phenomenon closely associated with high molecular weight material. This is illustrated by *Table 2* which gives estimates of the viscosities and relaxation times of the polymers that have been used. It is the last two which have given significant peaks at 150°C and it is only Hostalen GUR that also has a sufficiently long relaxation time for the melt to retain a memory to enable the material associated with the 150°C peak to be reconstituted on cooling. Hostalen GUR is not melt-processable by conventional extrusion technology and could not be used in our extrusion experiments. This molecular weight dependence could be a direct reflection of the fact that the formation of microshishkebabs in elongational flow fields is very sensitive to molecular weight. The absence of a 150°C peak in low molecular weight extrudates may be due to the very small proportion of microshishkebabs that form. Alternatively the 150°C peak may be the result of a Zachmann type of phenomenon where high molecular weight molecules can be expected to exacerbate the occurrence of entangled tie molecules and hence produce a greater proportion of superheatable material.

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References

1 Cogswell, F. N. and Jukes, A. W. UK Pat. Appl. 16291/73 (1973)
2 Cogswell, F. N. UK Pat. Appl. 26252/74 (1974)
3 Palmer, R. P. and Cobbold, A. J. *Makromol. Chem.* 1964, **74**, 174
4 Keller, A. and Willmouth, F. M. *J. Macromol. Sci. (B)* 1972, **6**, 493
5 Southern, J. M., Weeks, N., Porter, R. S. and Crystal, R. G. *Makromol. Chem.* 1972, **162**, 19
6 Hellmuth, E. and Wunderlich, B. *J. Appl. Phys.* 1965, **36**, 3039
7 Wunderlich, B. *Thermochim. Acta* 1972, **4**, 175
8 Pennings, A. J. and Kiel, A. M. *Kolloid-Z* 1965, **205**, 160
9 Pennings, A. J. and van der Mark, J. M. A. *Rheol. Acta* 1971, **10**, 174
10 Zachmann, H. G. *Kolloid-Z.* 1967, **216–217**, 180
11 Ferry, J. D. 'Viscoelastic Properties of Polymers', 2nd Edn, Wiley, New York, p 60

Unusual thermal energy transduction by means of a composite membrane system

Transport phenomena occurring across membranes separating two solutions of identical composition, kept at two different temperatures, have already been studied, and they are known as thermo-osmotic effects[1–5]. The temperature difference between the two semicelles of constant volume, separated by a membrane, causes a flow of matter which is called 'thermo-osmotic flow'. At the steady state a pressure difference between the two semicelles, called 'thermo-osmotic pressure', is established. Coupled to the flow of matter is a heat flow.

For a phenomenological description of such a non-isothermal system the thermodynamics of the irreversible processes[6,7] can be utilized.

The purpose of this Letter is to illustrate the experimental results obtained if a 'composite membrane' system is utilized instead of a simple cellulose membrane[11]. Our experimental set up is schematically shown in *Figure 1*. Two thermostatically controlled reservoirs R1 and R2, containing the same pure solvent, water, are separated by a chamber LM ('liquid membrane') filled up with an aqueous solution of poly(ethylene oxide) (PEO) having an average molecular weight of 20 000. The chamber LM is a plexiglass cylinder 4 mm thick, with an inner diameter of 30 mm, closed on the lower and upper sides by means of two pure cellulose dialysis membranes m_1 and m_2 (supplied by A. H. Thomas Co.), impermeable to the PEO.

If a temperature difference, measured by copper–constantan thermocouples placed on m_1 and m_2, is applied on the two sides of the composite membrane, a pressure difference is established as the steady state is reached. The pressure π^* on the hot side of our system was measured with a Bell and Howell pressure transducer, and it is plotted as a function of the PEO concentration inside the liquid membrane in *Figure 2*. In *Figure 3* is shown the dependence of π^* on the temperature difference applied to the composite membrane.

The more relevant points in these data are the values of the measured pressures, which are much higher than those previously obtained in thermo-osmosis experiments carried out on single membranes. In fact, a more than 300 fold amplification of the thermo-osmotic effect is now reached, as compared to the data quoted by Rastogi[5] and by Haase[8].

In order to account for the unusual pressures measured, the osmotic gradient established at the steady state within the 'liquid membrane', as a result of thermal diffusion effects, must be considered.

