Synthesis and characterization of new block copolymers of butadiene and 2-isopropenylpyridine

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Well defined diblock and triblock copolymers of butadiene and 2-isopropenylpyridine have been synthesized by anionic polymerization, using a difunctional lithium initiator. The structure of such a dilithium derivative was characterized by ^{13}C nuclear magnetic resonance and the reaction of the two lithium active centres was demonstrated. The characterization of the copolymers (by gel permeation chromatography and nuclear magnetic resonance) and the study of their thermomechanical properties (by differential scanning calorimetry and viscoelasticimetry) support the block structure and show that these materials would display better mechanical properties, at high temperature, than conventional styrene–butadiene–styrene and styrene–isoprene–styrene.

INTRODUCTION

In recent years, increasing effort has been devoted to the synthesis of novel copolymers and block copolymers, in order to develop materials with predictable and controllable properties. Such materials include thermoplastic elastomers (styrene–butadiene–styrene (SBS) and related polymers), which have been extensively studied[1-3].

Nevertheless, copolymers such as SBS present some drawbacks: in particular, a decrease in their mechanical properties has been observed at temperatures higher than 70°C[3,4]. Several authors have attempted to circumvent this problem by using as a vinylic block poly(α-methylstyrene) which exhibits a glass transition higher than that of polystyrene[5-7]; however, the direct anionic synthesis of triblock copolymers is relatively difficult using this approach due to the low stability of the active centres (e.g. poly(α-methylstyrene)yllithium), particularly in non-polar solvents[8]. Moreover, the few copolymers prepared have unexpectedly poor mechanical properties[6,9].

In previous comprehensive studies of the anionic polymerization of 2-isopropenylpyridine (2IP)[10] and of the thermal properties of the corresponding homopolymer[11], it has been demonstrated that:

(a) the poly(2-isopropenylpyridine)lithium active centres are stable even at temperatures as high as 80°C;

(b) poly(2IP) of low polydispersity can be obtained in good yields;

(c) the glass transition temperature (T_g) of poly(2IP) is one of the highest among those of vinylic polymers $(T_g \simeq 470 \text{ K})$.

This is why the synthesis of ABA copolymers with poly(2IP) as rigid block (A) turned out to be a new way to obtain thermoplastic elastomers displaying better mechanical properties, at high temperatures, than conventional SBS or styrene–isoprene–styrene (SIS).

In this paper, results on the anionic synthesis and characterization of diblock and triblock copolymers of 2IP and butadiene are reported.

EXPERIMENTAL

Synthesis and purification of monomers, purification of reactants, polymerizations and recovery of polymers were carried out as previously reported[10,12-14]. Monofunctional poly(butadiene)yllithium was prepared with tert-butyllithium as initiator[12]. Difunctional poly(butadiene)yldilithium was obtained by using difunctional initiator 2. Precursor 1 and initiator 2 (see later) were synthesized according to the method described by Guyot et al.[15,16]

Copolymerizations were performed by slowly adding 2IP monomer into a solution of mono- or difunctional poly(butadiene)yldilithium (following the onset of the addition, the colourless solution turns orange-red, indicating the formation of poly(2IP) anion). Active centre concentrations were measured by u.v. spectrometry using a CARY 219 spectrophotometer: poly(butadiene)yllithium[12]—in hexane, $\lambda_{max} = 275$ nm, $\varepsilon_{275} = 8300 \text{ l mol}^{-1} \text{ cm}^{-1}$, and in toluene, (shoulder) $\lambda = 290$ nm, $\varepsilon_{290} = 8000 \text{ l mol}^{-1} \text{ cm}^{-1}$; poly(2-isopropenylpyridine)yllithium[10]—in toluene, $\lambda_{max} = 300$ nm, $\varepsilon_{300} = 18\,000 \text{ l mol}^{-1} \text{ cm}^{-1}$.

