Carbocationic Polymerization in the Presence of Sterically Hindered Bases. VIII. High Efficiency Grafting of Poly(α-methylstyrene) Branches from Chlorobutyl and Polychloroprene Rubbers in the Presence of Proton Traps

Joseph P. Kennedy[a]; Suhas C. Guhaniyogi[a]

[a] Institute of Polymer Science The University of Akron, Akron, Ohio

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Carbocationic Polymerization in the Presence of Sterically Hindered Bases. VIII. High Efficiency Grafting of Poly(α-methylstyrene) Branches from Chlorobutyl and Polychloroprene Rubbers in the Presence of Proton Traps

JOSEPH P. KENNEDY and SUHAS C. GUHANIYOGI

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325

ABSTRACT

The syntheses of chlorobutyl rubber-g-poly(α-methylstyrene) and poly(chloroprene-g-α-methylstyrene) have been accomplished with 90-97% grafting efficiencies. The synthesis principle involves the initiation of α-methylstyrene polymerization by chlorobutyl rubber or polychloroprene rubber in conjunction with BCl_3 or $SnCl_4$ coinitiators in the presence of 2,6-di-t-butylpyridine proton trap. Selective solvent extraction coupled with molecular weight determination and molecular size distribution indicate satisfactory separation procedures and reliable grafting efficiency data. The close agreement between theoretical and experimental graft copolymer molecular weights suggests that backbone scission or gelation does not occur during grafting. According to graft composition and molecular weight data, 6 to 11 poly(α-methylstyrene) branches have been attached per chlorobutyl or polychloroprene rubber backbones.

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INTRODUCTION

As described in the previous papers of this series of publications [1] concerning the discovery of proton trapping during carbocationic polymerizations and elucidation of the mechanism of proton entrapment, certain nonnucleophilic hindered bases, e.g., 2,6-di-tert-butyl-pyridine (DtBP), are able to intercept the proton (or protonlike species) emerging during chain transfer in these polymerizations and thus lead to a variety of most remarkable phenomena. Depending on the nature of the particular system used, i.e., monomer, Friedel-Crafts acid coinitiator, solvent, and concentration range of these ingredients, the molecular weights may increase or decrease, the molecular weight dispersions may narrow or broaden, and the rates may accelerate or decelerate in the presence of DtBP. Extensive investigations have shown that the effects are system-specific, and generalization from one initiator/coinitiator/monomer/solvent system to another should not be made. However, whatever the specific phenomenon under investigation, the effect of DtBP on polymerization details could always be explained by the concept of terminative proton entrapment during chain transfer to monomer.
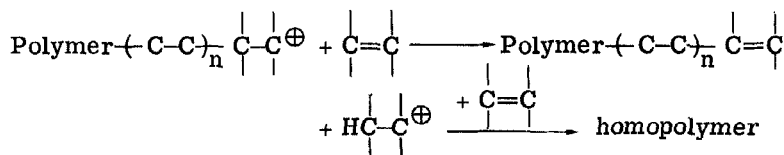
In the course of these fundamental investigations the thought occurred to us that proton entrapment by DtBP could be exploited in the field of cationic block and graft copolymerizations. It is well known [2] that carbocationic grafting is extremely inefficient in the presence of conventional Friedel-Crafts acids like BF_3, $SnCl_4$, $TiCl_4$, and $AlCl_3$, and attempts at grafting cationically polymerizable monomers (e.g., isobutylene) from halogenated backbones (e.g., chlorobutyl rubber, PVC) by these common Lewis acids yield far more homopolymer than grafted polymer. Evidently these coinitiators rapidly initiate cationic homopolymerizations in the presence of subanalytical amounts of protic impurities, and only few branches can arise because the desirable graft initiation step, e.g.,

$$\text{Polymer--Cl} + SnCl_4 + \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C} \longrightarrow \text{Polymer--}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^{\oplus}\ SnCl_5{}^{\ominus}$$
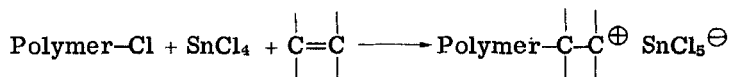
is relatively slow. The inefficiency of this grafting route is further aggravated by the fact that even the few branches that can be generated in this manner will lead to homopolymer by inevitable chain transfer to monomer, i.e., by proton loss from the propagating cation coupled by proton capture of the incoming monomer:

$$\text{Polymer}{+}\text{C--C}{\overset{}{\underset{n}{\big)}}}\ \overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^{\oplus} + \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C} \longrightarrow \text{Polymer}{+}\text{C--C}{\overset{}{\underset{n}{\big)}}}\ \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}$$

$$+\ H\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^{\oplus}\ \xrightarrow{\ +\ \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}\ }\ \text{homopolymer}$$

Invariably, the amount of true graft (or block) copolymer formed in such experiments must remain negligible.

