piece, by operating within the same limits of temperature, with constant f_2 force (90 g) and by varying force f_1. Cycles were performed by applying force $f_1 = 75, 60, 40, 30, 20, 10$ g. Also in this case on the axis of the abscissae, the absolute values of lengths are not reported, but only the variations in length with respect to length L_b of the test-piece, which was practically constant for all cycles. The data reported in Figs. 6 and 7 represent the steady-state values of ΔL, which in general have been reached (once the variation of the applied forces f_1 or f_2 had occurred) after 4–5 cycles.

Discussion of Results

By applying the principle of superimposition of the effects, we can conclude that every isodyne variation in length ΔL (that is $L_b–L_e$ or $L_a–L_t$), which is read on the horizontal lines (or segments) in diagram fL of Figs. 6 and 7, is the sum of the variations in length ΔL_s due to the phase transition and ΔL_t due to thermal expansions of the test-piece occurring on heating (or cooling).

Assuming that the above principle is valid, thermal expansions ΔL_t do not depend substantially on the applied force; therefore, when comparing cycles carried out under different forces, the differences that may be observed among total ΔL (at constant force) must be attributed to different values of the ΔL_s contributions. ΔL_s is a function of applied force; as demonstrated by us on theoretical and experimental grounds in previous papers[5], the absolute value of ΔL_s decreases in real and well oriented fibres with increasing the applied force. This is an agreement with that fores $\mathcal{S}$ n for an ideal fibre.

The following correlation allows to refer to actual length variation ΔL_s due to the phase transition of a real sample to the $\Delta L°_s$ one, which should be obtained at zero force, were the sample characterised by 100 per cent of orientation and of crystallinity:

$$\Delta L_s = \chi \Delta L°_s + \varphi$$

where χ is a numerical factor which allows the percentages of orientation and of crystallinity of the real sample, and φ is the additional deformation undergone by the fibre when transition occurs under force f instead of force zero. The expression of φ is fairly simple[6] in the case of the ideal fibre model ($\chi = 1$): in this case we demonstrated that φ is a function of the applied force, of the lengths and of the EA products (elastic modulus for the cross section) assumed by the test-piece both when in phase I and in phase II. In the real case φ becomes a complicated function of χ, even because the EA products become functions of χ. This is demonstrated, e.g. from Fig. 7, which shows that isothermal tensile runs, loading or unloadings (ab and ef) are characterised by a slope that depends on the difference $f_2–f_1$ of forces, which were applied in the cycle: with a constant f_2, the slope is generally lower when f_1 is lower. This is particularly evident in the case of

phase II (ef segments). As the slope is proportional to the EA product (by admitting that the Hooke law is valid), it is found that the fibre is less stiff for lower f_1 forces (f_2 being constant).

This might be related with the existence of a less ordered arrangement of the molecules (especially in phase II) under low f_1 forces: clearly, a good orientation is favoured by high forces. This is proved by the results shown in Fig. 6 revealing the very scarce dependence of the slopes of tensile isotherms on the difference of applied forces, in the case where they are fairly high.

Disorientations, once induced, do not permanently remain in the test-piece; in fact, by the experiments of Fig. 7, it is possible to pass subsequently with time from one cycle characterised by a high difference $f_2–f_1$ (with low isodyne ΔL value) to another with low force difference (and higher isodyne ΔL values).

The discrepancy existing, even from a qualitative point of view, between the behaviour of experimental isodyne ΔL of Fig. 7, which is obtained during the run fgha of the cycle, and that foreseen theoretically (5, 6) for crystalline ideal fibres, which should increase with decreasing the applied force, can also be justified on the basis of the dependence of factor χ on the applied forces.

In Fig. 8 we indicate the work obtained per cycle, which was calculated on the basis of formula (1) and of the experimental data illustrated in Figs. 6 and 7 valid for the real fibre described above, vs. the difference Δf between f_2 and f_1 forces. In the case of the data in Fig. 7, the work does not always increase with Δf; this is a consequence of the decrease of ΔL (along the isodynes) when increasing the difference of the applied forces.

The energy yield η of the cycle run from a test-piece having mass m, specific heats (at const. p.) C^I and C^{II} (in phase I and in phase II) is expressed by the ratio of the work supplied by the system to the environment, to the heat received, in a cycle:

$$\eta = \cfrac{W}{m\left[\displaystyle\int_{T_a}^{T_c} C^I dT + \Delta H + \int_{T_d}^{T_e} C^{II} dT\right]}$$

where ΔH is the specific variation of enthalpy during transition cd.