Molar mass determinations were performed either by size exclusion chromatography in tetrahydrofuran (THF) at 25°C using μ-Styragel columns in the 50 to 10^4 nm permeability range, or by osmometry in toluene at 25°C

Table 1 Copolymerization of butadiene and 2IP initiated by tert-butyllithium, in various experimental conditions

Expt.	Solvent[a]	Temperature (°C)	Butadiene blocks				2IP blocks			
			$[tBuLi] \times 10^3$ (mol l^{-1})	[Butadiene] (mol l^{-1})	$[B] \times 10^{3\,b}$ (mol l^{-1})	$\bar{M}_n$ (theor.)[c]	$[C] \times 10^{3\,b}$ (mol l^{-1})	$[2IP] \times 10$ (mol l^{-1})	$\bar{M}_n$ (theor.)[c]	Copolymers $\bar{M}_n$ (theor.)[c]
1	Toluene	−40	7.0	0.27	6.8	2100	6.8	0.57	1000	3100
2	Toluene	−40	5.0	0.52	4.8	5800	4.7	0.59	1500	7300
3	Toluene	−40	1.4	0.52	1.3	21600	1.2	0.71	7000	28600
4	Toluene	−40	0.47	0.52	0.45	62000	0.48	0.28	7000	69000
5	Toluene	−40	0.47	0.52	0.45	62000	0.47	2.1	53000	115000
6	Toluene	20	1.4	0.52	1.3	21600	1.2	0.71	7000	28600
7	Toluene	20	0.47	0.52	0.45	62000	0.44	0.25	7000	69000
8	THF	−70	1.4	0.52	1.3	21600	1.1	0.71	7000	28600
9	THF	−70	1.4	0.52	1.3	21600	1.0	0.82	7000	28600

[a] Initial polybutadiene block was obtained at 20°C in toluene for experiments 1 to 7 and in THF for experiments 8 and 9
[b] Measured by u.v. spectrometry; [B] = [poly(butadiene)yllithium]; [C] = [poly(butadiene-b-2IP)yllithium]
[c] Calculated from [monomer]/[initiator]

Table 2 Average molar masses of diblock copolymers poly(butadiene-b-2IP) obtained by anionic copolymerization

Expt.	Butadiene blocks			Copolymers		
	$\bar{M}_n$ (theor.)	$\bar{M}_n$ (expt.)[a]	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ (theor.)	$\bar{M}_n$ (expt.)[a]	$\bar{M}_w/\bar{M}_n$
1	2100	1800	1.1	3100	3000	1.3
2	5800	5600	1.05	7300	7600	1.2
3	21600	20900	1.1	28600	27000	1.1
4	62000	60100	1.05	69000	70100	1.2
5	62000	61300	1.05	115000	114000	1.1
6	21600	21800	1.05	28600	31000	1.2
7	62000	60500	1.05	69000	74500	1.2
8	21600	25600	1.2	28600	36600	1.4
9	21600	27300	1.3	28600	38100	1.6

[a] Determined by g.p.c.

using a Hewlett-Packard 5200 osmometer. In g.p.c. experiments, $\bar{M}_n$ and $\bar{M}_w$ values were calculated from a calibration curve obtained with polystyrene and polyisoprene standards.

N.m.r. measurements were carried out at 200 MHz for ^{1}H and at 50 MHz for ^{13}C in CDCl$_3$ or C$_6$D$_6$ (15 g/100 ml solvent) on a Bruker WP 200 spectrometer.

Glass transition (T_g) measurements were conducted using a Perkin-Elmer model DSC-4 differential scanning calorimeter. All measurements were made under argon at a heating rate of 10°C min^{-1}. T_g values were determined from d.s.c. traces and defined as the midpoint between the upper and lower intersections of the baseline projections with the tangent to the transition step, according to Garn et al.[17]

Dynamic mechanical measurements were made in the tensile mode, at 35 Hz, on a Rheo viscoelasticimeter. Samples were cylinders of 3–5 mm diameter, prepared by moulding under pressure (3 atm) at 180°C.

