Conversion of chemical into mechanical energy by contractile polymers performed by polymer complexation

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A mechanochemical energy conversion system working upon polymer—polymer complexation between poly(methacrylic acid) (PMAA) and poly(ethylene glycol) (PEG) was studied. It was found that among PEGs of various molecular weights used, PEG with molecular weight of 2000 provided the most rapid and significant contraction of crosslinked PMAA membrane loaded 100 times the weight of dry membrane, exhibiting about 2000 g/cm^2 of stress. Increasing and decreasing the molecular weight of PEG from 2000 brought about gradual decrease both in the contraction and stress of the membrane. The work done per contraction per gramme of contractile substance was studied for various loads. It was found that the work done increased linearly with increasing weight of load, reaching 200 g cm.

INTRODUCTION

It is necessary to introduce at least one feedback system to realize the self-regulating mechanochemical system in which the synthetic macromolecules involved are sensitive to change in enviroment, such as pH, ionic species and ionic strength, and temperature, and to make subsequent conformational changes of the polymers. In other words, the system must contain macromolecules possessing chemically active groups or functions sensitive to conformational changes at either the local or total macromolecular level.

During the last decade a large number of simple mechanochemical systems were investigated. They include polyelectrolyte fibres which expand and contract upon changing their degree of ionization[1-3]; ion-exchange fibres which change their dimension upon exchanging a monovalent counter-ion to divalent[4,5]; dialuric acid–alloxan redox reaction resulting in dimensional changes of polymer gels[6,7]; some fibrillar proteins, such as collagen, which perform mechanochemically upon interaction with strong salt solution[8,9]; polymers containing spiropyran groups which contract and dilate by lighting on-off owing to the *cis–trans* photo-isomerization[10,11].

Recently we have proposed a novel model of the mechanochemical system which works by polymer–polymer complexation between complementary polymers[12,13]. The dilations and contractions of our system were based on the drastic conformational changes of a three-dimensional network consisting of poly(methacrylic acid) (PMAA) due to thermoreversible complexation with poly(ethylene glycol) (PEG). Thus, it has been demonstrated that PEG of molecular weight 2000 could contract and dilate the PMAA membrane loaded 100 times the weight of dry membrane by over 90% of its length by repeated change in temperature. The results were explained by the formation of thermoreversible polymer complexes at the surface of the membrane for which a small temperature gradient was the driving force.

In this paper, we report detailed experimental results of mechanochemical behaviour of PMAA membrane by addition of PEG. The effects of chain length of PEG not only on the dimensional changes of the membrane, but on the contraction force at constant dimensions of the membrane (isometric contraction) are presented.

EXPERIMENTAL

Materials

PMAA membranes with a three-dimensional network were prepared by casting aqueous solutions of PMAA (molecular weight 150 000 or 1 090 000) on a glass plate. The procedures were identical to those described previously[12,13], i.e., cast on a glass plate with 3.3 g/100 ml aqueous PMAA solution containing a small amount of glycerol, followed by heating for 24 h at 120°C unless mentioned.

PEG of various molecular weights were of commercial origin and used without further purification.