The data reported in the literature are not sufficient to obtain an exact evaluation of the number value of the denominator with regard to C^I and C^{II}; in fact, the steric purity of the samples examined by us is far higher than that of the samples examined by other authors[7], who measured, the specific heats. With regard to ΔH, some discrepancies exist among the various authors [3, 7, 8]. Moreover, the dependence of ΔH on the applied force has not been investigated. However, the order of magnitude of η can be evaluated. For instance, by considering the experimental case that

Right:

Fig. 6. Group of cycles performed between $T_a = 35°C$ and $T_e = 82°C$ at constant f_1 and different f_2 on an oriented test piece (length 50 mm, cross section 1·02 mm² at 23°C)

Below:

Fig. 5. Same cycle as in Fig. 4 in the plane force (f), length (L)
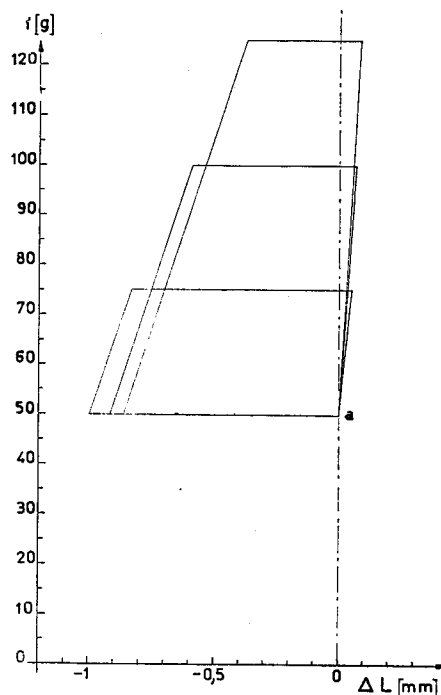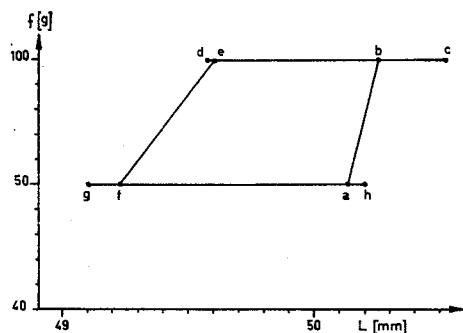
supplied us the highest value of the mechanical work (W = 49 g mm), and the mass of the test-piece (51 mm.g), and if a value of ΔH is assumed equal to 1,000 cal/u.m., the yield results of the order of 1/10,000.

Experimental Application

Although the yield of the cycles is low, the use of an evolving medium consisting of a solid polymer may be of a scientific interest and probably in some cases also of practical interest for the utilisation of thermal sources at temperatures of the order of 80°C, which are commonly little used.

Fig. 9 shows a small thermal motor which was built in the laboratory for the purpose of demonstrating one of the many possible ways of transformation of thermal energy into mechanical work. It consists of a disc of aluminium alloy, with diameter of 22 cm and thickness of 2 mm. The disc can rotate around its axis: on it, in proximity to its circumference, eight supports S are fixed: four on one face of the disc and four on the other, displaced by 45° with respect to those of the first face. On each of them a lever L is mounted which oscillates around a pivot, and which is connected on one side to a contractile fibre (dimensions of the fibre: cross section $0 \cdot 75$ mm²; useful length $9 \cdot 5$ cm) and on the other to a thread t joined to a mass M (20 g) sliding on a fixed C cylinder, fixed to the support and lubricated with graphitised oil.

We used a spring to hinder the approaches of M to support S having a deformation constant of $44 \cdot 10^{-4}$ cm/g. The disc bearing 4 fibres on the front and 4 fibres on the back is balanced by the movement of three balancing masses placed at 120° on one of the two faces of the disc (see photograph of Fig. 10). The disc was interposed between two thermal sources consisting of Osram Siccatherm (375 W) lamps with emission spectrum rich in IR radiations, so that the fibres placed on both faces were suitably heated.

Two screens consisting of expanded polystyrene sheets were placed between the disc and the two thermal sources: they had suitable fissures, which allowed the heating on both faces exclusively of the fibres connected with masses M situated, when viewed from the front of the face of Fig. 9, on the right of the vertical plane passing through the disc centre and orthogonal to it. Thus, on shrinking, a displacement of these masses and therefore of the baricentre of the system takes place as well as a rotation (in the sense of the arrow of the drawing). The fibres considered, after leaving the heating region, on cooling regain their original length, while other fibres enter into the heating region. With this apparatus it was thus possible to obtain a fairly regular rotation of the disc.

Under our conditions, we measured an average rate of about 2 turns/min. The phenomenon can be repeated for many cycles, provided that (in order to favour orientation) each fibre at room temperature is already under slight pre-tension. This was easily obtained by regulating the initial spring deformation. With time, the fibres underwent phenomena of ageing, thus losing at least in part their contractile properties.