Films for electron microscopy were cast from a toluene solution (10 g/100 ml solvent) and stained, for 3 days, in an aqueous solution of osmium tetroxide[18] (0.1 g/100 ml water).

RESULTS AND DISCUSSION

Synthesis of diblock copolymers, poly(butadiene-b-2-isopropenylpyridine)

It has previously been shown[10] that initiation of the polymerization of 2IP by 1,1-diphenyl-n-hexyllithium in
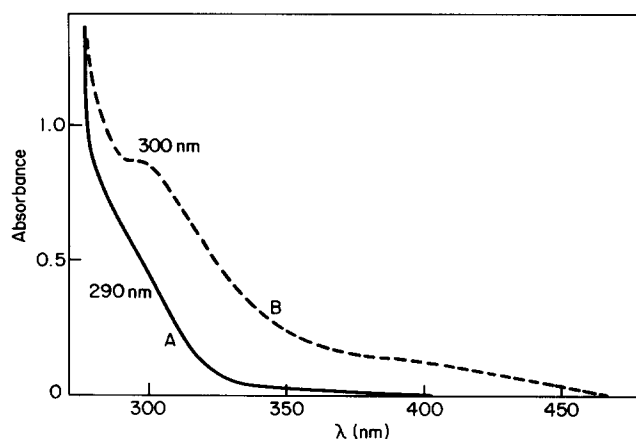

Figure 1 U.v. spectra of poly(butadiene)yllithium (curve A) and poly(2IP)yllithium (curve B) in toluene at 20°C

toluene is fast, complete and proceeds without perceptible side reactions. In order to verify if a similar behaviour is observed when initiating the polymerization of 2IP with poly(butadiene)yllithium, diblock poly(butadiene-b-2IP) copolymers were prepared under various experimental conditions (solvents, temperatures, concentrations). The results summarized in *Tables 1* and *2* and represented on *Figure 1* indicate the following:

(a) In a non-polar solvent (toluene) at low temperature, the transformation of poly-(butadiene)yllithium active centres into poly-(2IP)lithium anions is complete and no detectable

Table 3 Structures and glass transition temperatures of diblock copolymers poly(butadiene-*b*-2IP)

Expt.	$\bar{M}_n$ (expt.)[a]	Polybutadiene blocks				Poly(2IP) blocks				Copolymers	
		Structure[b]			T_g (°C)	Structure[b,c]			T_g (°C)	T_g (°C)	
		1–4 *cis*	1–4 *trans*	1–2		i	h	s			
1	3000	40.6	49.3	10.1	−92	1	15	84	−	−89	−
2	7600	40.1	49.3	10.7	−93	2	13	85	−	−91	−
3	27000	40.9	49.4	9.7	−95	2	12	86	174	−94	174
4	70100	40.6	49.2	10.2	−94	2	14	84	190	−95	190
5	114000	40.1	49.4	10.5	−94	1	14	85	193	−94	193
6	31000	40.1	49.1	10.8	−94	1	12	87	190	−93	190
7	74500	40.3	49.1	10.6	−93	2	13	85	193	−94	193
8	36600	1	9	90	−18	3	13	84	190	−18	190
9	38100	7	8	85	−20	5	13	82	191	−20	191

