Polymer Vol. 37 No. 20, pp. 4629-4631, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00 + 0.00

S0032-3861(96)00323-0

polymer communications

A convenient n.m.r. method for the measurement of Lewis acidity at boron centres: correlation of reaction rates of Lewis acid initiated epoxide polymerizations with Lewis acidity

Michael A. Beckett* and Gary C. Strickland
Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK

and John R. Holland and K. Sukumar Varma
Pilkington Group Research, Pilkington Technology, Lathom, Lancashire L40 5UF, UK
(Received 21 February 1996)

The reaction rates from viscosity measurements of Lewis acid catalysed epoxide (oxirane) polymerizations have been correlated with Gutmann's Acceptor Number (AN) scale derived from measurement of ^{31}P n.m.r. chemical shifts of Et$_3$PO (TPO) dissolved in the boron-containing Lewis acid. Copyright © 1996 Elsevier Science Ltd.

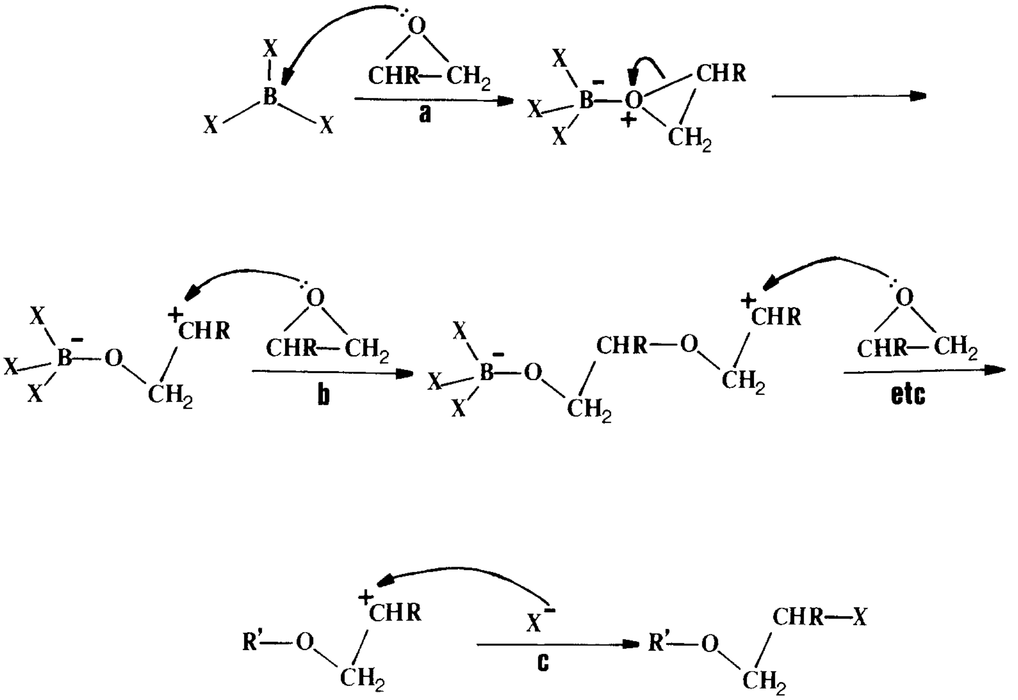
(Keywords: boron; Lewis acidity; n.m.r.)

The polymerization of epoxy resins is usually achieved by addition of an appropriate curing agent such as an amine or an anhydride[1]. Boron-containing Lewis acids, e.g. BF$_3$, (MeO)$_3$B$_3$O$_3$, serve well in this function, and have also been used as curing agents for the polymerization of epoxide (oxirane) monomers[1,2]. The reaction between the boron-based Lewis acid and the oxygen of the oxirane group of the monomer has been shown to be the initiation step leading to polymerization giving the polyether macromolecules. The reaction proceeds via nucleophilic attack by the oxirane oxygen on the electron deficient boron-centre giving rise to the ring-opening and formation of a carbocation which propogates the reaction by reacting with a neighbouring oxirane oxygen (*Scheme 1*). Hence, the Lewis acidity of the boron atom is crucial to its potential as a polymerization initiator and to the commercial utility of such compounds. The polymerization can be modelled by using 1,2-epoxy-3-phenoxy propane (phenylglycidyl either, PGE) as the epoxide monomer and the effectiveness of various curing agents can be assessed from viscosity measurements made over a specific timespan. Data for a selected range of curing agents, viz. (Me$_2$N)$_3$B, (EtO)$_3$B, (MeO)$_3$B, (^{n}BuO)$_3$B$_3$O$_3$, (MeO)$_3$B$_3$O$_3$, and BF$_3\cdot$OEt$_2$ are given in *Table 1*. The rate of polymerization is dependent upon the Lewis acidity at the boron centre with stronger Lewis acids producing faster cure. Thus, if the Lewis acidity of a particular compound could be determined then a useful estimate of its ability to act as a curing agent for epoxy resins should follow.

