Thermoplastic elastomers by sequential monomer addition

VI. Poly(*p*-methylstyrene-*b*-isobutylene-*b*-*p*-methylstyrene)*

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I. Abstract

The living carbocationic polymerization ($LC^{\oplus}Pzn$) of p-methylstyrene (pMeSt) was achieved by the use of the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ initiating system in the presence of triethylamine (Et_3N) electron donor in $CH_3Cl/\underline{n}C_6H_{14}$ mixed solvent at $-80°C$. Next, the synthesis, characterization, and some physical-mechanical characteristics of a series of poly(p-methylstyrene-<u>b</u>-isobutylene-b-p-methylstyrene)(PpMeSt-PIB-PpMeSt) triblocks is described. The latter synthesis involved two steps in one reactor: 1) The generation of diliving polyisobutylene dications ($^{\oplus}PIB^{\oplus}$) by the dicumyl chloride (DiCumCl)/$TiCl_4$ system under similar conditions followed by 2) The addition of pMeSt and growth of living $PpMeSt^{\oplus}$ cations. The PpMeSt-PIB-PpMeSt triblocks are soft thermoplastic elastomers (TPEs).

I. Introduction

In the course of our fundamental investigation on $LC^{\oplus}Pzn$, we have explored the synthesis by sequential monomer addition of a variety of glassy-rubbery-glassy triblock copolymers exhibiting TPE character (1-4). This paper concerns a demonstration of $LC^{\oplus}Pzn$ of pMeSt, and the subsequent synthesis of PpMeSt-PIB-PpMeSt triblocks. The latters were prepared in two steps in one reactor: The first step was the bidirectional $LC^{\oplus}Pzn$ of isobutylene (IB) to $^{\oplus}PIB^{\oplus}$ up to $\overline{M}_n \sim 50,000g/mole$, followed by the addition of pMeSt and growth of the $PpMeSt^{\oplus}$ blocks until $\overline{M}_n \sim 15,000g/mole$.

III. Experimental

The synthesis of 2-chloro-2,4,4-trimethylpentane (TMPCl) and 1,4-bis(2-chloro-2-propyl)benzene (or p-dicumyl chloride, DiCumCl) have been described (5,6). pMeSt was washed with 10% aqueous NaOH, with distilled water until neutral, dried over $CaCl_2$ and distilled over CaH_2 in vacuo. Et_3N was distilled over KOH. The source and purification of IB, $TiCl_4$, CH_3Cl and $\underline{n}C_6H_{14}$ have been described (7,8). Methanol and toluene (Fisher Scientific Co.) and $CDCl_3$ (Aldrich) were used as received. Polymerizations were carried out in a drybox under dry nitrogen

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in large (75mL) test tubes or 250mL round bottom flask equipped
with mechanical stirrer.

The synthesis of diliving $^{\oplus}$PIB$^{\oplus}$ by the DiCumCl/TiCl$_4$
initiating system in the presence of electron donors (EDs) has
been described (8,9). In the blocking step, prechilled dilute
pMeSt solution in the absence or presence of Et$_3$N was added to
charges stirred at -80°C. After one hour the charges were
poured into a large excess of methanol. The precipitated
products were dissolved in toluene, washed with aqueous HCl,
with distilled water, with aqueous NaHCO$_3$, with distilled water
until neutral, dried over MgSO$_4$, precipitated slowly into
methanol and dried under vacuum at 60°C.

Molecular weights and MWDs were obtained by a Waters high
pressure GPC assembly (Model 6000Å pump, Microstyragel columns
of 10^5, 10^4, 10^3, 500 and 100Å, UV and RI detectors). Elution
counts were calibrated by well-fractionated, narrow MWD PIB and
PSt standards. Block copolymer molecular weights were also
determined by ^{1}H-NMR spectroscopy. ^{1}H-NMR spectra were taken
on a Varian Gemini 200 MHz spectrometer using CDCl$_3$ solvent.

For mechanical property analysis of TPEs, microdumbells
were stamped from homogeneous bubble-free optically clear films
cast from toluene solution. Stress-strain measurements were
carried out on microdumbells at room temperature by an Instron
Tensile Tester Strain rate: 3.94 min^{-1}. Shore A hardness was
measured by a Shore Durometer, according to ASTM D2240. The
averages of 6 samples are recorded.

