

Figure 2 Arrhenius plot (A) of copolymerization of benzonitrile and propylene oxide and intrinsic viscosity $[\eta]$ (B) of copolymer vs. polymerization temperature. (PO = 2.96 mol/l; BzN = 2.94 mol/l; $n\text{-BuLi} = 1.6 \times 10^{-1}$ mol/l in THF at 0°, 30°, 80°C for 4 h)

Mechanism of copolymerization of BzN and PO

In order to clarify the mechanism of

the copolymerization of BzN and PO, the homopolymerization of BzN initiated with sodium ethoxide and that of PO by the anionic radical of BzN was studied. Oligomer of BzN was obtained according to equation (1). The anionic radical of BzN obtained by reaction of BzN with metal sodium polymerized PO in THF according to equation (2). The observations show that BzN anion adds to PO and that PO anion reacts with BzN. Sodium tetraphenyldihydrotriazine obtained by the reaction of tetraphenyldihydrotriazine with metal sodium in THF did not polymerize PO.

Since BzN reacts more easily than PO with $n\text{-BuLi}$, the above facts indicate the formation of an alternative

copolymer by the mechanism shown in equation (3).

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^{13}C n.m.r. studies of butadiene-styrene copolymers. A revised assignment

F. Conti

Istituto di Chimica Fisica, Università di Roma, Rome, Italy

and M. Delfini and A. L. Segre

Laboratorio di Chimica e Tecnologia dei Radioelementi, CNR, Padova, Italy
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A recent paper by Huckerby and Ebdon¹ gives a revised assignment of the ^{13}C n.m.r. spectrum of atactic polystyrene using a polymer selectively deuterated on the CH_2 of the backbone. The results reported show, definitively, that, contrary to previous reports in the literature^{2,3}, the signals due to methine carbon atoms are at higher fields than those due to methylenes. Moreover, the methine signal is almost insensitive to steric effects. It should be observed that this type of inversion has already been observed⁴ in the spectrum of 1,2-polybutadiene. However for polystyrene, the correct assignment¹ was not obvious^{5,6}, mainly as a result of the fact that when a styrene unit is interspersed between 1,4-butadiene units, this inversion is not present. As a consequence, in this case, the signal due to methine C atoms, is at lower fields (~ 45.9 ppm from TMS) than the signal due to methylene carbon atoms (~ 35.9 ppm from TMS).

In order to confirm the results reported^{1,5,6}, we have carried out an off-resonance experiment on an atactic polystyrene sample. The results obtained show that the assignment is indeed correct.

On this basis we considered the spectrum of a butadiene-styrene copolymer following the same method as in ref 3. The contributions due to the presence of a phenyl group in α , β and γ positions are: $\alpha = 15.3$ ppm; $\beta = 9.8$ ppm; $\gamma = -2.2$ ppm.

A comparison with the previous assignment shows that only the assignment of the signal lines 6, 12, 15, 16, 20, 29, are different in the case of the random copolymer (sample B, ref 3). Assignments are given in Table 1. The sequence attribution on block copolymers (samples C and D, ref 3) was correct and only an inversion between the assignment of the signals due to the groups CH_2 and CH of the styrene blocks was present. Inspection of the resonance lines: leads to the following conclusions (see Figure 1 and Table 1).

Peak 6 at 32.33 ppm: due to the weak intensity of this signal (partly overlapped on the strong signal at 32.76 ppm) this assignment is a tentative one, probably due to sequences $c\bar{v}\bar{\phi}$ and analogues.

Peak 11 at 35.86 ppm: the original assignment was correct, but probably other sequences might contribute to this peak.

Peak 12 at 37.72 ppm: assigned to

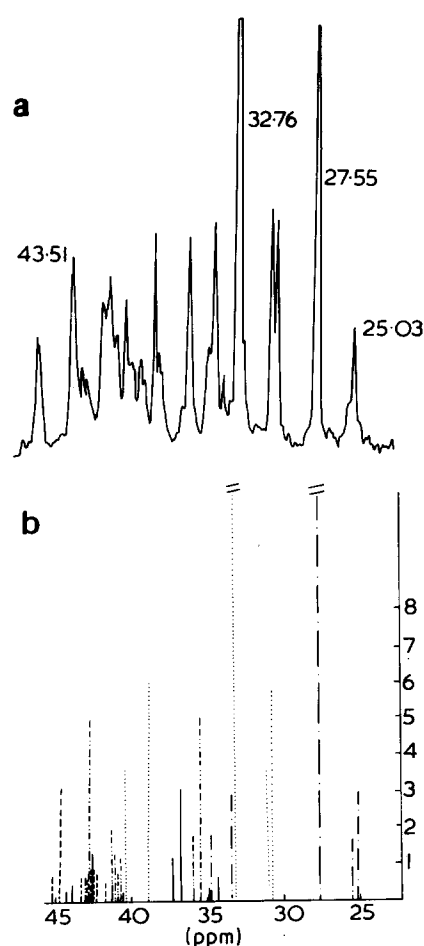


Figure 1 (a) Experimental and (b) calculated spectra of the aliphatic portion of a butadiene-styrene random copolymer., CH_2 butadiene *trans* 1,4; ----, CH_2 butadiene *cis* 1,4; —, CH vinyl; ———, CH_2 vinyl; - · - ·, CH styrene; - - - -, CH_2 styrene. The major multiplicity in the 37–43 ppm range of the experimental spectrum with respect to that calculated is due to configurational effects as also observed in the polystyrene spectrum

