

Figure 2 Arrhenius plot (A) of copolymerization of benzonitrile and propylene oxide and intrinsic viscosity [n] (B) of copolymer vs. polymerization temperature. (PO = 2.96 mol/l; BzN = 2.94 mol/l; n-BuLi = 1.6×10^{-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-BuLi, the above facts indicate the formation of an alternative copolymer by the mechanism shown in .equation (3).

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¹³C n.m.r. studies of butadiene—styrene copolymers. A revised assignment

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A recent paper by Huckerby and Ebdon¹ gives a revised assignment of the ¹³C n.m.r. spectrum of atactic polystyrene using a polymer selectively deuterated on the CH₂ 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 offresonance 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 the groups CH₂ 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 $c \vec{\nabla} \phi$ 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. ..., CH₂ butadiene *trans* 1,4; ------, CH₂ butadiene *cis* 1,4; ------, CH vinyl; ----------------, CH₂ vinyl; ------, CH vinyl; -----------------, CH₂ 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 Table 1

Number of exp.	Exp.	Calc.		
peaks	frequency	frequency	Group	Sequences
1	25.03	25.0	CH ₂	c ε ⊽ (C ₂), Ϋ ε ε (C ₁), t ε ⊽ (C ₂), Ϋ ε t (C ₁), Ϋ ε ⊽ (C ₁), ⊽ ε ⊽ (C ₂), ⊽ ε ⊽ (C ₁ , C ₂), ⊽ ε φ (C ₁), φ ε ⊽ (C ₂), ⊽ ε φ (C ₁), φ ε ⊽ (C ₂)
2	25.38	25.2	CH2	εεφ (C ₂), φεε (C ₁), τεφ (C ₂), φετ (C ₁), ⊽εφ (C ₂), φεν (C ₁), ⊽εφ (C ₂), φεν (C ₁), φεφ (C ₁), φεφ (C ₂). φεφ (C ₁ , C ₂)
3	27.55	27.4	CH ₂	ές ε΄ (C [, C 2], ες ε΄ (C 1, C 2), ες ε΄ (C 1, C 2), ες τν (C 1), ν΄ ες (C 2), ες τν (C 1), ν΄ ες ε΄ (C 2), ες τν (C 1), δ΄ ες (C 2), ες τν (C 2),
4	30.15	30.5	CH ₂	c t v (C2), v t c (C1), t t v (C2), v t t (C1), v t v (C1), v t v (C2), v t v (C2), v t v (C1), c t v (C2), v t f o (C2), v t f
5	30.51	30.7	CH ₂	c τῷ (C ₂), ở τ c (C ₁), τ τ ῷ (C ₂), ǿ τ τ (C ₁), Ϋ τ ῷ (C ₂), ở τ ῦ (C ₁), ῦ τ ῷ (C ₂), ở τ ῦ (C ₁), 후 τ ῷ (C ₁), ῷ τ ῷ (C ₁),
6	32.33	33.1	CH ₂	
7	32.76	32.9 33.3	CH ₂ , CH ₂	<u>c</u> c ⊈ (C ₂), ∇ c c (C ₁), t c ⊽ (C ₁), ∇ c t (C ₁), ∇ c ⊽ (C ₂), ∇ c ⊽ (C ₁), ∇ c ∨ (C ₁ , C ₂), ∇ c φ (C ₁), φ c ∨ (C ₂), ∇ c φ (C ₁),
				φεζν (C ₂), ετε (C ₁ , C ₂), ετε (C ₁ , C ₂), ετε (C ₁ , C ₂) ετζν (C ₁), ζτε (C ₂), ετζν (C ₁), ζτε (C ₂), ετζν (C ₁), ζτε (C ₂), ετζν (C ₁), ζτε (C ₂), εττ (C ₁ , C ₂), ετζν (C ₁), ζντε (C ₂) <u>τζν (C₃), ζτζι (C₂), ετζν (C₁), ψ</u> ξζτ (C ₃), <u>ε</u> τζν (C ₁), ζττ (C ₂)
8	33.65	33.6 34.3	CH ₂ , CH ₂	$\vec{v} \vec{v} \phi, \phi \vec{v} \vec{v}, \phi \vec{v} \phi, \phi \vec{v} \phi, c \phi \vec{v}, \vec{v} \phi c, t \phi \vec{v}, \vec{v} \phi t$
9	34.23	35.3	CH ₂	$\underline{c} \underline{v} c, c \underline{v} c, \underline{c} \underline{v} t, t \underline{v} c, \underline{t} \underline{v} c, c \underline{v} t, \underline{t} \underline{v} t, t \underline{v} t$
10	34.56	35.8	CH ₂	
11	35.86	34.7 36.7 34.8	CH ₂ , CH ₂ , CH ₂	ε ε φ (C ₂), φ ε ε (C ₁), τ ε φ (C ₂), φ ε τ (C ₁), ν ε φ (C ₂), φ ε ν (C ₁), ν ε φ (C ₂), φ ε ν (C ₁), φ ε φ (C ₁), φ ε φ (C ₁ , C ₂), ε φ ε, ε φ ε, τ φ ε, ν φ ν, ν φ ν, φ φ ν, ν φ φ
12	37.72	37.2	CH ₂	vēc, cēv, vēt, tēv, ēdc, cēb, tēb, tēdt
13	37.88	38.8	СН2, СН	c t v (C ₁), v t c (C ₁), t t v (C ₂), v t t (C ₁), v t v (C ₂), v t v (C ₁), v t v (C ₁ , C ₂), v t v (C ₁), v t v (C ₂), v t v (C ₁), v t v (C ₂), v t v (C ₁), v t v (C ₂), v t v (C ₁), v t v (C ₂), v t v (C ₁), v t v (C ₂), v t v (C ₁), v t v (C ₂), v t v (C ₁), v (
14	38.19			
15	38.89			
		38.6 39.0	СН	v v v#, v v v#, ¢ v ¢#, ¢ v ¢#
16	39.05			
17	39.60	40.5	СН	रे <i>रे c #, c रे रे म, t रे र</i> म, t रे रे म
18	39.83			
		40.2	CH2	ट र के (C2), के र ट (C1), र र के (C2), के र र (C1), ⊽ र के (C2), के र ⊽ (C1), ⊽ र के (C2), के र ⊽ (C1), के र के (C2), के र के (C1), के र के (C1, C2)
19	40.09			
20	40.68	40.4 40.6 40.7 40.8	CH. CH. CH. CH	
21	41.14	41.0 41.7	CH. CH-	
22	41.51	41.2 41.2 42.5	CH, CH ₂	c v of v ov c#, t v of ov t#, o v of a v of v o o c#, c o o #, o o o t#, t o o v, v v c, t v v, v v t
23	t 42 15		•	
24	42.62	42 3	сн	
25	42.93	42.5	CHa	
26	43.51	42.9 42.8 43.0 43.4	сн, сн, сн, сн	c v c#, c v c#, c v c#, c v v#, c v v#, c v v#, c v c#, c v c#, t v t#, t v t#, t v v#, o v t#, c v v#, v v c#, c v v#, v v v v
27	† 44.26			
28	45.82	44.5 44.7	CH1. CH	
29 30	45.92 146.22	45.2	СН	$c \phi \overline{v}$ #, $\overline{v} \phi c$ #, $t \phi \overline{v}$ #, $\overline{v} \phi t$ #

