Other derivatives gave different conversions; the 4,4′-DMBA showed an especially small yield. The amount of product formed varied also with the medium. In *Figure 16* we exhibit a simple configuration coordinate diagram where the mode involved is the reaction coordinate. In the original paper

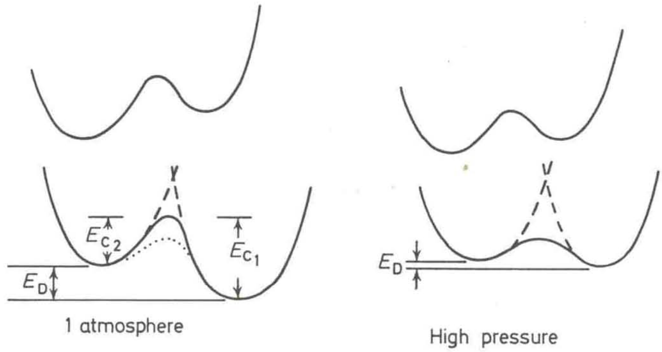

Figure 16. Configuration coordinate diagram for conversion between A and B forms

calculations using equation (1) demonstrate that the thermal process is directly from the A ground state to the B ground state to the B ground state; i.e. no thermal occupation of the excited A state is involved. In the steady state

$$(1 - x)\exp(-E_{c_1}/kT) = x\exp(-E_{c_2}/kT) \tag{2}$$

or

$$x = 1/[1 + \exp(E_D/kT)] \tag{3}$$

where x is the fraction converted and E_{c_1}, E_{c_2} and E_D are defined in *Figure 16*. A plot of E_D/kT vs pressure for BA is shown in *Figure 17*. If equilibrium has been reached, one can calculate the increase in yield upon raising the temperature, using E_D evaluated from room temperature data. As shown in

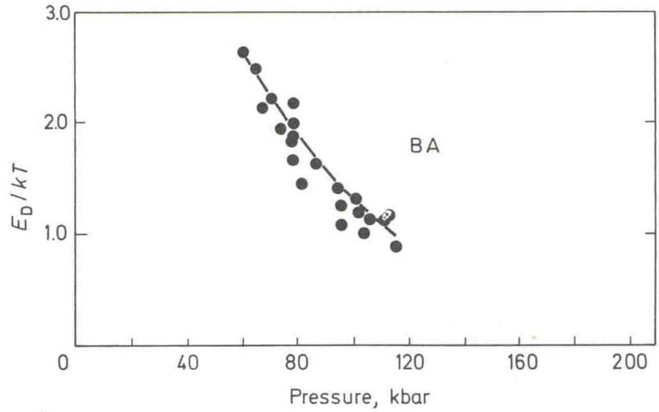

Figure 17. E_D/kT ($\Delta G_{AB}/kT$) against pressure: BA in PMMA

the original paper, equilibrium is indeed attained. One can then consider E_D as a free energy difference ΔG_{AB}, and write:

$$\partial \ln K/\partial p = -\partial \Delta G_{AB}/\partial p = -\Delta \overline{V}_{AB}/kT \quad (4)$$

where $\Delta \overline{V}_{AB}$ is the difference in partial molar volumes between the two states. Typical values appear in *Table 2*. The volume of the B state is less than that of the A state, but its compressibility is less also, so that at sufficiently high pressure they should attain the same volume. $\Delta \overline{V}_{AB}$ for 4,4′-DMB is noticeably smaller than that for the other derivatives. This is not surprising in view of its different conformation, but it is of interest to have a quantitative measure.

The difference in behaviour between BA in PMMA and in PS is illustrated in *Figure 18*, where E_D/kT ($\Delta G_{AB}/kT$) is plotted against ρ/ρ_0. The plots

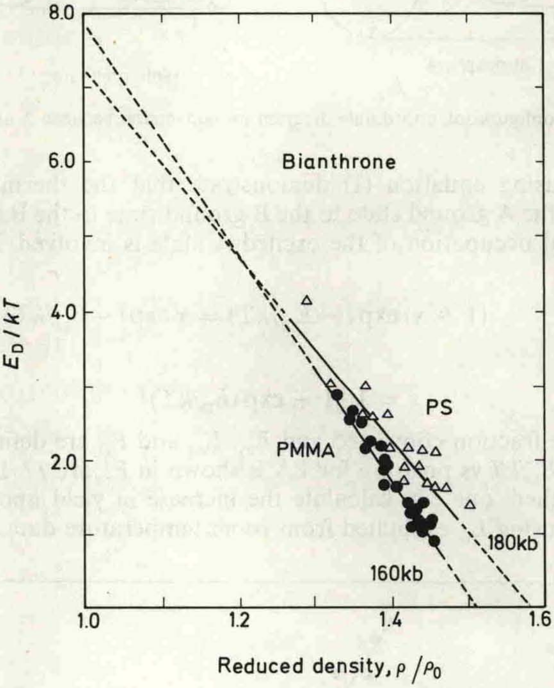

Figure 18. E_D/kT ($\Delta G_{AB}/kT$) against ρ/ρ_0: BA in PMMA and in PS

appear linear although there is considerable scatter, and the range is short, so this point should not be overemphasized.

Qualitatively one associates the decrease in E_D with increasing density with a stronger attractive interaction of the B state with the medium than that for the A state. This could be associated with a larger dipole moment and/or polarizability for the A state. While either state apparently has a permanent dipole moment, the electronic states of the two forms apparently differ enough to allow quite different polarizabilities. It may be relevant