Refractive index of polystyrene at 5461Å in the temperature range 30 to 260K

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A low temperature version of the Abbé refractometer[1] has recently been constructed[2] and used to measure the refractive index of liquid and solid argon at temperatures down to 35K. The reference prism of the refractometer was machined in the workshops of Sussex University from Q. 200.5 cross-linked polystyrene supplied by Polypenco Engineering Plastics, Welwyn Garden City and polished flat to 1 fringe by G. Hole and Son Ltd, Brighton.

A self-calibration of the instrument provided the refractive index of polystyrene at a wavelength of 5461Å over the temperature range 30 to 260K with a maximum experimental uncertainty of 0.001, about 0.06%. The refractive index n was fitted to a polynomial $n = A + BT + CT^2 + DT^3$, where T is the temperature in degrees Kelvin, with the coefficients listed in *Table 1*. Selected values of n are listed in *Table 2*.

Table 1 Polynomial coefficients giving refractive index of polystyrene as a function of temperature with T in degrees kelvin

Coefficients	Variance
$A = 1.6200$	0.60149×10^{-5}
$B = 0.806459 \times 10^{-4}$	0.47040×10^{-8}
$C = -0.126896 \times 10^{-5}$	0.30728×10^{-12}
$D = 0.261742 \times 10^{-8}$	0.17249×10^{-17}

$n = A + BT + CT^2 + DT^3$

Table 2 Refractive index of polystyrene

Temperature, T (K)	Refractive index, n	Temperature, T (K)	Refractive index, n
30	1.6214	160	1.6112
40	1.6214	180	1.6087
60	1.6209	200	1.6063
80	1.6197	220	1.6042
100	1.6180	240	1.6025
120	1.6159	260	1.6012
140	1.6136		

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Copolymerization of benzonitrile and propylene oxide initiated by *n*-butyllithium

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INTRODUCTION

It is known that strong acidic and basic catalysts cause dimerization and trimerization of cyano compounds[1]. Kabanov *et al.*[2] reported that stoichiometric complexes of some nitriles with $TiCl_4$ and BF_3 polymerized through the cyano bond giving a polymer with conjugated bonds in chains. The polymerization of acetonitrile by $ZnCl_2$ was also reported by Oikawa *et al.*[3].

Using sodium methoxide, Johns[4] polymerized succinontrile to *DP*'s of 6–65. On the other hand, Panayotov *et al.*[5] found that the anion radical and dianion of aromatic nitriles was the initiator of the ring opening polymerization of alkylene oxide. The above facts pointed to the possibility of copolymerization of benzonitrile (BzN) and propylene oxide (PO) and in this paper, this reaction was studied using n-butyllithium (n-BuLi) as the anionic initiator.

EXPERIMENTAL

Reagents

Benzonitrile (BzN) and propylene oxide (PO) were distilled over calcium hydride under reduced and atmospheric pressure, respectively, immediately before use. The concentration of commerical n-butyllithium (n-BuLi) used as initiator was determined by Gillman's double titration method[6,7]. THF was refluxed and distilled over sodium. Other solvents were dried and purified by conventional methods.

Copolymerization

The copolymerization was carried out in sealed glass tubes, containing given weights of BzN, PO and THF added in that order. After degassing, the system was cooled in a dry ice–methanol bath, n-BuLi added under nitrogen, the tube degassed, sealed and placed in a thermostat.

The reaction was stopped by adding water and the oil layer was extracted with benzene. The copolymer was precipitated by adding n-hexane, filtered, washed with n-hexane and dried under vacuum to a constant weight.

The copolymer was characterized by elementary analysis and infra-red spectra.

Reaction of propylene oxide with the anionic radical of benzonitrile

The anionic radical of BzN was obtained by reaction with metal sodium in THF at 30°C for 30 min. The polymerization of PO was carried out in THF by heating at 30°C for 4 h.

The poly(propylene oxide) was confirmed by i.r. and elementary analysis.

Reaction of BzN with sodium ethoxide

The oligomerization of BzN was carried out by using sodium ethoxide as catalyst in THF at 30°C for 3 h and the product was confirmed by i.r. and elementary analysis.