[a] Determined by g.p.c. (see *Table 2*)
[b] Determined by ^{13}C n.m.r. at 50 MHz
[c] i = isotactic triad, h = heterotactic triad, s = syndiotactic triad
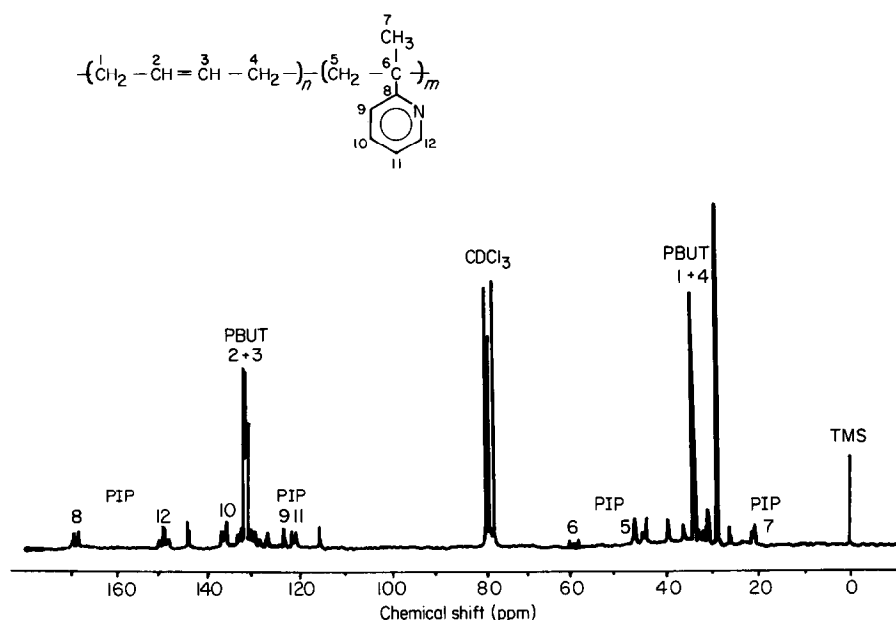
Figure 2 ^{13}C n.m.r. spectrum, at 50 MHz, of poly(butadiene-*b*-2IP) copolymer

side reactions (particularly on pyridine rings) occur; indeed, experimental concentrations of active species (measured by u.v.) agree well, within experimental error, with theoretical concentrations. Moreover, in such a medium, the experimental molar masses $\bar{M}_n$ are in good agreement with theoretical ones (calculated from [M]/[C] ratio) and the polydispersity of both the butadiene blocks and the copolymers is always relatively low.

(b) In contrast, in either polar (THF) or non-polar solvent at room temperature, theoretical calculations and experimental measurements of both concentrations and $\bar{M}_n$ values disagree. This result may be explained by the low stability of poly(butadiene)yllithium active species in THF[19,20] and the occurrence of nucleophilic reactions on the pyridine ring, at room temperature, even in a non-polar solvent[14,21-24].

The structure and the thermomechanical properties (T_g, dynamic modulus) of the different copolymers prepared were studied.

^{1}H and ^{13}C n.m.r. studies allowed the identification of polybutadiene and poly(2IP) blocks, along with the measurement of both the content of 1–4 and 1–2 units in

the diene block[25] and the stereoregularity of the vinylic block[26] (*Table 3* and *Figure 2*). The structure and the T_g of the polybutadiene block are in good agreement with those reported in the literature[25,27]. The values of T_g measured for the poly(2IP) block are similar to those previously determined for homopolymer[11]*. It is worth noting that two glass transition temperatures in the copolymer (with values being equal to those of each homopolymer) support the block structure of the copolymers.

A preliminary study of thermomechanical behaviour of the diblock copolymers was also carried out. The variations of the storage modulus E' and the loss modulus E'' were studied as a function of temperature (*Figure 3*). The results corroborate both the values of T_g determined by d.s.c. and the block structure; moreover, they show that the copolymers poly(butadiene-*b*-2IP) would present good mechanical properties (low decrease of the modulus E') at temperatures up to 140°C.

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* Nevertheless, when the length of the poly(2IP) block is short $(\overline{DP}_n \simeq 30)$, it was not possible to detect any glass transition

Synthesis of triblock copolymers, poly(2IP-b-butadiene-b-2IP)

On the basis of the optimal experimental conditions determined previously in the diblock synthesis, triblock copolymers poly(2IP-*b*-butadiene-*b*-2IP) with various molecular weights were synthesized.

The initial difunctional polybutadiene block was prepared at room temperature using dimethyl-2,17-diphenyl-4,15-octadecane-diyllithium (2) as initiator. Indeed, Guyot *et al.*[16] have demonstrated by u.v. spectrophotometry and g.p.c. experiments that such an initiator leads to monodisperse difunctional polybutadiene.

