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Carbocationic Polymerization in the Presence of Sterically Hindered Bases. IX. High Efficiency Blocking of Poly(α-methylstyrene) from Linear and Radial Polyisobutylenes Carrying tert-Chlorine Termini in the Presence of Proton Traps

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ABSTRACT

Di-, tri-, and tristar block copolymers consisting of rubbery poly(isobutylene) (PIB) and glassy poly(α-methylstyrene) (PαMeSt) sequences have been synthesized with 70 to >95% efficiency. The syntheses involved initiation of α-methylstyrene polymerization by linear or three-arm star PIB's carrying 1,2, or 3 tertiary chlorine termini in conjunction with $SnCl_4$ coinitiator in the presence of 2,6-di-tert-butylpyridine (DtBP). Blocking efficiencies (B_{eff}) increased with the amount of DtBP and approached 100% under suitable conditions.

INTRODUCTION

The grafting of αMeSt from chlorobutyl and polychloroprene rubbers with conventional Friedel-Crafts acids, e.g., $SnCl_4$ and BCl_3, in the presence of DtBP resulted in 90-97% grafting efficiencies [1].

These results could be achieved because of controlled cationic initiation of α-methylstyrene polymerization and suppression of chain transfer to monomer in the presence of DtBP. These findings encouraged us to design experiments for the high efficiency synthesis of block copolymers with common Friedel-Crafts acids in the presence of DtBP.

This paper concerns the synthesis of PIB and PαMeSt diblocks, triblocks, and three-arm star-blocks. The syntheses involved the initiation of αMeSt polymerization from PIB's carrying $\sim CH_2C(CH_3)_2Cl$ termini (i.e., linear PIB's carrying one or two tert-chlorine termini, or three-arm PIB stars carrying three such termini) in the presence of $SnCl_4$ coinitiator and DtBP proton trap. Scheme 1 helps to visualize the syntheses. These block copolymers are expected to be useful in a large variety of applications, e.g., oxidation resistant thermoplastic elastomers and impact resistant thermoplastics.

EXPERIMENTAL

Polymerization

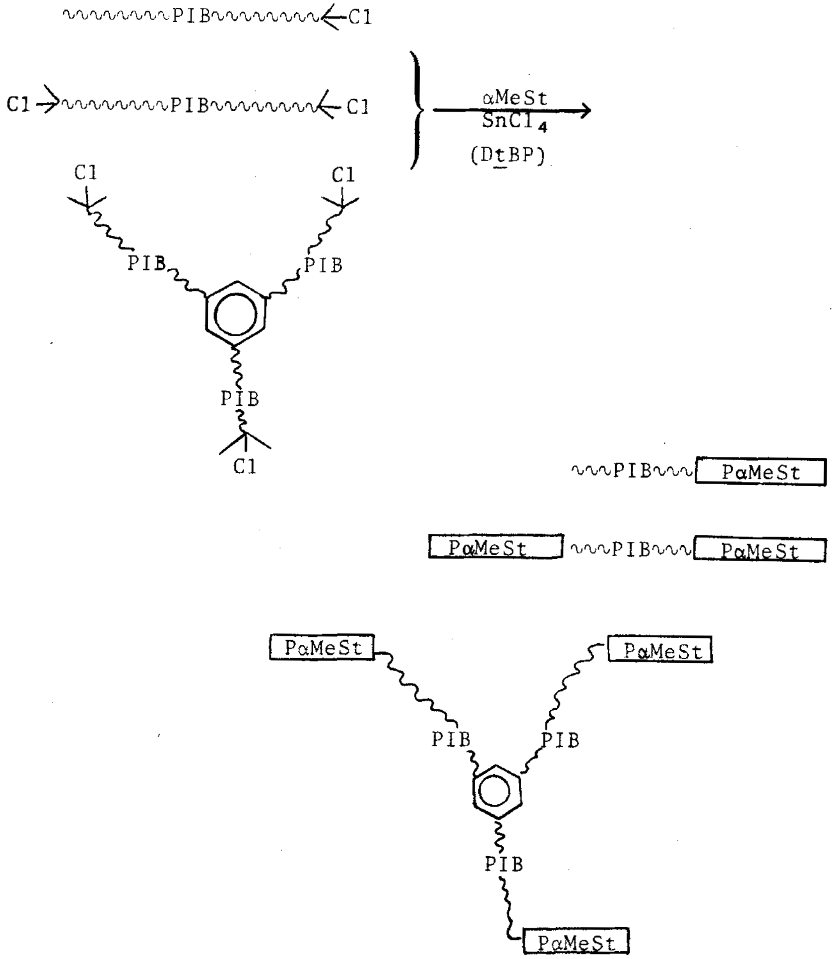
Purification of solvents, monomer, coinitiator, DtBP, and the polymerization procedures used for the open systems and high vacuum experiments have been described [1]. The preparation of telechelic polyisobutylenes has been described [2, 3]. The propolymers were precipitated in methanol, dissolved in hexane, washed with water, and dried with $MgSO_4$. The n-hexane was removed and the polymer films were dried under high vacuum at room temperature for 1 week. They were then redissolved in n-hexane and CH_2Cl_2 was added to obtain desired CH_2Cl_2:n-hexane ratios. Polymerizations were triggered by adding the $SnCl_4$ coinitiator solutions to charges containing the prepolymer, monomer, and DtBP. Polymerizations were stopped by the addition of prechilled methanol. After precipitation with methanol, the products were dried and weighed.