We theorized that the above undesirable reactions leading to massive homopolymer formation could be avoided and high grafting efficiencies could be achieved by conducting graftings in the essential absence of moisture and in the presence of DtBP proton trap. This paper concerns an experimental exploration of this idea; specifically, the grafting of α-methylstyrene (α-MeSt) from chlorobutyl rubber (Cl-IIR) and polychloroprene rubber (CR) in the (absence and) presence of DtBP, and a demonstration that virtually complete graftings can be obtained under routine laboratory conditions by the use of DtBP.

EXPERIMENTAL

αMeSt (Aldrich, 99%) was purified by removing the inhibitor, refluxing over CaH_2, and distilling under dry nitrogen. The middle cut was dried over a shiny Na-film under vacuum, distilled, dried again over a shiny Na-film, sealed in ampules with calibrated breakseals, and stored at -30°C in the dark. DtBP (Chemical Samples, Co., 99%) was dried over dry BaO under vacuum and distilled. $SnCl_4$ (Alfa, Ultrapure) was purified according to Overberger [3]. It was further treated several times with anhydrous P_2O_5 under vacuum, distilled, and the middle fraction was taken. BCl_3 (Linde, Specialty Grade) was dried over a series of Na-films. CH_2Cl_2 (Eastman Kodak, Reagent Grade) was refluxed with Et_3Al under dry nitrogen and distilled. The middle fraction of the distillate was transferred to the vacuum line where it was dried over BaO and a series of shiny Na-films before use. Methylcyclohexane (Eastman Kodak, Reagent Grade) was refluxed with fuming sulfuric acid, washed till neutral, dried, and distilled under nitrogen. The middle fraction was further dried over shiny Na-films under vacuum. The solutions of DtBP, $SnCl_4$, and BCl_3 were prepared with CH_2Cl_2 under vacuum and sealed into ampules with calibrated breakseals. The materials were stored in the dark at -30°C.

Purification of CR (Neoprene W, E. I. du Pont de Nomours and Co.) and Cl-IIR (Enjay HT-1066, Exxon Chemicals Co.) has been described [4, 5].