Measurements

The infra-red spectrum of the copolymer was measured as KBr pellets

Table 1 Copolymerization of benzonitrile (BzN) and propylene oxide (PO) with n-butyllithium (n-BuLi) in THF (n-BuLi = 1.6×10^{-1} mol/l, at 30°C, for 3 h)

[PO] / [BzN]	PO (ml)	BzN (ml)	Yield (wt%)	N-Content (%)	d[PO] / d[BzN]
0.24	0.7	4.3	4.2	9.4	0.8
0.64	1.5	3.5	4.0	9.0	0.9
1.00	2.0	3.0	2.4	9.0	0.9
1.45	2.5	2.5	2.9	8.8	1.2

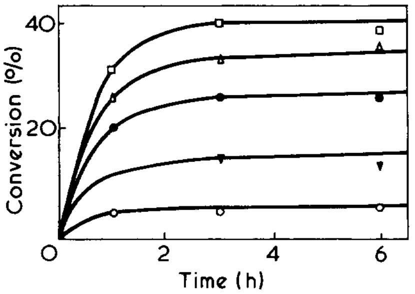


Figure 1 Variation of polymerization rate with mol ratio of benzonitrile (BzN) and propylene oxide (PO) with n-BuLi. (n-BuLi = 0.8 mol/l in THF at 50°C). ○, PO = 5.92 mol/l, BzN = 0.0 mol/l; ▼, PO = 4.44 mol/l, BzN = 0.98 mol/l; △, PO = 2.96 mol/l, BzN = 1.96 mol/l; □, PO = 1.48 mol/l, BzN = 2.94 mol/l; ●, PO = 0.0 mol/l, BzN = 3.92 mol/l

on an infra-red spectrometer (Jasco IR-E Japan Spectroscopic Co. Ltd) and the intrinsic viscosity [η] with an Ubbelohde viscometer in benzene at 30° ± 0.01°C.

The molecular weight of the copolymer was determined by use of a Knauer vapour pressure osmometer in chloroform.

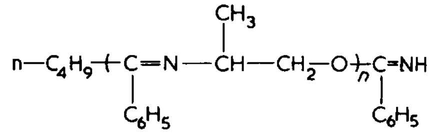
RESULTS AND DISCUSSION

Copolymerization of benzonitrile and propylene oxide

Copolymerization of BzN [M_2] and PO [M_1] initiated by n-BuLi at 30°C and at various monomer mole ratios are shown in *Table 1*. The copolymer composition(d [PO] /d [BzN]) was calculated from N(%) of elemental analysis and was almost independent of the monomer mole ratio. The values of $r_1 = 0.04$ and $r_2 = 0.1$ determined by the Fineman–Ross method indicate that the copolymer is an alternative copolymer.

The infra-red spectrum of this copolymer showed absorption bands at 1650 cm^{-1} due to the –C=N– linkage, 1390 cm^{-1} due to the $-CH_2-$ group, 1100 cm^{-1} due to the ether linkage and 700 cm^{-1} due to the phenyl group and the absence of absorption bands due to triphenyl-*s*-triazine and tetraphenyldihydrotriazine groups. The latter observation shows that the trimerization of BzN has not occurred.

The rate of copolymerization increased with the decrease of mole ratio of PO/BzN as shown in *Figure 1* and it is suggested that the polymer end group is BzN and that the copolymer has the structural formula (I):



$$n{-}C_4H_9{+}\underset{C_6H_5}{\underset{|}{C}}{=}N{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_2{-}O{+}_n\underset{C_6H_5}{\underset{|}{C}}{=}NH$$

Degree of polymerization

Using a ratio ([PO] / [BzN]) of 1.45, the copolymer of BzN and PO was obtained with n-BuLi in THF. The elementary analysis of this copolymer was: C = 77.0%; H = 7.6%; N = 8.7% [calculated for copolymer $(C_{10}H_{11}NO)_n$. C = 74.53%; H = 6.83%; N = 8.69%]. The *n* value in I as calculated from the carbon content was 2.0 (calculated values for *n* = 2.0 are C = 77.02%; H = 7.66%; N = 8.70%).

The molecular weight of a copolymer having *n* = 2.0 is 483 and this agrees with the observed molecular weight of the copolymer of 475 as determined by vapour pressure osmometry.

Copolymerization of BzN and PO under various conditions

Figure 1 shows the time conversion curve of various ratios of PO/BzN in THF at 50°C. BzN alone formed triphenyl-*s*-triazine, while poly(propylene oxide) was obtained from PO.

The yield of copolymer increased with an increase in the mole fraction of BzN and this suggested that n-BuLi reacted more easily with BzN than PO.

On the other hand, the molecular weight of the copolymer was almost constant and independent of the polymerization time (1–6 h).