Measurement of mechanochemical reactions

Mechanochemical measurement of PMAA membrane was carried out in a similar manner to that described previously[13], i.e., a strip of PMAA membrane, 10 mm wide and 20 mm long, of dry weight 4–6 mg was loaded with a prescribed amount at the lower end and was suspended over 69 ml of water. A 1 ml portion of aqueous PEG solution(1.05 unit mol/l) was then added to the embedding fluid and a change in length was measured using a cathetometer in the case of isotonic contraction. In case of isometric measurement, instead of attaching a load, the lower end of the membrane was hooked to the bottom of the cell and the change in equilibrated internal stress caused by addition of PEG was measured. The
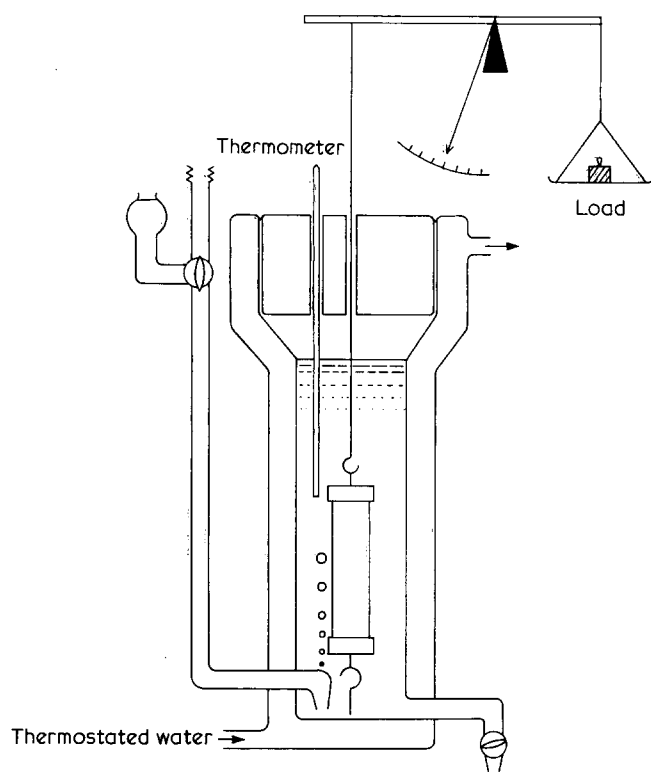
between the two membranes. Although these membranes were prepared in the same manner, the increased viscosity of the casting solution prepared from PMAA molecular weight of 1 090 000 somehow resulted in a decreased pliability, presumably due to the higher crosslinking of the membrane. In fact, the membrane prepared from PMAA molecular weight of 1 090 000 swells 20–30% less of its length by immersing in the water than the membrane prepared from PMAA molecular weight of 150 000.
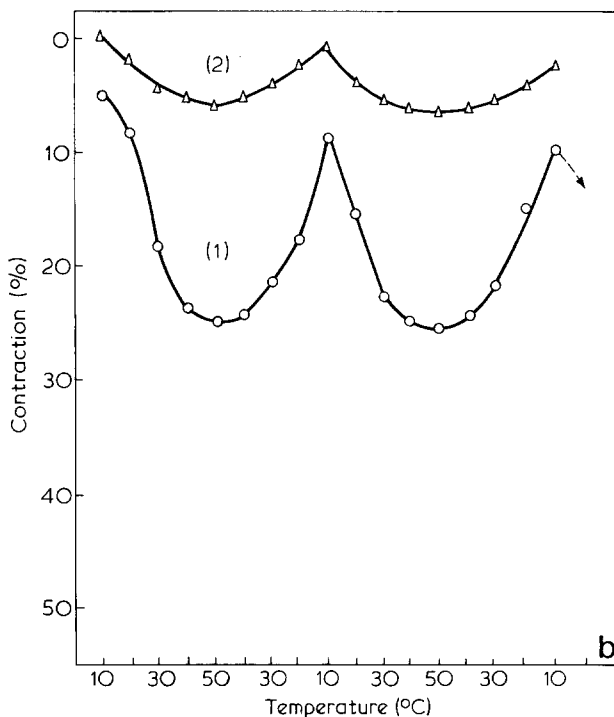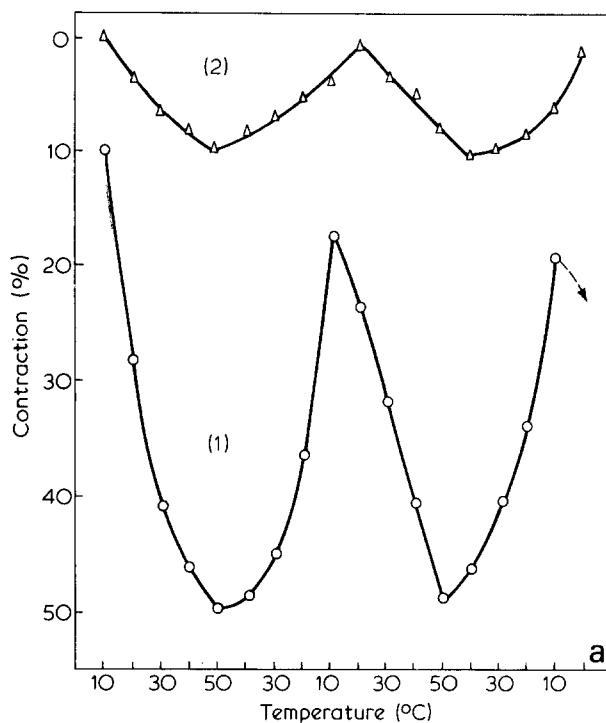

Figure 1 Apparatus for the mechanochemical reaction (used for the measurement of stress of PMAA membrane)

apparatus used for isometric experiment is shown in *Figure* 1.