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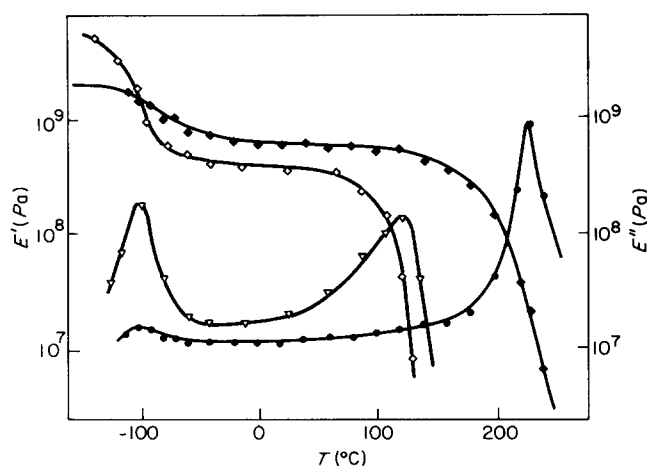
Figure 3 Variations *versus* temperature, at 35 Hz, of storage modulus E' (◆) and loss modulus E'' (●) of copolymer poly(butadiene-*b*-2IP). Variations of E' (◇) and E'' (▽) of copolymer SBS (from ref. 3; $M_n = 53\,000$)
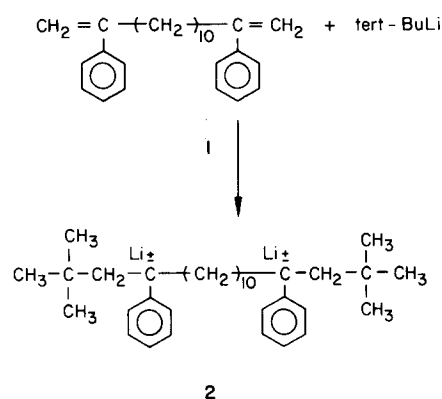
Our observations corroborated these results:

(a) Experimental concentrations of poly(butadiene)-yllithium [C] and the experimental molar mass of polybutadiene blocks agree, within experimental error, with theoretical concentrations (calculated from initial concentrations of 1) and theoretical M_n (calculated from 2[butadiene]/[C]) (*Tables 4* and *5*).

(b) [13]C n.m.r. spectra of protonated initiator 2' and protonated oligomers of butadiene 3 showed that 2 is a dianion and that the initiation occurs on both active centres (*Figures 4* and *5*).

(c) The transformation of dianionic poly(butadiene)-yllithium into dianionic poly(2IP)yllithium is complete (*Table 4*).

2'
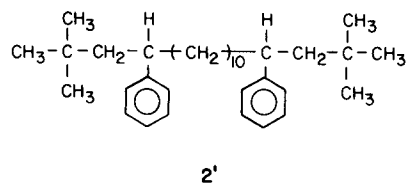
Table 4 Synthesis of triblock copolymers poly(2IP-*b*-butadiene-*b*-2IP) in toluene at $-30°C^a$

	[1] (mol l⁻¹)	[2] (mol l⁻¹)	[Butadiene] (mol l⁻¹)	[B] × 10³ ᵇ (mol l⁻¹)	Polybutadiene $\bar{M}_n$ (theor.)ᶜ	[C] × 10³ ᵇ (mol l⁻¹)	[2IP] (mol l⁻¹)	Copolymer $\bar{M}_n$ (theor.)ᵈ
1	3.1	6.3	0.47	6.5	7800	6.6	0.11	11900
2	0.72	1.4	0.39	1.7	25000	1.6	0.03	29000
3	3.4	6.3	0.47	6.5	7800	6.4	0.25	17000
4	0.76	1.4	0.39	1.7	25000	1.8	0.08	35000
5	0.72	1.5	0.39	1.7	25000	1.6	0.25	60000