IV. Results and Discussion

IV.1. LC$^{\oplus}$Pzn of pMeSt

Preparatory to the synthesis of PpMeSt-PIB-PpMeSt, con-
ditions for the Lc$^{\oplus}$Pzn of pMeSt have been developed. This
phase of our research was guided by information accumulated
earlier during research with pMeSt (10,11) and similar systems
(1-4). After some orienting experimentation we found that the
LC$^{\oplus}$Pzn of pMeSt can be achieved by the TMPCl/TiCl$_4$ initiating
system in the presence of Et$_3$N. Figure 1-1 shows the $\bar{M}_n$ versus
W_p (g of polymer obtained) and $\bar{M}_n$ versus I$_{eff}$ (initiator effic-
iency, (g polymer/$\bar{M}_n$)/TMPCl)) plots. Evidently the experimen-
tal $\bar{M}_n$'s are higher than theoretical, i.e., expected by assum-
ing I$_{eff}$ = 100% (see dotted lines in Figure 1-1). Higher than
theoretical $\bar{M}_n$'s are obtained because the rate of initiation
(R$_i$) is relatively lower than that of propagation (R$_p$); in
other words TMPCl/TiCl$_4$ induces relatively slow initiation and
the pMeSt is rapidly consumed by a fraction of initiating
entities leading to I$_{eff}$ <100%.

By plotting the data in Figure 1-1 according to
$-\ln(1-I_{eff})-I_{eff}$) versus [M$_0$] (monomer concentration), i.e., by
the diagnostic plot of a slowly initiating LC$^{\oplus}$Pzn (12), a
straight line without intercept is obtained (see Figure 1-2).
According to this evidence the polymerization of pMeSt under
the above conditions is living with the rate of initiation
lower than that of propagation. This treatment has been used
previously to gain insight into the mechanism of LC$^{\oplus}$Pzn of
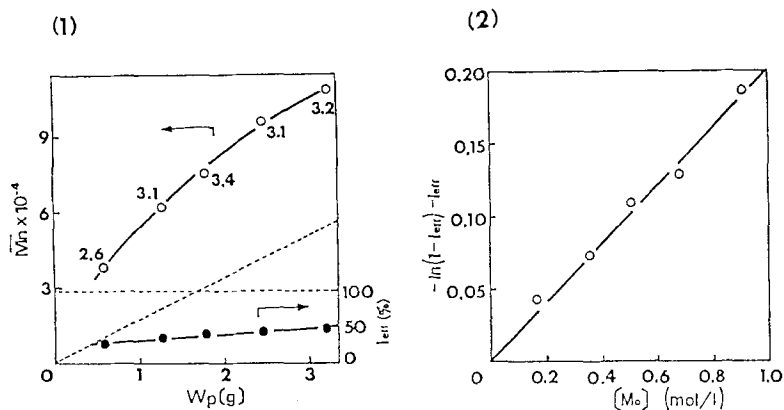p-tert-butylstyrene (ptBuSt) (4) and indene (In) (3).

Figure 1. Living polymerization of pMeSt with slow initiation.
(1) $\overline{M}_n$ versus W_p, and I_{eff} versus W_p plots (the
numbers are $\overline{M}_w/\overline{M}_n$ values). The dotted lines are
theoretical calculated for I_{eff} = 100%.
(2) $-\ln(1-I_{eff})-I_{eff}$ versus $[M_0]$ plot (slow initi-
ation plots). Conditions: $CH_3Cl/\underline{n}C_6H_{14}$ = 4/6(v/v),
-80°C, V_0 = 30 mL, 30 min., AMI method. TMPCl =
6.0×10^{-5}mole, $TiCl_4$ = 6.0×10^{-4}mole, Et_3N =
1.5×10^{-4}mole.

Evidently the $\overset{\oplus}{LC}$Pzn of styrene and styrene-derivatives can be
initiated by living $PIB\overset{\oplus}{}$ or $\overset{\oplus}{}PIB\overset{\oplus}{}$ cations, however, the second
step of these syntheses leading to the target TPEs is
characterized by $R_i < R_p$, which leads to somewhat broad MWDs
products.

IV.2. The Synthesis of PpMeSt-PIB-PpMeSt

Having demonstrated the $\overset{\oplus}{LC}$Pzn of pMeSt, we proceeded with
the synthesis of the PpMeSt-PIB-PpMeSt. Table 1 summarizes the
results obtained in experiments in which pMeSt, $TiCl_4$ and Et_3N
were added to living $\overset{\oplus}{}PIB\overset{\oplus}{}$ charges under various conditions.