RESULTS AND DISCUSSION

Results of isotonic contraction and dilation of PMAA membranes, 0.3 mm thick (dry state) prepared from PMAA of molecular weight 150 000 and 1 090 000 are shown in *Figure* 2 as a function of temperature. As shown in the Figure, PMAA membranes exhibit pronounced contraction in the presence of a small amount of PEG (mol. wt. 2000) which by decreasing temperature returned to values very near the starting points. A reference was also made when the dimensional change was measured in the absence of PEG. The results show that PEG provides evident effect on contraction and that the magnitude of contaction-dilation of the membrane prepared from PMAA molecular weight 150 000 exceeds that of the membrane prepared from PMAA of molecular weight 1 090 000. As discussed in previous papers[14–18] contraction of the membrane with increasing temperature can be associated with the endothermic complexation favoured by rise in temperature due to the hydrophobic interaction between α-methyl groups of PMAA and the ethylene backbone of PEG. It should be noted that the cycle of contraction–dilation could be repeated many times quite reproducibly.

A study was made on the internal stress of the membranes measured at constant length for corresponding systems. The results are given in *Figure* 3. On may note that the membrane prepared from PMAA molecular weight 150 000 exhibits higher stress at corresponding temperatures than the membrane from PMAA molecular weight of 1 090 000. The results in *Figures* 2 and 3 seem to be associated with the different swelling tendencies

Figure 2 Temperature dependences of the contraction—dilation (in % of dry membrane) of PMAA membrane in the presence (1) and absence (2) of PEG with mol. wt of 2000; load, 500 mg; (a) membrane prepared from PMAA mol. wt 15 x 10⁴; (b) membrane prepared from PMAA mol. wt 109 x 10⁴
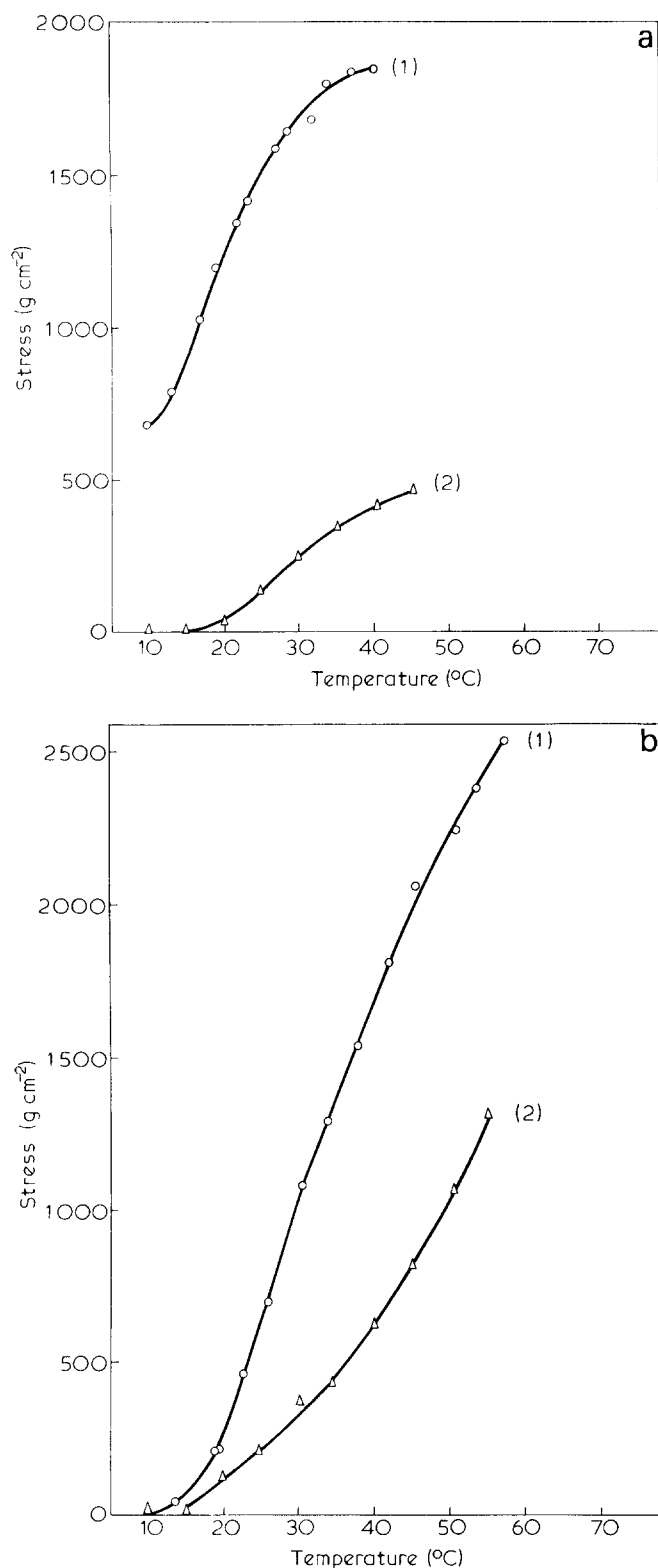
and 83 000, resulted in gradual contractions over a long period of time and their response was rather slow, especially in the initial stage of contraction. On the other hand, PEGs with low molecular weight, such as 1000 or 600, produced the contraction rapidly at first and then leveled off. The same relation of the contraction to the chain length of PEG was also found using PMAA membranes having a smaller swelling property. As shown in *Figure 4b*, although these membranes swell less in water due to the heat-treatment for longer duration in the course of membrane preparation, and therefore, the values of contraction are smaller than those obtained by the membrane in *Figure 4a*. The qualitative features are the same as those for highly swollen membranes.