Characterization

The composition of the various fractions obtained by selective solvent extraction was determined by ^1H NMR spectroscopy (Varian T-60 spectrophotometer). The $\overline{M}_n$ of block copolymers was determined by membrane osmometry (Hewlett-Packard instrument, Model 503).

Block Separation and Purification

The crude products of block copolymerizations were extracted with a series of selective solvents. The extraction scheme is outlined in

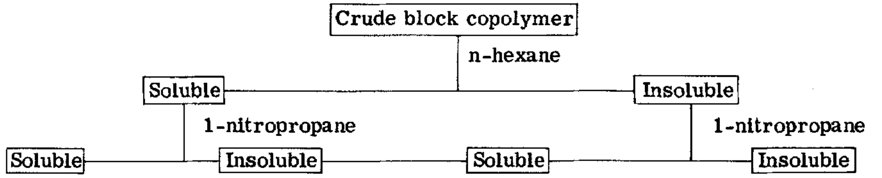


SCHEME 1. Synthesis outline of the various block copolymers.

Table 1. Each extraction step was carried out for 72 h and the soluble and insoluble fractions were separated. n-Hexane or n-pentane were equally suitable for separating the PIB; 1-nitropropane was the solvent of choice for PαMeSt [1].

This separation procedure was tested by quantitatively separating a blend of PIB and PαMeSt. Thus a quantity of PIB ($\overline{M}_n$ = 50,000) and PαMeSt ($\overline{M}_n$ = 15,000) was dissolved in THF and precipitated into

TABLE 1. Extraction Scheme, Amount, and Composition of Various Fractions Obtained



	(low molecular weight products)		(PIB-rich fraction)		(PαMeSt-rich fraction)		(blocks with long PIB/PαMeSt sequences)		
Expt	Wt%	Composition wt% PαMeSt	Wt%	Composition wt% PαMeSt	Wt%	Composition wt% PαMeSt	Wt%	Composition wt% PαMeSt	$\overline{M}_n \times 10^{-3}$
3	-	50	-	3	-	100	-	93	25
4	8	43	12	10	36	95	44	87	26
5	4	60	19	12	29	90	48	89	25
6	8	38	11	4	22	98	67	87	16
7	6	34	8	2	15	100	71	90	34
8	11	49	33	8	42	98	44	75	23
9	-	55	-	7	-	96	-	80	50
10	-	46	-	5	-	100	-	78	80
11	21	61	52	10	11	86	16	70	25
12	7	68	43	11	13	94	36	82	39
13	13	28	23	10	4	82	60	81	33
14	1	49	17	10	22	91	60	86	48
15	4	70	12	8	20	90	63	78	50
16	20	65	12	9	14	89	54	70	55
17	15	60	10	17	10	89	64	49	-

methanol. The precipitate was separated, dried, and subjected to selective extraction as shown in Table 1. The purity of the fractions recovered were greater than 98%.