ᵃ Initial difunctional polybutadiene block was prepared at 20°C
ᵇ See *Table 1* for definition of [B] and [C]. Measured by u.v. spectrometry
ᶜ Calculated from 2[butadiene]/[B]
ᵈ Calculated from 2[2IP]/[C] + 2[butadiene]/[B]

Table 5 Experimental molar masses of triblock copolymers poly(2IP-*b*-butadiene-*b*-2IP)

	Polybutadiene blocks				Poly(2IP) blocks	Copolymers			
Expt.	$\bar{M}_n$ (theor.)	$\bar{M}_n$ (expt.)ᵃ	$\bar{M}_n$ (expt.)ᵇ	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ (theor.)	$\bar{M}_n$ (theor.)	$\bar{M}_n$ (expt.)ᵃ	$\bar{M}_n$ (expt.)ᵇ	$\bar{M}_w/\bar{M}_n$
1	7800	8000	8200	1.1	4100	11900	11000	13000	1.2
2	25000	24000	26000	1.2	4000	29000	39000	32000	1.3
3	7800	8300	8100	1.1	9200	17000	20000	18100	1.4
4	25000	24500	26100	1.1	10000	35000	45000	34000	1.3
5	25000	26000	26600	1.1	35000	60000	75000	62200	1.2

ᵃ Determined by g.p.c.
ᵇ Determined by osmometry

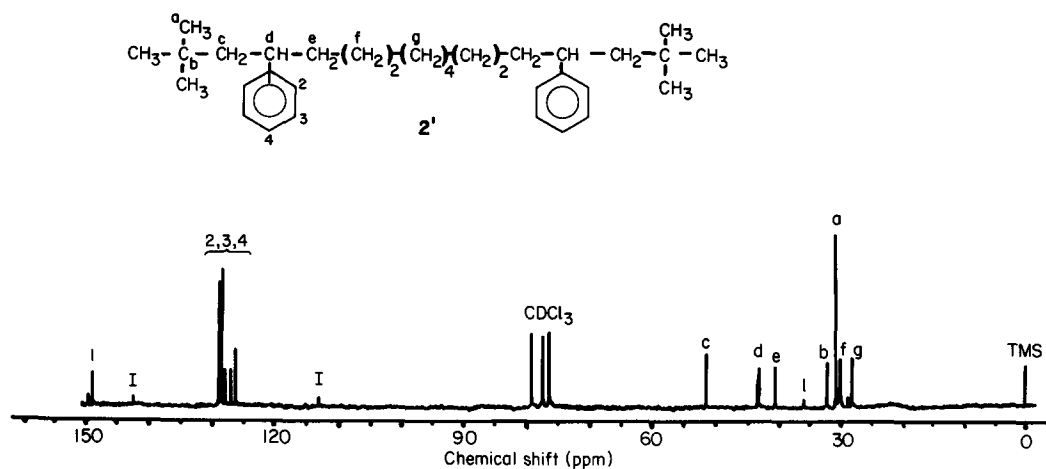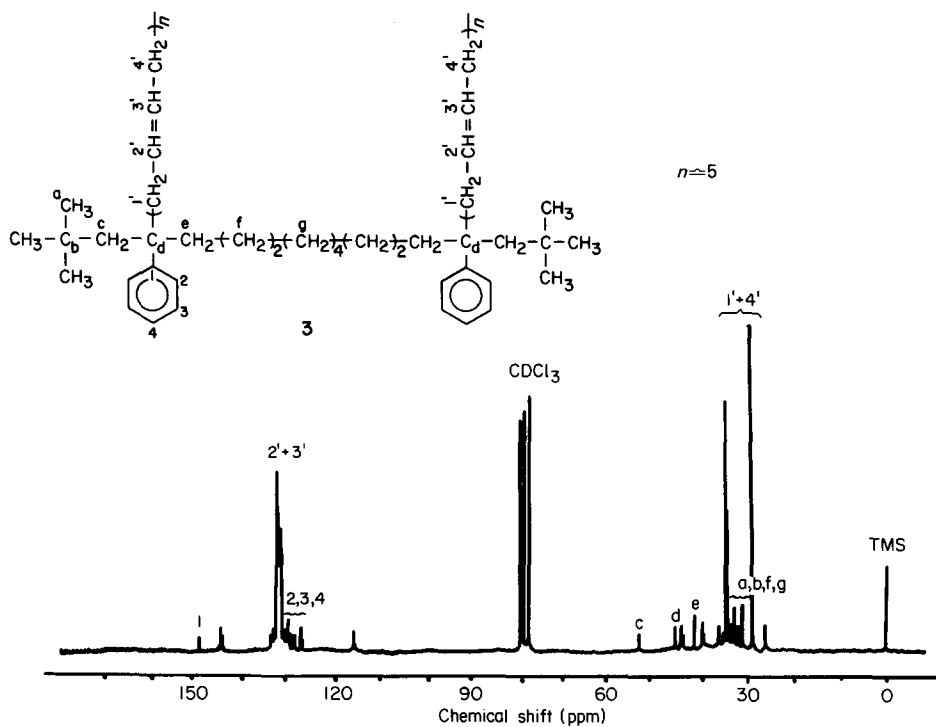**Figure 4** ^{13}C n.m.r. spectrum, at 22.5 MHz, of protonated initiator **2'**