It should be remembered here that PEGs with molecular weight of 1000 or 600 cannot form any conplexes with PMAA and cannot bring about any conformational changes in solution[14-18].

Taking account of the results described above, as well as the experimental fact obtained in an earlier paper[19], in which the contraction and dilation of PMAA membrane upon change in pH in the presence of PEG of molecular weight 1000 or 600 has been demonstrated, it should be mentioned that PEG with molecular weight of 1000 or 600 apparently can form a complex with a three-dimensional network of PMAA, despite its short chain length. This effect, caused by crosslinking of PMAA on
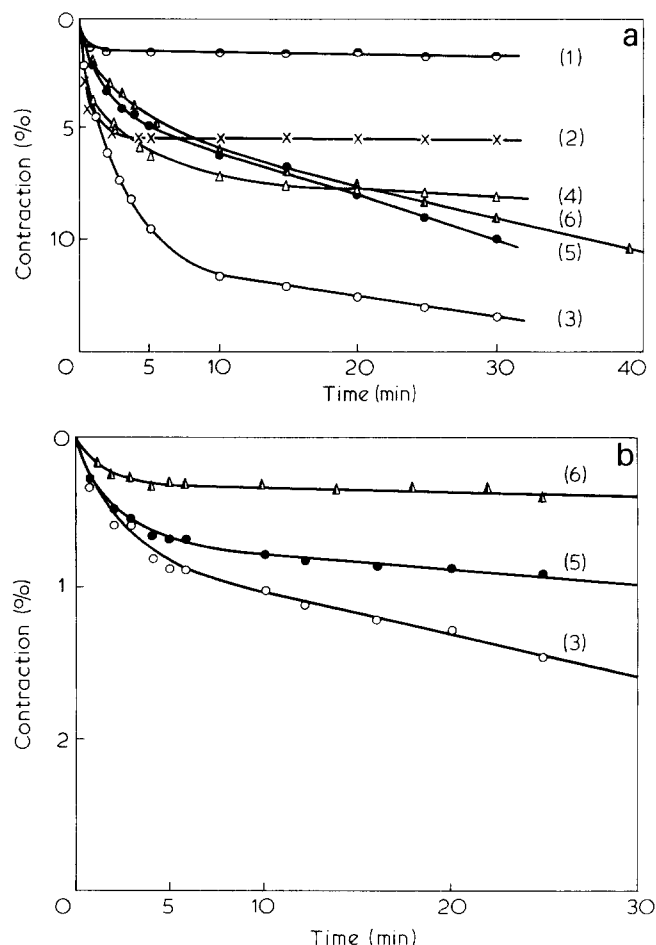

Figure 3 Temperature dependences of stress of PMAA membrane in the presence (1) and absence (2) of PEG with mol. wt. of 2000; (a) membrane prepared from PMAA mol. wt. 15 x 10⁴; (b) membrane prepared from PMAA mol. wt. 109 x 10⁴