PROCEDURES

Graft Copolymerization. Ampules equipped with breakseals and magnetically activable hammers containing the $SnCl_4$ or BCl_3 coinitiator, DtBP, αMeSt, and methanol were connected to a 5-arm reaction vessel (150 mL capacity) sealed to the high vacuum apparatus. The chlorinated rubber initiators Cl-IIR or CR were

```
                    ┌─────────────────────────────────┐
                    │ CR + CR-g-PαMeSt + PαMeSt        │
                    └─────────────────────────────────┘
                                    │
                          Methyl ethyl ketone
              ┌─────────────────────┴──────────────────────┐
         Soluble                                        Insoluble
┌──────────────────────────────┐        ┌──────────────────────────────────┐
│ CR-g-PαMeSt + PαMeSt          │        │ CR + CR-g-PαMeSt                  │
│ #3   53%       -              │        │ #3   47% (23 wt.% PαMeSt)         │
│ #4   15% (35 wt.% PαMeSt)     │        │ #4   85% (30 wt.%    "    )        │
└──────────────────────────────┘        └──────────────────────────────────┘
              │                                           │
      1-Nitropropane                            60% acetone +
                                                40% n-Pentane
    ┌─────────┴──────────┐
 Soluble            Insoluble
┌──────────┐   ┌──────────────────────────────┐
│ PαMeSt   │   │ CR-g-PαMeSt                   │
│ #3  52%  │   │ #3   1%                       │
│ #4  2.5% │   │ #4   12.5%  (24 wt.% PαMeSt)  │
└──────────┘   └──────────────────────────────┘
    ┌─────────────────────┴──────────────────────┐
 Soluble                                      Insoluble
┌──────────────────────────────┐   ┌──────────────────────────────┐
│ CR + CR-g-PαMeSt              │   │ CR-g-PαMeSt                   │
│ #3   negligible               │   │ #3   47% (23 wt.% PαMeSt)     │
│ #4   2% (10 wt.% PαMeSt)      │   │ #4   83% (10 wt.% PαMeSt)     │
└──────────────────────────────┘   └──────────────────────────────┘
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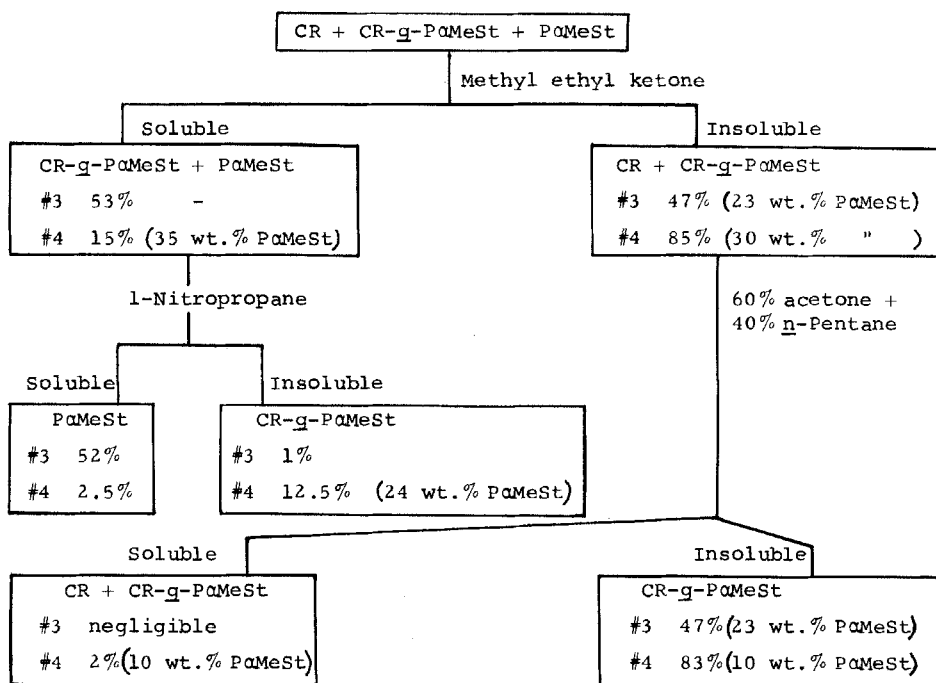
FIG. 1. Selective solvent extraction scheme used in experiments with polychloroprene rubber (MEK Method). The numbers in the boxes refer to experiments summarized in Tables 1 and 2.

introduced into the reactor via the 5th arm. The rubbers were dried under high vacuum (10^{-7} mmHg) for 24 h. The whole assembly was covered with aluminum foil to exclude light. αMeSt was kept at 0°C during these manipulations. The solvents were introduced into the reaction vessel and after a few freeze-thaw cycles the reactor was sealed under vacuum and removed from the vacuum line. The reactor was equilibrated at -50 ± 1°C and after the rubber had dissolved, αMeSt and DtBP solutions were added. The charge was mixed and the polymerization was triggered by introducing the coinitiator and thoroughly mixing the reactants. After suitable times at -50°, during which period the homogeneous charges were frequently agitated, graftings were terminated by adding methanol through the shattered breakseal. The reactor was brought to room temperature, the glass arms were filed and broken off, and the clear, homogeneous charges were filtered to remove glass pieces. Grafts were precipitated into methanol and dried in vacuum (20°C, with occasional dry nitrogen purging) to constant weight.

```
                    ┌─────────────────────────────────┐
                    │  CR + CR-g-PαMeSt + PαMeSt       │
                    └─────────────────────────────────┘
                                    │
                              1-nitropropane

   Soluble │                                    │ Insoluble
   ┌────────────────┐         ┌──────────────────────────────────────┐
   │  PαMeSt        │         │      CR + CR-g-PαMeSt                 │
   │                │         │                                      │
   │  #9    42%     │         │  #9    58% (29 wt.% PαMeSt)          │
   │                │         │                                      │
   │  #10   10%     │         │  #10   90% (35 wt.% PαMeSt)          │
   └────────────────┘         └──────────────────────────────────────┘
                                              │
                              60% Acetone + 40% n-Pentane