The four fractions obtained from the blocking experiments are: 1) low molecular weight products (n-hexane-1-nitropropane-soluble), 2) a fraction rich in PIB (n-hexane-soluble-1-nitropropane-insoluble), 3) a fraction rich in PαMeSt (n-hexane-insoluble-1-nitropropane-soluble), and 4) a fraction composed of block copolymer that has long sequences of both PIB and PαMeSt (n-hexane-inxoluble-1-nitropropane-insoluble). The low molecular weight products are typically oily materials that elute near the GPC trash peak. The composition of this minor fraction was not analyzed. The n-hexane-soluble-1-nitropropane-insoluble fraction was taken as the amount of free PIB for the I_{eff} calculation, and the n-hexane-insoluble-1-nitropropane-soluble fraction was taken as the free PαMeSt for the B_{eff} calculation.

Initiation efficiency, i.e., the moles of block copolymer formed/ moles of PIB prepolymer charged, has been calculated by

$$I_{eff} = \frac{PIB - PIB_{fr} PIB_{\%}}{PIB} \times 100$$

where PIB is the weight of the PIB prepolymer charged, PIB_{fr} is the weight of the n-hexane-soluble-1-nitropropane-insoluble fraction and $PIB_{\%}$ is the weight percent PIB in this fraction (assuming that the molecular weights of the charged PIB prepolymer and that of the product in the n-hexane-soluble–1-nitropropane-insoluble fraction are identical, all the quantities are available from Table 1; the correctness of this assumption has been directly tested by determining the molecular weight of select samples in the PIB_{fr} fraction).

I_{eff} data shown in Table 2 are minimum values because block copolymers with only a few PαMeSt units cannot be separated from PIB. Since this uncertainty is greater in experiments with very low αMeSt concentrations and higher molecular weight PIB samples, the data in Table 2 reflects only those I_{eff} values in which PIB prepolymer molecular weights were low ($\overline{M}_n$ = 5-8,000) and [αMeSt] higher than 0.5M.

Blocking efficiency is expressed by

$$B_{eff} = ((B_{P\alpha MeSt}/(B_{P\alpha MeSt} + H_{P\alpha MeSt})) \times 100$$

where $B_{P\alpha MeSt}$ and $H_{P\alpha MeSt}$ are blocked and homo-PαMeSt, respectively. The B_{eff} data in Table 2 are minimum values since the hexane-insoluble–1-nitropropane-soluble (PαMeSt) fraction is contaminated

TABLE 2. Syntheses of Block Copolymers with $SnCl_4$ in the Absence and Presence of DtBP

Expt	Prepolymer		Solvents, CH_2Cl_2/ n-hexane	$SnCl_4$ ($\underline{M} \times 10^2$)	DtBP ($\underline{M} \times 10^3$)	αMeSt ($\underline{M}$)	Temperature (°C)	Time (h)	αMeSt conversion (%)	B_{eff} (%)	I_{eff} (%)
	$\underline{M} \times 10^3$	$\overline{M}_n \times 10^{-3}$									
		Controls									
1^a	-	-	100/0	2.0	-	2.3	-50	0.3	20	-	-
2^a	-	-	100/0	4.0	1.0	2.3	-50	5	3	-	-
		PIB-Cl									
3	6.0	5	70/30	2.0	-	0.61	-50	5	100	40	40
4	6.0	5	70/30	2.0	0.017	0.61	-50	5	100	49	59
5	6.0	5	70/30	2.0	0.034	0.61	-50	5	100	60	35
6	6.0	5	70/30	2.0	0.067	0.61	-50	5	100	74	63
7	6.0	5	70/30	2.0	0.168	0.61	-50	5	100	79	73
8^a	2.0	5	60/40	0.8	2.10	0.08	-50	4	86	92	-

	PIB-Cl_2									
9[a]	3.7	8	70/30	0.5	1.0	0.19	-40	6	97	90	-
10[a]	0.8	30	55/45	0.3	7.2	0.23	-40	3	80	90	-
	PIB-Cl_3										
11	15.0	8	60/40	3.8	1.6	0.24	-50	5	100	70	-
12	15.0	8	60/40	3.8	1.6	0.48	-50	5	100	73	-
13	15.0	8	60/40	3.8	1.6	0.72	-50	5	100	70	53
14	15.0	8	60/40	3.8	1.6	1.44	-50	5	100	75	39
15	15.0	8	60/40	3.8	1.6	2.43	-50	5	100	78	37
16[a]	1.6	14	60/40	0.5	0.15	0.11	-40	6	100	83	-
17[a]	1.5	27	60/40	0.5	0.15	0.07	-40	6	100	88	-
18	0.9	50	60/40	1.4	2.5	0.38	-40	8	74	90	-
19	4.5	5	60/40	6.5	70.0	0.08	-40	6	22	> 95	-

[a] High vacuum experiments.

by block copolymers with long PαMeSt blocks. These fractions cannot be separated using the solvent extraction method shown in Table 1.