The cycle in the f,L plane run by each test-piece working on the engine differs from that previously studied, because every fibre

is subjected to the resultant of the force weight due to mass M and of the force due to the spring deformation. The value of this resultant varies, the spring deformation being equal, depending on the angular position of support S: it reaches the lowest value in the lower position and the highest in the upper position. It follows that the cycle is run by each test-piece under continuously variable forces, which are higher when transition phase I→ phase II takes place. Thus the cycle yields work.

Experimental Data

Preparation of Polymer· Trans-1,4 polybutadiene having a steric purity over 99 per cent was prepared by polymerising the monomer at room temperature for 70 hours, using VCl_3 and $Al(C_2H_5)_3$ in n-heptane (molar ratio Al/V = 7) [1].

The residue to the ether extraction of the purified polymer was compression moulded at 170°C and at a pressure of 50 kg/cm² for 5 min. thus obtaining a sheet.

Preparation of Sample. Test-pieces were successively obtained at 50°C from the sheet with a cutting compression die and were then oriented (immersed in glycerine at 138°C) by applying an axial stress to them, by a tensile machine having clamps that separated at a speed of 9 mm/min.

After reaching a 50 per cent elongation, test-pieces were cooled immediately, keeping them under tension, by removing the thermostating liquid. Then, after cutting the upper and lower ends, test-pieces were examined by X-rays: fairly well oriented fibre spectra have been observed. In general, the test-pieces thus obtained had sections of the order of 1 mm², lengths of 50–110 mm.

Measurement of the Work· In order to measure the mechanical work that can be obtained in the cycles, we used a two-arm analytical balance, which had been modified by replacing one of the scalepans by a clamp hung by a steel thread to the upper knife. During the runs, the test-piece was fixed between this clamp and a lower fixed clamp.

We used as thermostatting liquid glycerol circulating in a glass jacket in contact with the clamped test-piece so that the temperature could be kept constant at $\pm 0 \cdot 2°C$; the balance was put in equilibrium with the test-piece free. Then after having clamped the test-piece, suitable forces were applied, by putting convenient loads on the scalepan opposite to the test-piece.

Shifts of the upper clamp and therefore variations in length of the test-piece (generally of the order of 1–2 mm) were read with a $0 \cdot 02$ mm accuracy, by observing the horizontal shifts of the lower extremity of the balance index with a Salmoiraghi tacheometer (precision 1/400 of angular centesimal grade).

Conclusions

The above considerations show that production of work from heat can take place through cycles that utilise the contraction due to the polymorphous transformation of an oriented heated fibre of trans-1,4 polybutadiene under a load followed by cooling under a smaller load.

Where the system is thermodynamically reversible, we have demonstrated[6] that the yield would be (for an ideal fibre) of the

f [g]

Left:

Fig. 7. Group of cycles performed at constant f_2 and different f_1 on the fibre used for the experiences of Fig. 6. Same temperature range

Fig. 8. Work obtained in the cycles run by the described test piece calculated by Figs. 6 and 7 against f_2-f_1

W [g.mm]