   Soluble │                                    │ Insoluble
   ┌──────────────────────────────┐   ┌──────────────────────────────────────┐
   │  CR + CR-g-PαMeSt            │   │      CR-g-PαMeSt                      │
   │                              │   │                                      │
   │  #9   negligible, < 0.2%    │   │  #9    58% (29 wt.% PαMeSt)          │
   │                              │   │                                      │
   │  #10  0%                    │   │  #10   90% (35 wt.% PαMeSt)          │
   └──────────────────────────────┘   └──────────────────────────────────────┘
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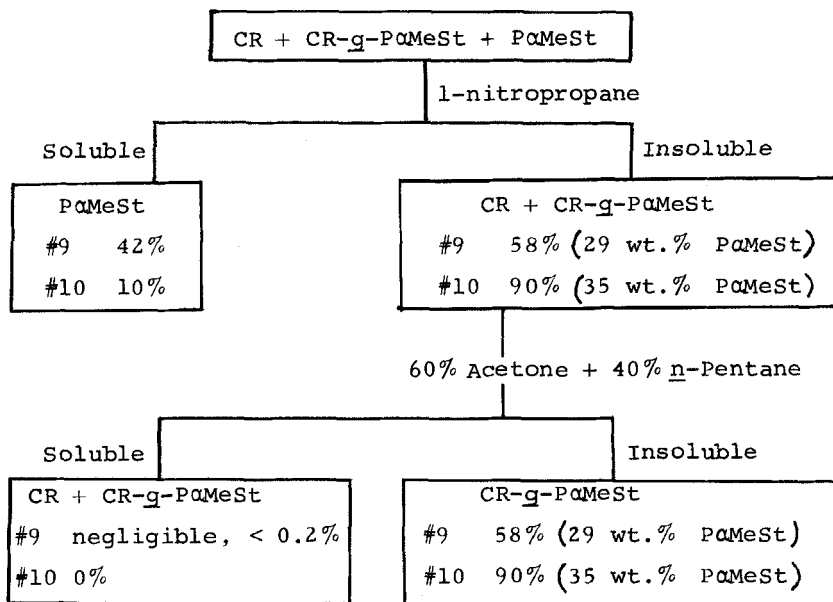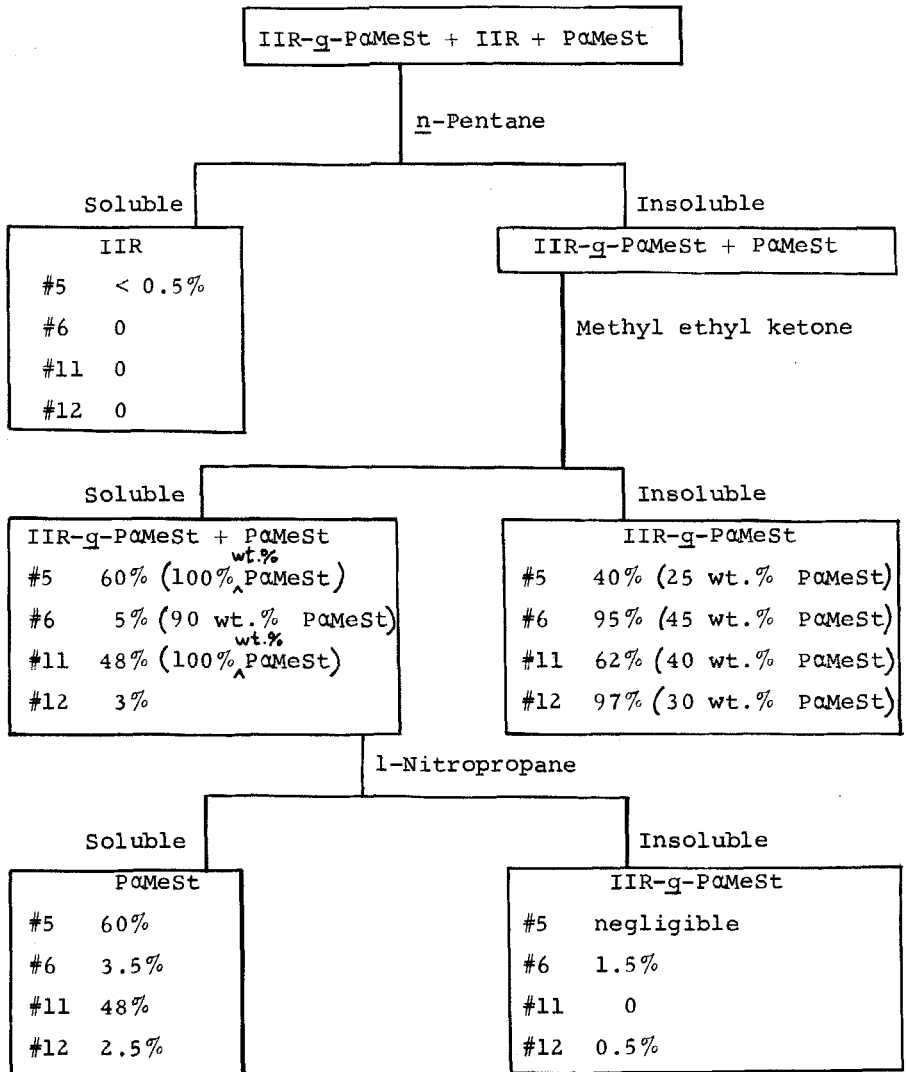
FIG. 2. Selective solvent extraction scheme used in experiments with polychloroprene rubber (1-Nitropropane Method). The numbers in the boxes refer to experiments summarized in Tables 1 and 2.