Figure 4 Contraction profiles of PMAA membrane by addition of PEG of various mol. wts.; load, 500 mg; temp., 40°C; mol. wt. of PEG: (1) 600; (2) 1000; (3) 2000; (4) 7500; (5) 20 000; (6) 83 000. (a) Membrane prepared from PMAA mol. wt. 109 x 10⁴ by heating at 120°C for 24 h; (b) membrane prepared from PMAA mol. wt. 109 x 10⁴ by heating at 120°C for 48 h

It would be of interest to study the effects of chain length of PEG on the contraction of the membrane. *Figure 4a* shows time–contraction relationship of PMAA membrane observed at 40°C on addition of PEG of various molecular weights. It is seen that the most rapid and significant contraction is obtained by addition of PEG with a molecular weight of 2000. PEGs with molecular weight higher than 2000, such as 7500, 20 000
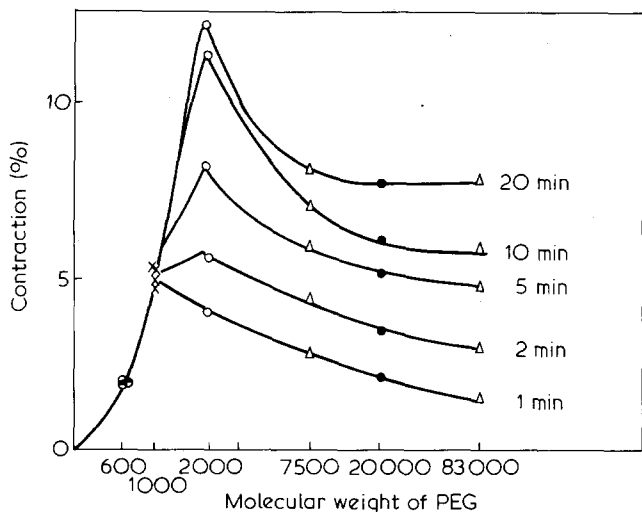
Figure 5 Dependence of contraction of PMAA membrane on mol. wt. of PEG at various intervals after addition of PEG, Experimental conditions are identical to those described in *Figure 4*
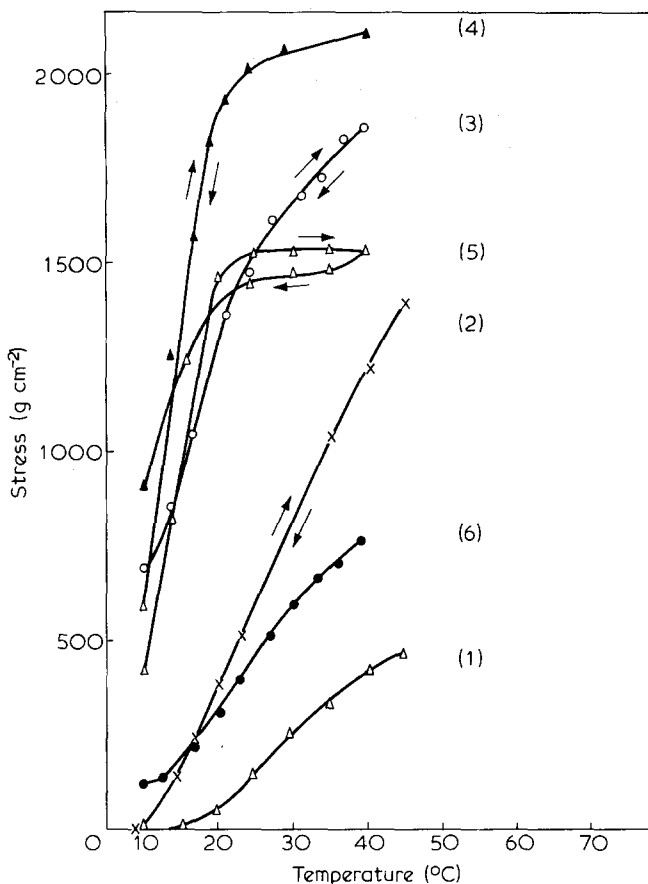

Figure 6 Temperature dependences of stress of PMAA membrane in the presence (2–6) and absence (1) of PEG; membrane was prepared from PMAA mol. wt. 15 x 10^4. Mol. wt. of PEG: (2) 1000; (3) 2000; (4) 3000; (5) 7500; (6) 20 000

of molecular weight of 2000 or higher keep the contraction over a long period of time, whereas in PEG solution of low molecular weight they do not.