Figure 5 ^{13}C n.m.r. spectrum, at 22.5 MHz, of protonated oligomers of polybutadiene **3**

Table 6 Structures and glass transition temperatures of triblock copolymers poly(2IP-*b*-butadiene-*b*-2IP) prepared by anionic polymerization in toluene at $-30°C$

	Polybutadiene blocks				Poly(2IP) blocks T_g (°C)	Copolymers		
	Structure^a (%)			T_g (°C)		Composition^b (mass %)		
Expt.	1–4 cis	1–4 trans	1–2			Butadiene	2IP	T_g (°C)
1	36.5	52.0	11.5	−90	−	66	34	−87
2	38.3	51.4	10.3	−93	−	86	14	−89
3	39.1	50.8	10.1	−92	190	46	54	−91	190
4	38.8	51	10.2	−93	191	69	31	−93	190
5	39.2	50.8	10	−93	197	41	59	−94	197

^{a} Measured by ^{13}C n.m.r. at 50 MHz
^{b} Calculated from [butadiene]/[2IP]
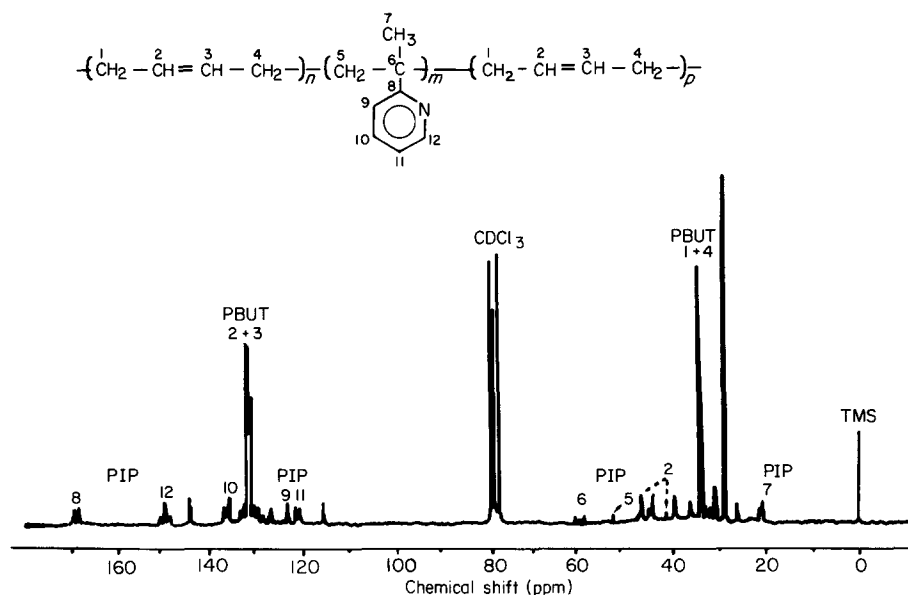
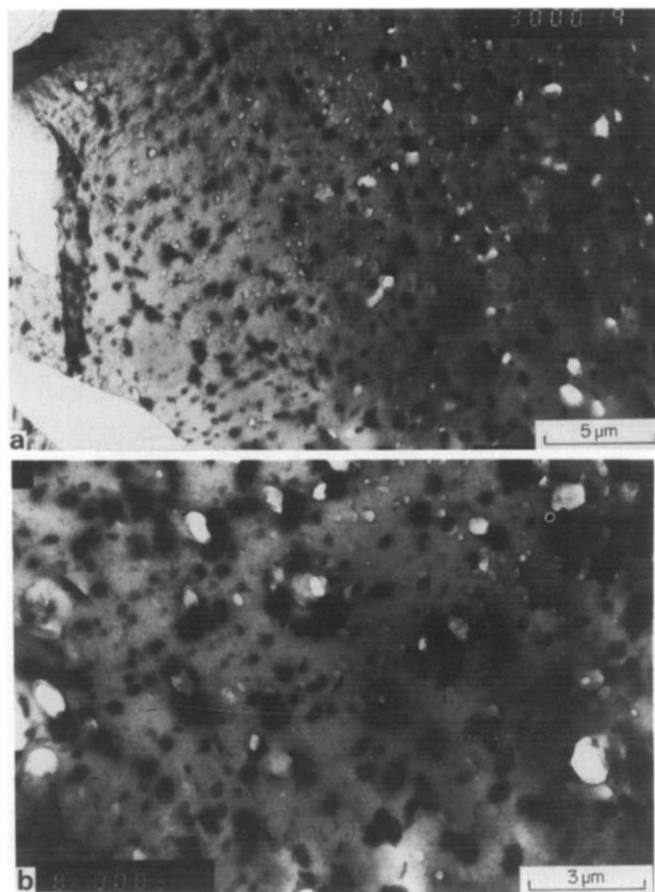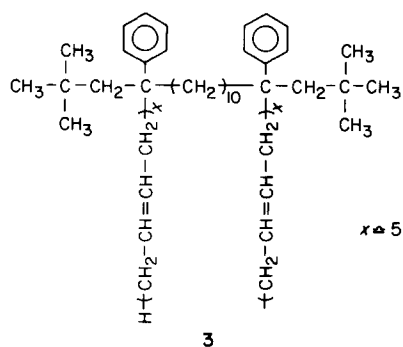**Figure 6** ^{13}C n.m.r. spectrum, at 50 MHz, of triblock copolymer poly(2IP-*b*-butadiene-*b*-2IP)

The various copolymers prepared and the corresponding initial polybutadiene blocks were characterized (*Table 6* and *Figure 6*).

The structure and the T_g of each block are in good agreement with those determined for the corresponding homopolymers. On the contrary, some deviations were observed between calculated and experimental $\bar{M}_n$ measured by g.p.c. and the polydispersity of triblock copolymers is higher than that of diblock copolymers. Nevertheless, it can be noticed that the g.p.c.-based values of $\bar{M}_n$ and of $\bar{M}_w/\bar{M}_n$ were calculated from a polystyrene standards calibration curve; the conformation in solution of the triblock copolymers must be far different from that of polystyrene, and therefore these values are approximate ones and a better agreement is observed when the experimental $\bar{M}_n$ are determined by osmometry (*Table 5*).

A preliminary determination of the morphology of the triblock copolymers was performed by scanning electron microscopy. Photomicrographs of triblock copolymer 5 stained by osmium tetroxide indicate the existence of phase separation between the elastomeric blocks (dark spheres) and the vinylic blocks (grey matrix), thus corroborating the block structure of the copolymers (*Figure 7*).

Figure 7 Electron photomicrographs of a triblock copolymer poly(2IP-*b*-butadiene-*b*-2IP)

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