Molecular weights were determined using a Hewlett Packard 503 High Speed Membrane Osmometer with toluene at 37°C. GPC analyses were carried out with a Waters Model 6000A high pressure pump and a R401 differential refractometer detector. A series of Styragel columns (pore sizes: 500, 10^3, 10^4, 10^5, and 10^6 Å) were used. Flow rate of THF solutions was 2 mL/min.

Graft Separation, Purification.   The crude products of graft copolymerizations were subjected to a series of selective extractions to determine the individual components obtained.

The procedures outlined in Figs. 1 to 3 were developed for the characterization and analysis of products obtained in experiments with CR and Cl-IIR initiators. The schemes are self-explanatory. The amounts of the individual fractions obtained (wt% by gravimetry) and their PαMeSt contents (wt% by NMR) are shown. 1-Nitropropane was found to be an excellent selective solvent for PαMeSt, see Fig. 2. PαMeSt of $\overline{M}_n \approx 5 \times 10^4$ was found to be soluble after agitating with 1-nitropropane for 20 h whereas Cl-IIR and CR were completely insoluble. IIR in Fig. 3 denotes butyl rubber (isobutylene-isoprene rubber); this abbreviation is meant to indicate that the Cl atom in Cl-IIR has been lost during grafting.
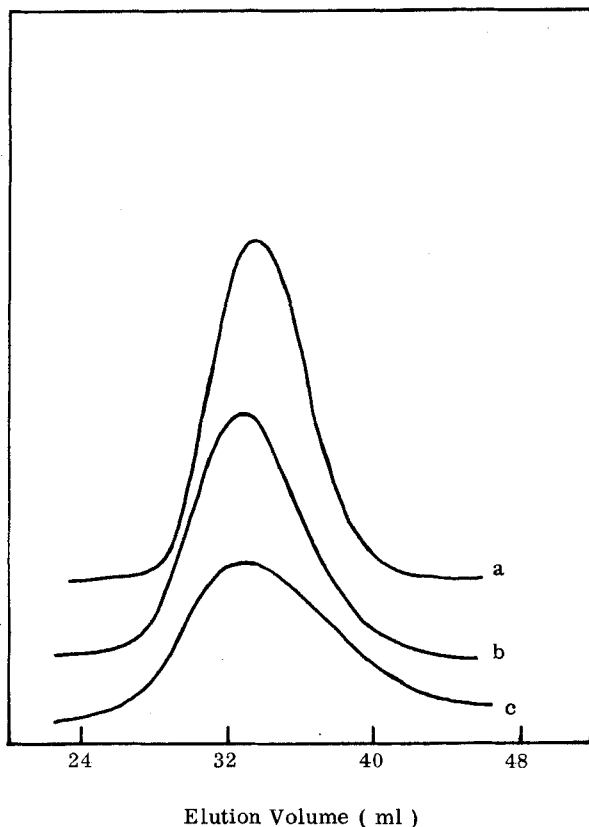
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              ┌─────────────────────────────────────┐
              │  IIR-g-PαMeSt + IIR + PαMeSt         │
              └─────────────────────────────────────┘
                              │
                         n-Pentane
           ┌──────────────────┴──────────────────────┐
        Soluble                                  Insoluble
   ┌──────────────┐                    ┌──────────────────────────┐
   │     IIR      │                    │  IIR-g-PαMeSt + PαMeSt    │
   │ #5   < 0.5%  │                    └──────────────────────────┘
   │ #6    0      │                              │
   │ #11   0      │                    Methyl ethyl ketone
   │ #12   0      │
   └──────────────┘
           ┌──────────────────┴──────────────────────┐
        Soluble                                  Insoluble
```

IIR-g-PαMeSt + PαMeSt

#5	60% (100% wt.% PαMeSt)
#6	5% (90 wt.% PαMeSt)
#11	48% (100% wt.% PαMeSt)
#12	3%

IIR-g-PαMeSt

#5	40% (25 wt.% PαMeSt)
#6	95% (45 wt.% PαMeSt)
#11	62% (40 wt.% PαMeSt)
#12	97% (30 wt.% PαMeSt)

1-Nitropropane

Soluble — PαMeSt

#5	60%
#6	3.5%