Such a kind of membrane can be

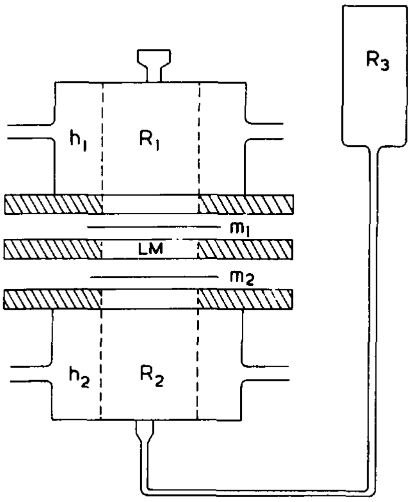

Figure 1 Experimental apparatus: R_1, R_2, R_3, solvent reservoirs; h_1, h_2, heating jackets; m_1, m_2, cellulose membranes; LM, plexiglass chamber containing the polymer solution

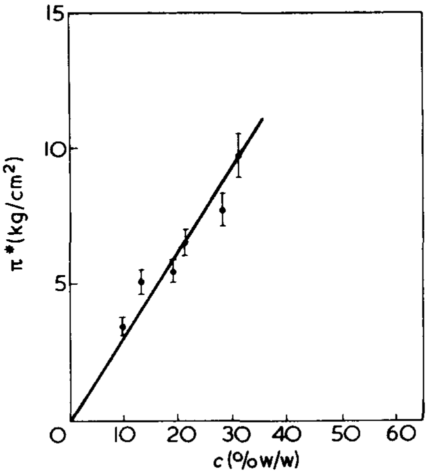

Figure 2 Dependence of the pseudo-thermo-osmotic pressure π^* upon the PEO concentration c inside the liquid membrane LM (ΔT = 25.0°C; T_m = 44.0°C)

regarded as a 'dissymmetrical membrane', following the Liquori's model[9] In our case, the composite membrane we have studied is dissymmetrical with respect to the PEO concentration, the dissymmetry arising at the expense of a driving force which is the temperature gradient.

It is interesting to note that the unusual amplitude of the effects reported in this Letter are caused by small temperature differences. The composite membrane system could therefore be regarded as a possible device to transduce waste thermal energy into mechanical work.

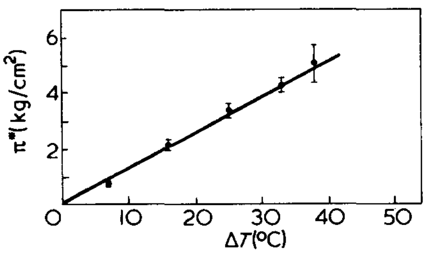

Figure 3 Dependence of the pseudothermo-osmotic pressure π^* upon the temperature difference ΔT applied to the composite membrane (c = 10%, T_m = 44.0°C)

A more detailed investigation on the 'pseudothermo-osmotic effects' across composite membranes will be discussed in a forthcoming paper[10].

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References

1 Haase, R. *Z. Phys. Chem.* 1959, **21**, 244
2 Haase, R. and Steinert, C. *Z. Phys. Chem.* 1959, **21**, 270
3 Carr, C. W. and Sollner, K. *J. Electrochem. Soc.* 1962, **109**, 616
4 Rastogi, R. P., Blokhra, R. L. and Agarwal, R. K. *Trans. Faraday Soc.* 1964, **60**, 1386
5 Rastogi, R. P. and Singh, K. *Trans. Faraday Soc.* 1966, **62**, 1754
6 Prigogine, I. 'Thermodynamics of Irreversible Processes', Interscience, London, 1967
7 De Groot, S. R. and Mazur, P. 'Non-Equilibrium Thermodynamics', North-Holland, Amsterdam, 1969
8 Haase, R. and De Greiff, H. J. *Z. Phys. Chem.* 1965, **44**, 301
9 Liquori, A. M., Pispisa, B. and Acampora, G. *Ric. Sci.* 1969, **58**, 308
10 D'Ilario, L. and Canella, M. *Polym. J.* in press
11 D'Ilario, L. and Canella, M. Ital. Pat. Appln 23557 A/73 (1973)