tPresent only in block copolymers and due to $\phi \phi \phi$ (CH₂). C₁ is on the left and C₂ is on the right side in triads having a 1,4 butadiene as a central unit. #Tertiary carbon atoms in $\phi \phi \phi$, $\overline{\psi}$. c = cis 1,4 butadiene; c = cis 1,4 butadiene;

V =CHCH₂-	v =CH2CH
CH	cH
	u
CH ₂	CH ₂
$\vec{\phi} = -CH - CH_2$	$\phi = -CH_2 - CH$
φ	φ

a central phenyl surrounded by vinyl and cis or trans units.

Peaks 13-14 at 37.88 and 38.19 ppm: these peaks are due to the effect of vinyl on trans-butadiene, and probably also methines due to the sequences reported in Table 1.

Peaks 15-16 at 38.89 and 39.05 ppm: these are due to short vinyl blocks (methines) as observed in 1,2polybutadiene homopolymers. This assignment is confirmed by offresonance data. The intensity of these peaks shows that in the polymerization process short blocks of $\vec{\nabla} \vec{\nabla} \vec{\nabla}$ type are formed. Thus the polymer is not strictly random. The assignment is also supported by the fact that all the peaks of 1,2-polybutadiene have been observed (see peak 21).

Peak 17 at 39.60 ppm: only part of the assignment (ref 3) was correct, such as that for sequences $\vec{v} \cdot \vec{v} c$ etc. No other units are involved.

Peaks 18-19 at 39.83 ppm and

40.09 ppm: β -effect of a phenyl on a trans-butadiene units. The splitting into two peaks, whereas the calculations predict only one, is probably due to long range effects. The total intensity of the two peaks supports this assignment.

Peak 20 at 40.68 ppm: this peak contains contributions by methines (by off-resonance) of many sequences. This assignment (see Table 1) is tentative.

Peak 24 at 42.62 ppm: phenyl units (methines) interspersed between 1,2and 1,4-butadiene units. The assignment is a tentative one.

Peaks 28-29 at 45.82 ppm and 45.92 ppm: the two peaks are due to methines of phenyl groups interspersed between 1,4-butadiene units. Other sequences (methines) may contribute to these peaks, as shown in Table 1.

With this new assignment, (see Figure 1), the standard error between calculated and experimental frequencies is <1 ppm, which is quite good considering the approximations involved. It should be noted that the calculated intensities, apart from the presence of 1,2-butadiene blocks, show a reasonable agreement which is also in agreement with the low Overhauser effect, as observed by Allerhand and Hailstone⁶.

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