Several methods have been used to measure the relative Lewis acidity of boron compounds, e.g. dipole moments of Me$_3$N and pyridine (py) adducts[3], heats of reaction in solution of py and nitrobenzene adducts[4], and i.r. spectroscopy[5–7]. In particular, Lappert[5] has prepared BX$_3$L adducts (X = F, Cl, Br; L = ethyl acetate) and used the decrease of the ν(CO) vibrational frequency of the ethyl acetate ligand upon coordination as a measure of Lewis acidity at boron. These $\Delta\nu$(CO) shifts were found to be qualitatively in agreement with their condensed phase heats of formation[8]. Drago and co-workers[9] have found a linear correlation between the gas-phase heats of formation ΔH_f of ethyl acetate adducts and Lappert's $\Delta\nu$(CO) values[5]. Thus, the i.r. method gives a reliable estimate of the Lewis acidity but it has the disadvantage that it requires the synthesis and subsequent i.r. measurements on the isolated adduct. N.m.r. spectroscopy might be considered an ideal analytical tool for measuring Lewis acidity in boron compounds. Unfortunately, the upfield ^{11}B n.m.r. shifts which are observed upon coordination of a Lewis base are variable and often broadened due to chemical exchange, and so do not give useful information on the Lewis acidity of the boron centre[10]. Gutmann and co-workers[11,12] have described a quantitative parameter (Acceptor Number, AN) derived from the ^{31}P n.m.r. shifts produced in triethylphosphine oxide (TPO) by electrophilic solvent actions which lead to deshielding of the phosphorus atoms by inductive effects involving electron donation from oxygen to the solvent. Gutmann's solvent scale has arbitary fixed points of hexane (AN = 0) and SbCl$_5$ (AN = 100) calculated from observed chemical shifts extrapolated to infinite dilution and corrected for differences in volume susceptibilities of the solvents under analysis[11]. In general the AN number depends upon how well the heteroatom bound to boron competes against the oxygen donor atom of the TPO for the boron acceptor orbital. We report here that a simplified procedure in which the TPO (*ca.* 50 mg) when dissolved in the boron-containing liquid (0.5 ml) in a 5 mm OD n.m.r. tube centred in a 10 mm OD n.m.r. tube filled with 2 ml of CDCl$_3$ for use as a lock, gave AN values in reasonable agreement (within 5 percentage points) with values obtained by Gutmann. A comparison of our data with Gutmann's for a selected range of

---

* To whom correspondence should be addressed.



Scheme 1 Role of BX_3 in epoxide polymerizations (R = $PhOCH_2$– for PGE): (a) formation of a Lewis base–Lewis acid adduct and initiation of polymerization; (b) propagation; (c) termination

Table 1 ^{31}P chemical shifts and acceptor numbers and PGE polymerization rates for selected boron compounds

Compound[a]	$\delta(^{31}P)$[b]	AN[c]	PR[d] (centipoise min^{-1})
$(Me_2N)_3B$	45.1	9.1	$<3.3 \times 10^{-4}$
$(^nBuO)_3B$	46.3	11.8	—
$(EtO)_3B$	48.7	17.1	$<3.3 \times 10^{-4}$
$(MeO)_3B$	51.4[e]	23.1	$<3.3 \times 10^{-4}$
$(^nBuO)_3B_3O_3$	70.3	65.0	1×10^{-2}
$BH^3 \cdot THF$	75.8[f]	>77.1	—
$(MeO)_3B_3O_3$	76.4	78.5	7×10^{-2}
$BF_3 \cdot Et_2O$	80.9	88.5	2.4×10^{5}[g]
BCl_3	88.7	105.7	—
BBr_3	90.3	109.3	—
BI_3	92.9	114.9	—

[a] Boron compounds are neat solvents for TPO unless otherwise stated

[b] Spectra were recored at room temperature (except for BI_3) on a Bruker AC 250 CP/MAS n.m.r. instrument operating at 101.25 MHz

[c] The relationship $AN = (\delta_{(sample)} - 41.0) \times \{100/(86.14 - 41.0)\}$ was used to calculate AN values throughout this publication

[d] Relative initial rate of polymerization of PGE from gradient of viscosity/time measurements of PGE (10 g; 0.0665 mol) with 0.0145 mol (or 0.0145/3 mol for boroxines) added Lewis acid at 50°C