It is also seen that PEG with molecular weight of 2000 provides the best response from the viewpoint of its magnitude and velocity among all PEGs applied.

A mechanism of the described effect of PEGs of various molecular weights is not fully understood, however, in view of the preliminary nature of the mechanochemical reaction, the speculated penetration process of PEG through the swollen network of the membrane must be considered, because the results obtained could be associated with the mobility of PEG in the PMAA membrane. In other words, PEG of low molecular weight could cause a contraction rapidly due to high mobility, but increased molecular weight of PEG resulted in a decreased mobility and gradual contraction. In an earlier paper it has been shown that poly(vinyl pyrrolidone) of molecular weight of 10 000, 40 000, 360 000, poly(vinyl alcohol) of molecular weight of 22 000, and poly(methyl vinyl ether) of molecular weight of 64000 could form a complex with PMAA in solution resulting in a drastic conformational change, but caused no obvious contraction of PMAA membrane[19]. Considering the importance of chemical and steric structures of these polymers for the diffused penetration in the membrane, this result also seems to support the postulated penetration mechanism described.

A similar effect of the chain length was found on the study of isometric measurement. Results are given in *Figure 6* where the equilibrated stress of the membrane caused by addition of PEG was plotted as a function of temperature. Greatest values of internal stress were obtained by PEG having molecular weight of 2000 and 3000; decreasing and increasing molecular weight led to a corresponding decrease in stress. This result for the stress of the membrane was compared with that of isotonic contraction and is given in *Figure 7* in good correlation with that predicted by the results of dimensional changes.

A study was also made on the effect on the contraction

favouring the equilibrium of the complexation, could be explained by the local concentration effect of PEG near the PMAA network or decrease in apparent dissociation constant of PMMA by crosslinking[20].

The time–contraction relationship of the membrane can be understood clearly in *Figure 5*, where degree of contraction at various intervals after addition of PEG was plotted as a function of molecular weight of PEG. It is clear that the membranes embedded in the PEG solutions
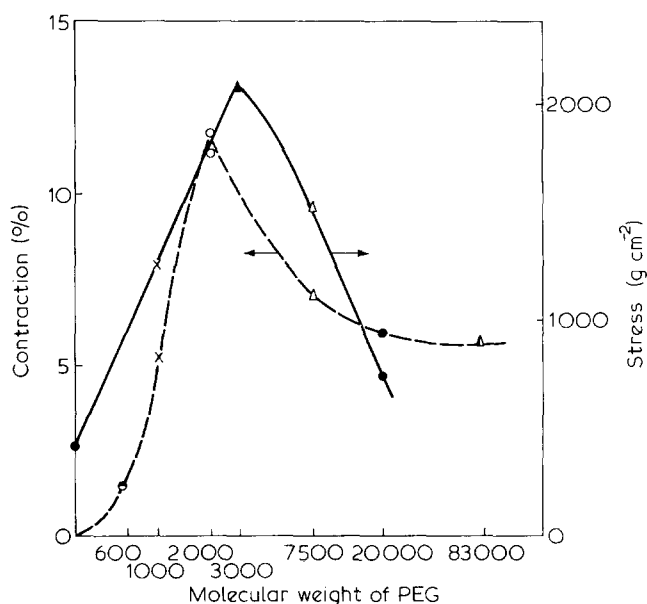