#11	48%
#12	2.5%

Insoluble — IIR-g-PαMeSt

#5	negligible
#6	1.5%
#11	0
#12	0.5%

FIG. 3. Selective solvent extraction scheme used in experiments with chlorobutyl rubber. The numbers in the boxes refer to experiments shown in Tables 1 and 2.

Elution Volume (ml)
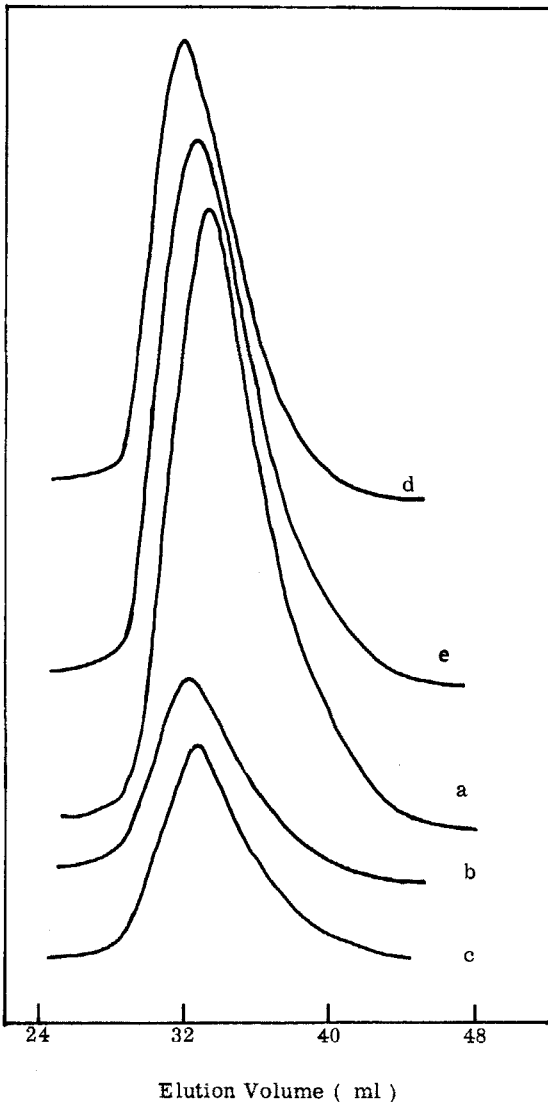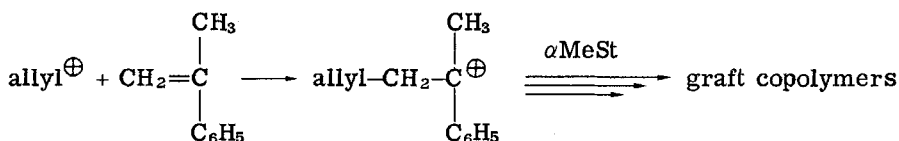
FIG. 4. Gel permeation chromatograms of CR and CR-g-PαMeSt (nonnormalized): (a) pure CR; (b) and (c) pure CR-g-PαMeSt obtained from Experiments 4 and 10, respectively.

Characterization. The composition of the various fractions obtained by selective solvent extractions was determined by ^{1}H NMR spectroscopy using a Varian T-60 instrument.

Grafting efficiency is expressed by $G_{eff} = G_{P\alpha MeSt}/(G_{P\alpha MeSt} + H_{P\alpha MeSt})$ where $G_{P\alpha MeSt}$ and $H_{P\alpha MeSt}$ are the grafted- and homo-PαMeSt, respectively. The measure of branch frequency is the b/B ratio (b = branch, B = backbone) calculated by

$$\frac{b}{B} = \frac{\overline{M}_B X_b/100}{\overline{M}_b(1 - X_b/100)}$$

FIG. 5. Gel permeation chromatograms of Cl-IIR and IIR-g-PαMeSt (nonnormalized): (a) pure Cl-IIR; (b) and (c) crude IIR-g-PαMeSt obtained from Experiments 6 and 12, respectively; (d) and (e) pure IIR-g-PαMeSt from Experiments 6 and 12, respectively.

where $\overline{M}_B$, $\overline{M}_b$, and X_b are the $\overline{M}_n$ of backbone, $\overline{M}_n$ of a branch, and wt% PαMeSt in the pure graft, respectively. $\overline{M}_B$ has been determined directly by osmometry, $\overline{M}_B$ of Cl-IIR = 150,000 and of CR = 140,000, whereas $\overline{M}_b$ has been obtained indirectly by determining $\overline{M}_n$'s of PαMeSt's produced in graftings in the presence of DtBP and assuming that the $\overline{M}_n$ of the free PαMeSt obtained by extraction is equal to the $\overline{M}_n$ of PαMeSt branches. That this assumption provides correct $\overline{M}_n$ estimates has been substantiated earlier by direct experiments in the similar poly(chloroprene-g-styrene) system [4].

The homogeneity of select fractions has been examined by GPC. Figures 4 and 5 show GPC traces of the "naked" backbones used and representative graft copolymers.

RESULTS AND DISCUSSION