Table 2 Effect of solvent on copolymerization of benzonitrile (BzN) and propylene oxide (PO) (BzN = 3.0 mol/l; PO = 3.0 mol/l; n-BuLi = 1.5×10^{-1} mol/l, at 80°C, for 24 h)

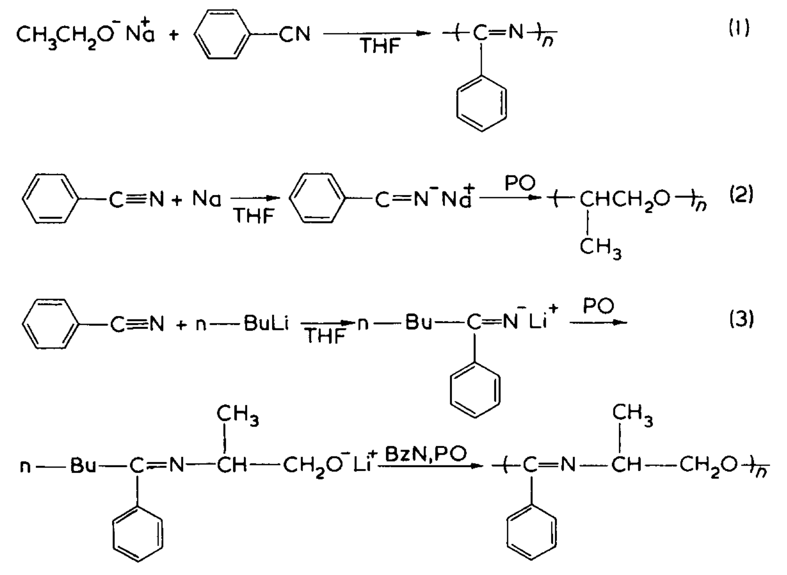
Solvent	(μ)	Yield (wt%)	M_w [1]	$[\eta]$ [2]
Benzene	(0)	13.7	–	0.018
Toluene	(0.37)	13.6	391.6	–
THF	(1.68)	11.6	–	0.022
Diglyme	(1.97)	10.3	–	0.017
No solvent		15.8	–	–

[1] In chloroform; [2] in benzene

Table 2 shows the effect of solvent on the yield, intrinsic viscosity and molecular weight of the copolymer. Solvents such as DMSO and DMF could not be used since they reacted with n-BuLi. A plot of dipole moment (μ) vs. yield of copolymer was linear and the yield of copolymer decreased with an increase in the dipole moment (μ). This result indicates that ion pair of the copolymer end formed a contact ion pair.

The rates of polymerization at 0°, 30° and 80°C shown in *Figure 2* correspond to an activation energy of 12.6 kcal/mol.

The intrinsic viscosity of the copolymer increased slightly with an increase in the polymerization temperature.



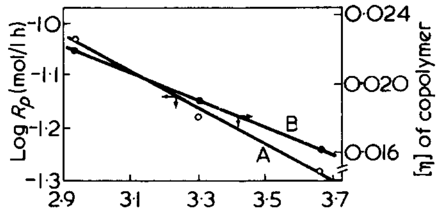


Figure 2 Arrhenius plot (A) of copolymerization of benzonitrile and propylene oxide and intrinsic viscosity [η] (B) of copolymer vs. polymerization temperature. (PO = 2.96 mol/l; BzN = 2.94 mol/l; n-BuLi = 1.6×10^{-1} mol/l in THF at 0°, 30°, 80°C for 4 h)

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

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A recent paper by Huckerby and Ebdon[1] 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 observed[4] in the spectrum of 1,2-polybutadiene. However for polystyrene, the correct assignment[1] 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 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 $c\,\overrightarrow{v}\,\overleftarrow{\phi}$ 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

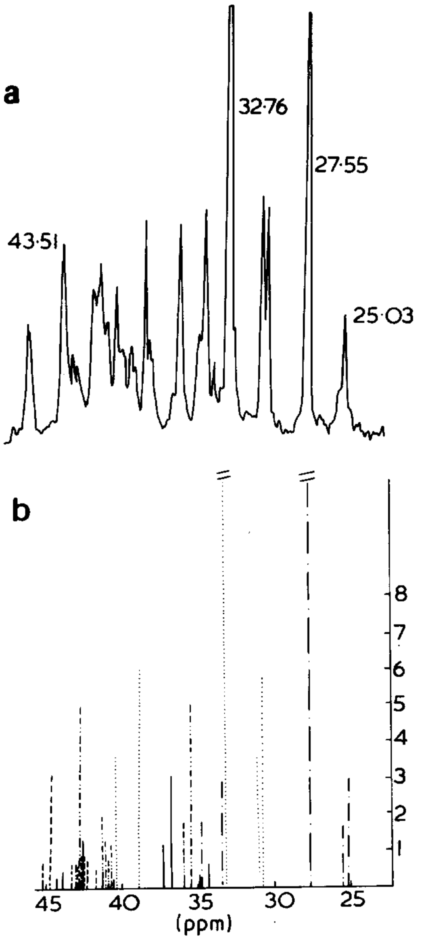

Figure 1 (a) Experimental and (b) calculated spectra of the aliphatic portion of a butadiene–styrene random copolymer. . . . ., CH_2 butadiene *trans* 1,4; —·—·—·—, CH_2 butadiene *cis* 1,4; ——··——, CH vinyl; ———·····——— CH_2 vinyl; ————, CH styrene; ———, CH_2 styrene
The major multiplicity in the 37–43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