In Expt. M1 a mixture of pMeSt and Et_3N was added to the
living $\overset{\oplus}{}PIB\overset{\oplus}{}$ charge. Although the product exhibited a rela-
tively narrow MWD (Aw/An = 1.6), the GPC trace was skewed
toward low elution counts, i.e., it suggested the presence of
high molecular weight constituent (see Figure 2). According to
these results, the blocking in solution of pMeSt from
relatively high molecular weight living $\overset{\oplus}{}PIB\overset{\oplus}{}$ cations is
influenced by a diffusion effect which helps to narrow the MWD
and leads to high I_{eff}. This beneficial diffusion effect is
discussed in detail elsewhere (13).

Subsequently, efforts were made to increase R_i relative to
R_p by increasing the concentration of $TiCl_4$ (Expt. M2) and of
Et_3N (Expt. M3); however, the results were disappointing as
indicated by the relatively broad MWDs (i.e., Aw/An values).
Evidently the rate of pMeSt propagation was still too rapid and
Et_3N added in admixture with the monomer did not sufficiently
reduce R_p.

Table 1. Synthesis of PpMeSt-PIB-PpMeSt

A. Synthesis of the Mid PIB Block[*],[a]

conv.(%)	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[a]	I_{eff}(%)
100	77,600	1.08	90

[*]Conditions: DiCumCl=2.25×10^{-4} mole, TiCl$_4$=3.0×10^{-3} mole, IB=2.81 mole, Et$_3$N=3.0×10^{-4} mole, CH$_3$Cl/$\underline{n}$C$_6$H$_{14}$= 4/6 (v/v), V$_0$=150mL, 4 hours, -80°C

[a]By GPC using PIB calibration.

B. Synthesis and Characterization of Triblocks[*]

Expt.	conv. of pMeSt(%)	$\bar{M}_n$ PpMeSt[a],[b]	$\bar{M}_n$ Triblock[b]	B$_{eff}$[c] (%)	PIB/PpMeSt[d] (wt%)	Aw/An[b]
M1	100	25,600	133,300	92	61/39	1.63
M2	100	33,100	144,000	82	57/43	3.27
M3	100	32,100	145,300	83	61/39	2.88
M4	88	18,200	114,000	97	67/33	1.24
			116,000[d]			

[*]Conditions. The following systems were added to the above living [⊕]PIB[⊕] charges at -80°C.

M1: pMeSt(0.076 mole)+Et$_3$N(4.5×110^{-4} mole) in CH$_3$Cl 12mL/ $\underline{n}$C$_6$H$_{14}$ 18mL

M2: 1)TiCl$_4$(3.0×10^{-3} mole) in CH$_3$Cl 4mL/$\underline{n}$C$_6$H$_{14}$ 6mL, followed by 2)pMeSt(0.076 mole) + Et$_3$N(4.5×10^{-4} mole) in CH$_3$Cl 12mL/$\underline{n}$C$_6$H$_{14}$ 18mL

M3: pMeSt(0.075 mole)+Et$_3$N(1.35×10^{-3} mole) in CH$_3$Cl 12mL/ $\underline{n}$C$_6$H$_{14}$ 18mL

M4: 1)Et$_3$N(4.5×10^{-4} mole) in CH$_3$Cl 4mL/$\underline{n}$C$_6$H$_{14}$ 6mL, followed by 2) pMeSt(0.076 mole) in CH$_3$Cl 12mL/$\underline{n}$C$_6$H$_{14}$ 18mL

[a]Calculated from ($\bar{M}_n$$_{Triblock}$-$\bar{M}_n$$_{PIB}$)/2

[b]By GPC, from peak-height data

[c]Blocking efficiency of pMeSt from [⊕]PIB[⊕]