[e] TPO has $\delta(^{31}P)$ of +50.6 ppm when dissolved in a 4.4 M solution of $(MeO)_3B$ in THF. Based on the $(MeO)_3B_3O_3$ calibration data an AN value of 21.8 can be calculated for $(MeO)_3B$

[f] 1.0 M solution in THF

[g] Normalized (obtained at 1/6 concentration of Lewis acid, 40 000 cp min^{-1} from first minute only)

non-boron containing solvents is as follows: solvent, $\delta(^{31}P)$, our AN value, Gutmann's AN value; hexane, +41.0, 0.0, 0.0; THF, +46.8, 12.9, 8.0; EtOH, +57.4, 36.4, 37.1; H_2O, +64.2, 51.4, 54.8; $SbCl_5$, +86.14, 100.0, 100.0. ^{31}P chemical shifts of TPO in a THF/$(MeO)_3B_3O_3$ solution at various $(MeO)_3B_3O_3$ concentrations (mole fractions) were also obtained [conc. (M), mole fraction (%/100), δ (ppm); 0.00, 0.000, 46.8; 0.44, 0.044, 54.4; 2.00, 0.187, 64.5; 4.00, 0.442, 75.6; 5.50, 0.679, 76.4; 8.95. 1.000, 76.4]; at concentrations > 4 M(mole fraction 0.44) the chemical shift was very similar to that obtained for neat (8.95 M) $(MeO)_3B_3O_3$ and at lower concentrations the ^{31}P chemical shift of TPO approaches that observed in neat THF. With the assumption that compounds with similar chemical structures will have similar behaviour in THF solution then a shift approximating to that which we ought to observe as a 'neat liquid' can be estimated from an observed shift at a known mole fraction by use of a calibration curve. This THF solution method would also allow for estimates of AN values of solids to be calculated.

The AN numbers obtained by the simplified Gutmann method (*Table 1*) are in the order generally accepted for Lewis acidity at boron centres ($BH_3 \sim BF_3 < BCl_3 < BBr_3$) obtained by other methods[3–9]. This n.m.r. method gives a qualitative order for weaker Lewis acids as follows: $(Me_2N)_3B < (MeO)_3B < BF_3$ indicative of the strongest B–X π interaction for $(Me_2N)_3B$. The much weaker Lewis acidity of an orthoborate ester (e.g. R = Me; AN = 23.1) when compared to a metaborate ester (R = Me, AN = 78.5) is a probable consequence of their B:O ratios being 1:3 and 1:2, respectively. The AN drops by *ca.* 10–15 on changing R from Me to ^nBu for both the orthoborate $(RO)_3B$ and metaborate $(RO)_3B_3O_3$ esters, and this may be attributable to steric effects. BI_3 was also measured (at 40°C) and its Lewis acidity was higher than that of BBr_3. The calculated AN numbers for the series of boron containing compounds reported in *Table 1* correlate qualitatively with the viscosity measurements and thus enable an estimate, by a simple n.m.r. experiment, to be made of the reactivity of boron-containing Lewis acids with regards to curing epoxy resins, and hence to other important reactions.

References

1 Chen, C. S., Bulkin, B. J. and Pearce, E. M. *J. Appl. Polym. Sci.* 1982, **27**, 1177
2 Lopata, E. S. and Riccitiello, S. R. *J. Appl. Polym. Sci.* 1975, **19**, 1127; 1977, **21**, 91

3 Bax, C. M., Katritzky, A. R. and Sutton, L. E. *J. Chem. Soc.* 1958, 1258

4 Brown, H. C. and Holmes, R. R. *J. Am. Chem. Soc.* 1956, **78**, 2173

5 Lappert, M. F. *J. Chem. Soc.* 1962, 542; 1961, 817

6 Frazer, M. J., Gerrard, W. and Twaites, R. *J. Inorg. Nucl. Chem.* 1963, **25**, 637

7 Shriver, D. F. and Swanson, B. *Inorg. Chem.* 1971, **10**, 1354

8 Lappert, M. F. and Smith, J. K. *J. Chem. Soc.* 1965, 5826

9 Brown, D. G., Drago, R. S. and Bolles, T. F. *J. Am. Chem. Soc.* 1968, **90**, 5706

10 Nöth, H. and Wrackmeyer, B. in 'N.m.r. Basic Principles and Progress', Vol. 14, Springer, Berlin, 1978

11 Mayer, U., Gutmann, V. and Gerger, W. *Monat. Chem.* 1975, **106**, 1235

12 Gutmann, V. *Coord. Chem. Rev.* 1975, **18**, 225.