Figure 7 Dependence of contraction (broken line) and stress (solid line) of PMAA membrane on mol. wt. of PEG at 40°C. Contraction is the value measured at 10 min after addition of PEG. Experimental conditions are the same as in *Figure 4* and *Figure 6*
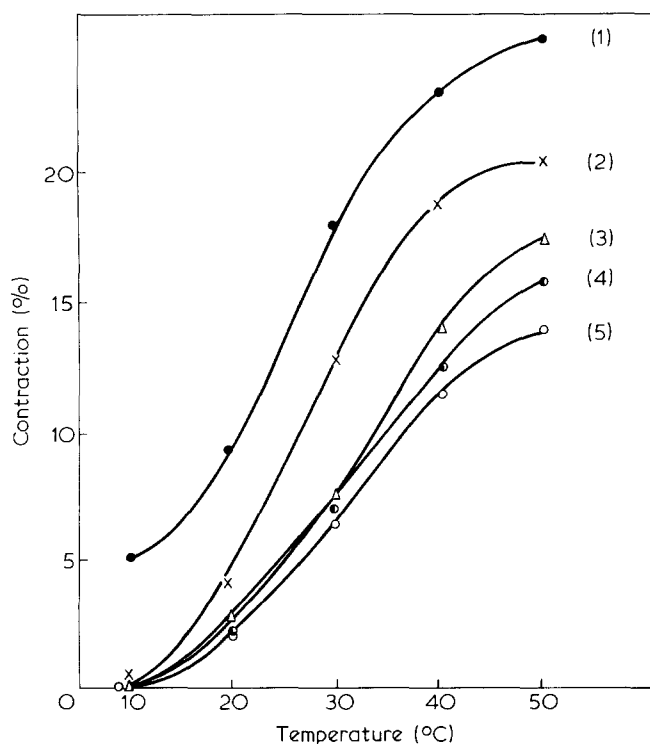
Figure 8 Temperature dependences of contraction of PMAA membrane with various amounts of load; mol. wt. of PEG, 2000; load (mg); (1) 500; (2) 818; (3) 1145; (4) 1700; (5) 4440; membrane was prepared from PMAA mol. wt. 109 x 10⁴
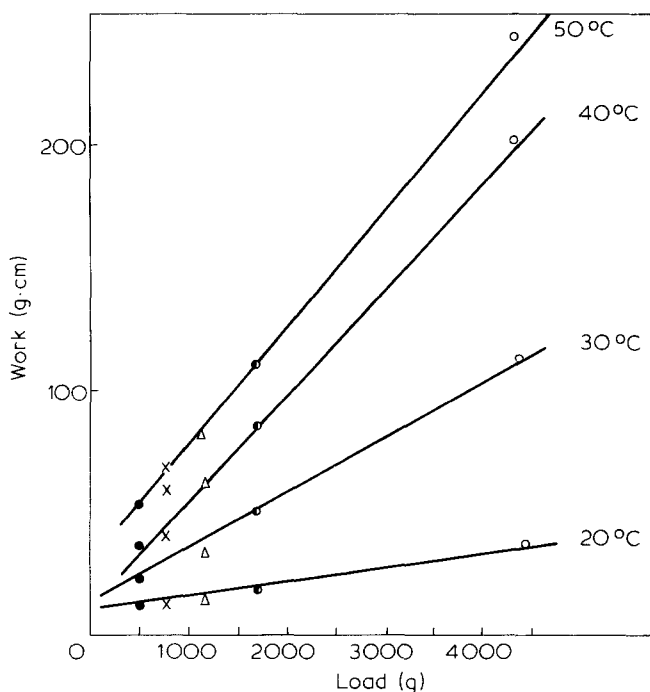

Figure 9 Relationship between work done per contraction per gramme of PMAA membrane and load, Experimental conditions are identical to those described in *Figure 8*

when the weight of load attached at the lower end of the membrane was varied. It is seen from *Figure 8* and 9 that the contraction of the membrane decreases gradually under higher weight of load, although the work done in g cm per contraction per gramme of contractile substance increases almost linearly. The highest value of the load that the PMAA membrane could lift in the presence of PEG of molecular weight 2000 was 4400 mg, which corresponds approximately to 15 kg/cm², exceeding that

of natural muscle[21]. An attempt was also made to lift 5000 mg of weight, however, the membrane could not sustain it and tore off.

Both sets of isotonic and isometric experiments proved that it is possible to realize the contraction and dilation of the synthetic membrane to which a load nearly 1000 times the weight of dry membrane has been attached, exhibiting a few kg/cm² of stress. The work done per contraction per gramme of contractile substance becomes 200 g cm or 5 x 10⁻³ cal. Different from mechanochemical reactions working a change in pH, exchanging counter-ions or redox reactions taking place in the local domain of macromolecules, the present system was operated through polymer–polymer complexation which induces a drastic conformational change at the total macromolecular level. The pronounced effect of this system described above could be in part related to this principle of the reaction.

The origin of the mechanochemical energy of the given system was taken from the free energy of the complexation between PEG and crosslinked PMAA, for which a small temperature gradient is necessary for reversible operation. The quantitative theoretical treatment of these mechanochemical phenomena is based on the same arguments as those used for the explanation of polymer–polymer complexation of dissolved polymers[14–16,21,22]. They include a statistical consideration[14] concerning the enthalpy and entropy changes of the complexation as a function of temperature.

ACKNOWLEDGEMENT

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