Previous experience in the area of graft copolymerization [2] dictated the particular system selected for this study. It has been amply demonstrated that both chlorinated butyl rubber [6] and poly-chloroprene [7, 8] contain a sufficient number of substituted allylic chlorines for efficient cationic grafting with alkylaluminum compounds. It was assumed that the same chlorines will also be effective graft-initiating sites with the conventional Lewis acids, SnCl₄ and BCl₃, selected for these investigations. Figure 6 shows the overall struc-tures of these rubbers, the allylic chlorines they are known to contain [6-8], and the allylic cations they would yield in the presence of conventional Lewis acid coinitiators such as SnCl₄ and BCl₃. The substituted allylic carbocations arising along either the Cl-IIR or

CR chains (allyl$^{\oplus}$) would be expected to induce the polymerization of αMeSt and lead to PαMeSt branches:

$$\text{allyl}^{\oplus} + CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}} \longrightarrow \text{allyl}{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}{\oplus} \xrightarrow{\;\;\alpha MeSt\;\;} \text{graft copolymers}$$

In the absence of H₂O, grafting could only start at the backbone car-benium ion, and homopolymer formation, at least by this process, could be avoided.
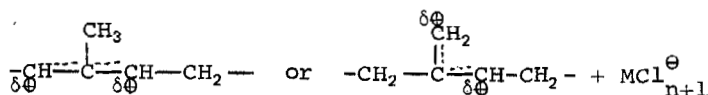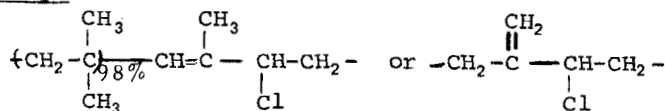
The second source of homopolymer could also be avoided in the presence of DtBP since the proton trap would intercept the proton emerging during chain transfer to monomer, a process known to occur during carbocationic growth of PαMeSt$^{\oplus}$:

$$\sim CH_2-\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^{\oplus} \quad \underset{N}{\bigotimes} \quad \longrightarrow \quad \sim CH_2-\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_2}{\parallel}}{C}} \quad + \quad \underset{N}{\overset{H}{\underset{\oplus}{\bigotimes}}}$$

(Proton loss may also occur from the $-CH_2-$ group or may involve indane formation; however, the exact site of proton loss would not change the fundamentals.)

In view of these principles, grafting experiments have been carried out in the absence of moisture (under high vacuum conditions) by

Chlorobutyl

$$\underset{\underset{CH_3}{|}}{+CH_2-\overset{\overset{CH_3}{|}}{\underset{98\%}{C}}}CH=\overset{\overset{CH_3}{|}}{C}-\underset{\underset{Cl}{|}}{CH-CH_2}- \quad or \quad -CH_2-\overset{\overset{CH_2}{\parallel}}{C}-\underset{\underset{Cl}{|}}{CH-CH_2}-$$

$$\Big\downarrow MCl_n$$

$$-\overset{\delta\oplus}{CH}\overset{\overset{CH_3}{|}}{\underset{\delta\oplus}{C}}CH-CH_2- \quad or \quad -CH_2-\overset{\overset{\delta\oplus}{CH_2}}{\underset{\delta\oplus}{C}}CH-CH_2- \quad + \quad MCl_{n+1}^{\ominus}$$