[d]By ^{1}H-NMR

Table 2. Physical-Mechanical Properties of Select TPEs Comprising a Rubbery PIB Mid-Segment and Glassy Polystyrenic Outer Segments

|	Triblock $\bar{M}_n\times10^{-3}$	Tensile Strength (MPa)	Elong- ation (%)	Modulus at 100% (MPa)	200% (MPa)	300% (MPa)	Shore A	Ref
M4	PpMeSt-PIB-PpMeSt 18-78-18	14.1	420	1.5	4.2	9.1	53	This work
M5	PpMeSt-PIB-PpMeSt 13-42-13	10.1	300	1.9	6.8	–	–	11
S1	PSt-PIB-PSt 13-79-13	13.3	720	0.7	0.9	1.3	–	11
S2	PSt-PIB-PSt 24-62-24	18.7	380	1.9	5.9	12.0	52	1
I1	PIn-PIB-PIn 13-57-13	17.0	400	2.8	6.2	12.0	55	3
B1	Ppt̲BuSt-PIB-Ppt̲BuSt 13-75-13	13.0	590	2.3	3.0	3.8	68	4
B2	Ppt̲BuSt-PIB-Ppt̲BuSt 21-66-21	16.0	550	3.2	4.0	5.0	76	4
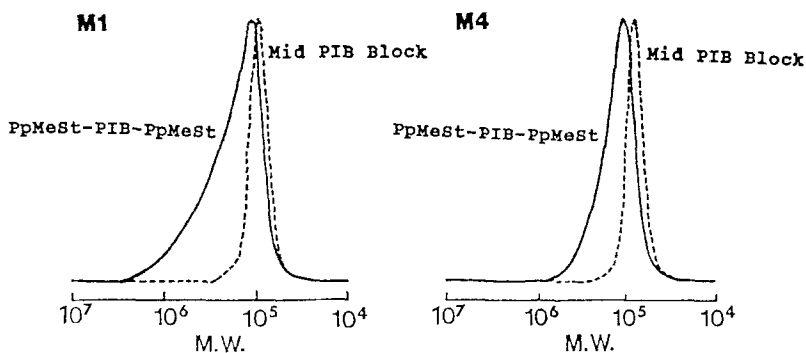
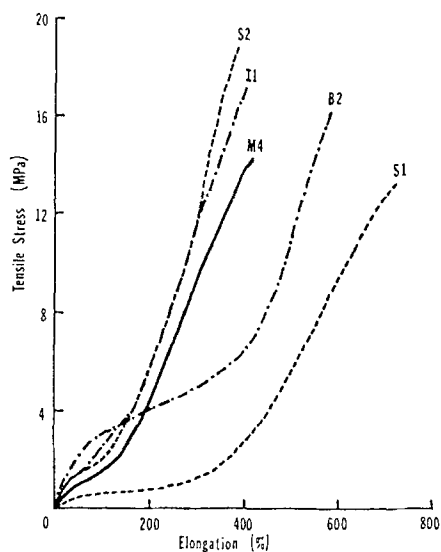Figure 2. GPC (RI) traces of Mid PIB blocks and PpMe-St-PIB-PpMeSt triblocks. Samples M1 and M4 of Table 1.

Figure 3. Stress-Strain traces of PpMeSt-PIB-PpMeSt (M4), PSt-PIB-PSt (S1 and S2), PIn-PIB-PIn (I1) and PptBuSt-PIB-PptBuSt (B2) triblocks (see Table 2).

In Expt. M4 we have added Et_3N to the living $^{\oplus}PIB^{\oplus}$ charge before the pMeSt was introduced. The triblock contained 33 wt% PpMeSt of $\overline{M}_n$ = 18,200 and the blocking efficiency (B_{eff}) was close to quantitative (~97%). The MWD was narrow ($\overline{A}w/\overline{A}n$ = 1.24) and the GPC trace was close to symmetrical (see Figure 2).

It appears that the addition of EDs to living $^{\oplus}$PIB$^{\oplus}$ charges prior to the introduction of the second monomer increases the blocking efficiency. Similar observations have also been made with the poly(indene-<u>b</u>-isobutylene-<u>b</u>-indene) (3) and poly(p-<u>tert</u>-butylstyrene-<u>b</u>-isobutylene-<u>b</u>-p-<u>tert</u>-butyl-styrene) (4) systems.

IV.3. <u>Physical-Mechanical Properties of PpMeSt-PIB-PpMeSt</u>
The tensile properties and hardness of select PpMeSt-PIB-PpMeSt triblocks have been determined. Table 2 and Figure 3 show representative data and stress-strain traces, respectively, obtained with films cast of unextracted triblocks. For comparison, the table and figure also include data of similar TPEs comprising a rubbery PIB mid segment flanked by two polystyrenic outer-segments. All these triblocks combine good mechanical properties with desirably low hardness. Investigations on the synthesis of new PIB-based TPEs are continuing.

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