RESULTS AND DISCUSSION

The objectives of this research were: 1) to achieve complete blocking of PαMeSt sequences from tertiary chlorine endgroups, 2) to control the molecular weight of PαMeSt blocks, and 3) to minimize or altogether eliminate PαMeSt homopolymer formation by the use of DtBP.

The results are organized in Tables 1 and 2. Table 1 shows experimental conditions together with αMeSt conversion, B_{eff}, and I_{eff} obtained. The data in Table 2 are subdivided into three groups depending on the nature of the prepolymer: PIB-Cl, $PIB\text{-}Cl_2$, and $PIB\text{-}Cl_3$, i.e., linear PIB carrying one $-CH_2C(CH_3)_2Cl$ endgroup, linear PIB carrying two such endgroups, and three-arm star PIB carrying three such endgroups, respectively.

The data in Table 2 can be divided into systems where [DtBP] is less than $-\!\![CH_2C(CH_3)_2Cl]$ and where [DtBP] is in excess of $-\!\![CH_2C(CH_3)_2Cl]$. In Experiments 3-7 [DtBP] is less than $-\!\![CH_2C(CH_3)_2Cl]$ and conversions are virtually 100%. This suggests incomplete proton entrapment. The escaped protons generate PαMeSt and thus B_{eff} is less than 100%.

High B_{eff} values can be obtained even at relatively low [DtBP], i.e., when [DtBP] is much lower than that of the initiating $-\!\![CH_2C(CH_3)_2Cl]$. For example, in Experiments 7 and 11-17, [DtBP] is 30 and 10 times lower than $-\!\![CH_2C(CH_3)_2Cl]$, respectively, still B_{eff} = 79 and ~75%. The I_{eff}'s obtained in Experiments 7 and 13-15 are much less than 100%. These data suggest that the rate of initiation is relatively slow while that of propagation (or rather $k_p/k_{tr,M}$) is very large. This conclusion is substantiated by results of Sigwalt et al. [4] who found $k_p = 2.2 \times 10$ and $k_{tr,M} = 30$ in a similar system. Previously investigations in our laboratories have also yielded large $k_p/k_{tr,M}$ values [5].

I_{eff} is apparently not affected by [DtBP] (Experiments 3-7) and [αMeSt] (Experiments 13-15) under our experimental conditions, i.e., at low [αMeSt].

In Experiments 8, 10, 18, and 19, [DtBP] is higher than $-\!\![CH_2C(CH_3)_2Cl]$ and conversions fall below 100% due to terminative proton entrapment. Simultaneously B_{eff}'s increase because the events leading to the formation of free PαMeSt, i.e., protic initiation and chain transfer to monomer, are reduced.

CONCLUSIONS

The objectives set for this research have largely been attained. Thus complete blocking of PαMeSt sequences from all available $-CH_2C(CH_3)_2Cl$ termini has probably been achieved since, for example, according to Experiments 18 and 19, in spite of very long blocking times (6-8 h), monomer conversions did not reach 100%. However, these data do not exclude the possibility of incomplete blocking if at the moment of initiating cation formation ($-CH_2C(CH_3)_2Cl + SnCl_4 \longrightarrow \sim\!\sim CH_2C^{\oplus}(CH_3)_2SnCl_5^{\ominus}$) proton elimination to DtBP occurs faster than cationation of monomer.

Our second objective of controlling the molecular weight of PαMeSt blocks has been achieved by varying [DtBP] and/or [αMeSt]. For example, $\overline{M}_n$'s increase from 25,000 to 50,000 by increasing [αMeSt] (see Experiments 12-15). Similarly, according to the results obtained in Experiment 19, in the presence of large [DtBP] the molecular weight of the PαMeSt sequence decreases to such an extent that the block copolymer becomes completely n-hexane soluble. Further, yet unpublished data indicate that the $\overline{M}_n$ of PαMeSt sequence can be controlled by varying the relative concentrations of αMeSt/DtBP/$-CH_2C(CH_3)_2Cl$ in the presence of excess $SnCl_4$ [6].

The third objective of obtaining high B_{eff}'s was readily attained by either using low [αMeSt] and/or high [DtBP] in the charge as shown by the data in Table 2.

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