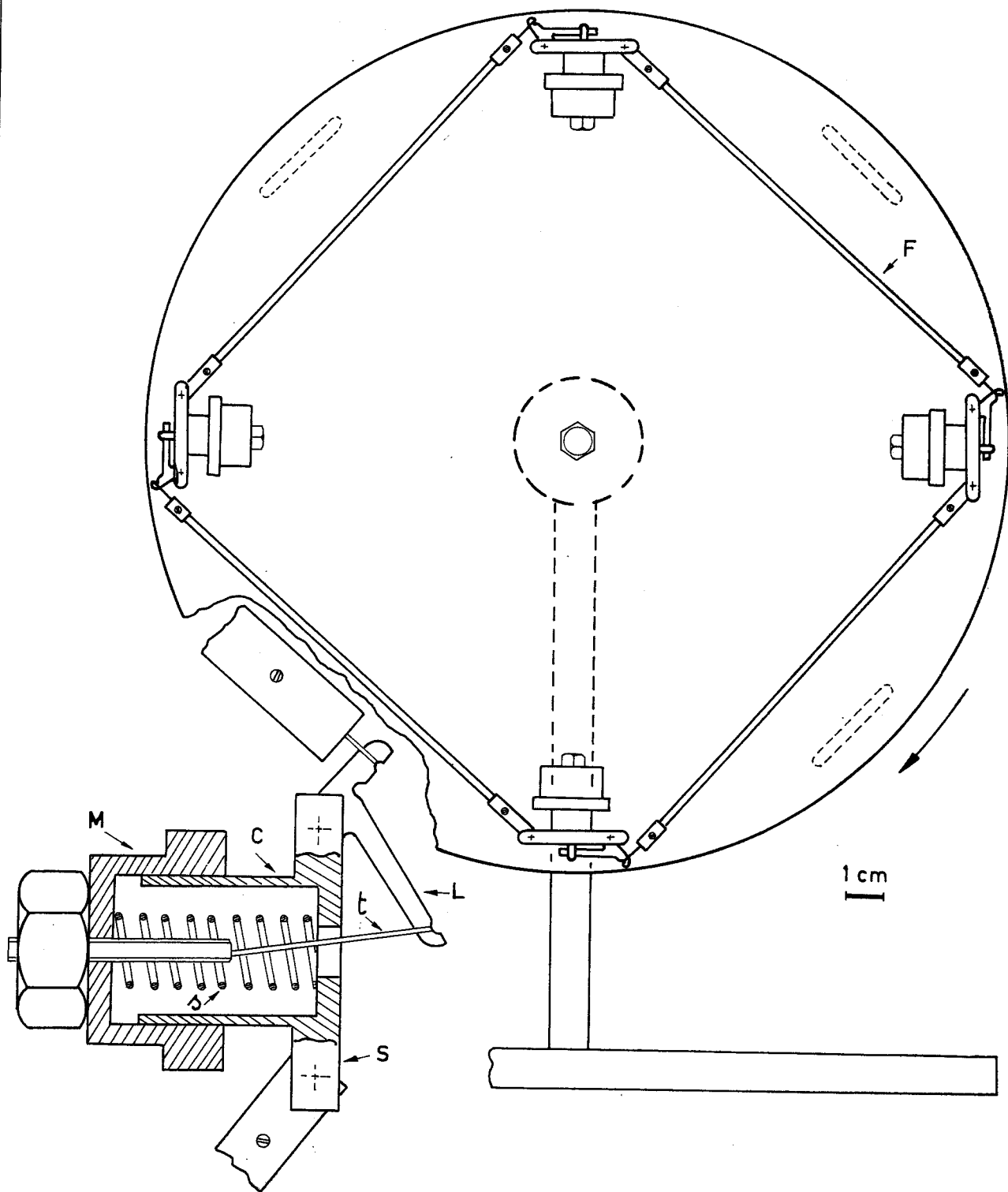$\oplus$ $f_2 = 90$ g.

$+$ $f_1 = 50$ g.

Δf [g]
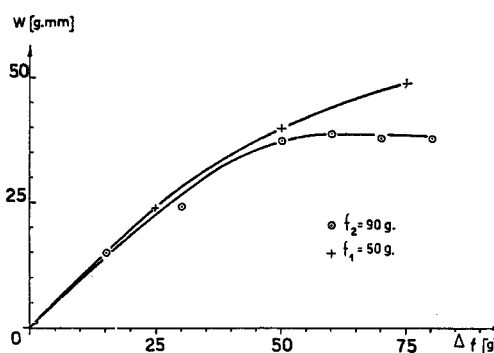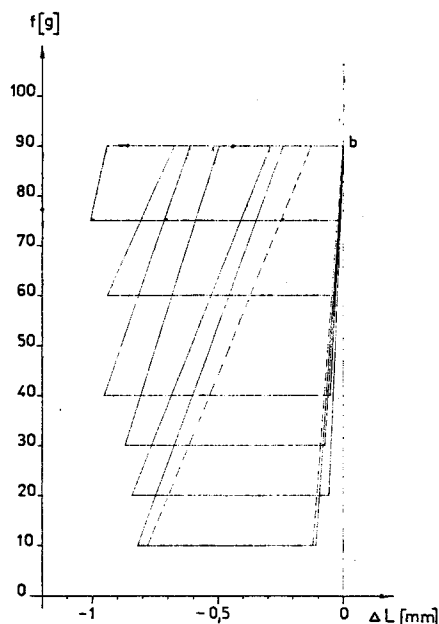
Fig. 9. View of the thermal machine; F = fibre; S = support;
L = oscillating lever; M = mobile mass; C = fixed cylinder;
t = thread; s = spring

same order of magnitude as a Carnot cycle which uses the same interval of temperature. Such a comparison is far more unfavourable in the case of real fibres, in which the practical yield, as we have seen before, is very small.

Notwithstanding this, possibility to produce work was proved by us experimentally also by an experimental mechanical model (the disc). From the quantitative point of view, however, it results that such cycles do not allow practical applications of any importance, owing to the very low energetic yield depending on various reasons:

1. very high slope of the force temperature equilibrium curve and impossibility to reach high forces due to the mechanical properties of the material (breaking or viscous flow);
2. low entity of shrinkage;
3. thermodynamic irreversibility of the cycle, as a thermal drop of at least twenty degrees is needed to obtain spontaneously the inverse transformation under the same load conditions;
4. possible ageing of the unsaturated polymer, for which fibres should be replaced after some time.

Other polymeric materials are being examined: we will refer to them in another paper.

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Right: View of the thermal machine with balancing weights, and of the side view.