Polychloroprene

$$\underset{96\%}{+CH_2-\overset{\overset{Cl}{|}}{C}=CH-CH_2+} \quad \underset{1.7\%}{+CH_2-\underset{\underset{HC=CH_2}{|}}{\overset{\overset{Cl}{|}}{C}}+} \quad or \quad \underset{0.8\%}{+CH_2-\underset{\underset{HC-CH_2Cl}{\parallel}}{C}+} \quad or \underset{\underset{CH}{\parallel}}{+CH_2-\underset{\underset{C-Cl}{|}}{CH}+}$$

$$\Big\downarrow MCl_n$$

$$-CH_2-\overset{\overset{\delta\oplus}{C}}{\underset{HC\cdots\overset{\delta\oplus}{CH_2}}{\parallel}}- \quad + \quad MCl_{n+1}^{\ominus}$$
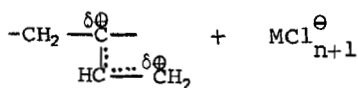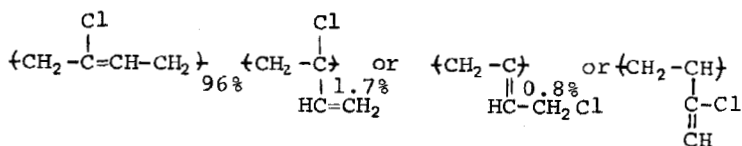
FIG. 6. Structural elements in chlorobutyl rubber and polychloroprene rubber that yield graft-initiating allylic cations.

TABLE 1. Syntheses of CR-g-PαMeSt and IIR-g-PαMeSt with $SnCl_4$ and BCl_3 in the Absence and Presence of DtBP at -50 ± 1°C

No.	Polymer (g)	Solvents		Coinitiator: mol × 10^4	DtBP (mol × 10^4)	αMeSt (mol × 10^2)	Time (h)	αMeSt conversion (%)	Free PαMeSt (%)	G_{eff} (%)
		CH_2Cl_2 (mL)	MeCH (mL)							
1	-	100	-	$SnCl_4$: 4.00	-	2.30	5	100	-	-
1a	-	100	-	$SnCl_4$: 2.00	-	2.30	0.3	20	-	-
2	-	100	-	$SnCl_4$: 4.00	1.00	2.30	5	3	-	-
3	CR: 0.85	90	10	$SnCl_4$: 4.00	-	2.30	5	97	52.0	48.0
4	CR: 1.20	90	10	$SnCl_4$: 5.34	1.45	1.15	5	85	2.5	97.5
5	Cl-IIR: 0.80	50	50	$SnCl_4$: 4.00	-	1.15	5	100	60.0	40.0
6	Cl-IIR: 0.92	50	50	$SnCl_4$: 10.70	0.70	1.15	6	93	3.5	96.5
7	-	100	-	BCl_3: 9.66	-	2.30	5	88	-	-
7a	-	100	-	BCl_3: 2.15	-	2.30	0.3	8	-	-
8	-	100	-	BCl_3: 9.66	0.60	2.30	4	Negligible	-	-
9	CR: 0.79	90	10	BCl_3: 8.60	-	2.30	5	98	42.0	58.0
10	CR: 1.06	90	10	BCl_3: 11.00	0.60	1.15	3	90	10.0	90.0
11	Cl-IIR: 0.74	50	50	BCl_3: 8.60	-	2.30	5	95	36.0	64.0
12	Cl-IIR: 0.92	50	50	BCl_3: 8.00	2.02	1.15	4	96	2.5	97.5

TABLE 2. Characterization of Cr-g-PαMeSt and IIR-g-PαMeSt

No.		$\overline{M}_B$ $\times 10^{-3}$	X_b (overall) (%)	$\overline{M}_n$ (graft) Theoretical $\times 10^{-3}$	Experimental $\times 10^{-3}$	Free PαMeSt, $\overline{M}_n$ $\times 10^{-3}$	b/B
3	CR-g-PαMeSt	140	23	182	170	6	6.9
4	"	140	30	200	180	10	6.0
5	IIR-g-PαMeSt	150	25	200	185	20	2.5
6	"	150	45	270	230	15	8.0
9	CR-g-PαMeSt	140	29	197	180	7	8.2
10	"	140	35	215	200	10	7.5
11	IIR-g-PαMeSt	150	40	250	220	17	5.9
12	"	150	30	210	200	6	11.0

adding BCl_3 or $SnCl_4$ coinitiator solutions to quiescent Cl-IIR/αMeSt/ DtBP or CR/αMeSt/DtBP systems in suitable solutions at -50°C. Tables 1 and 2 show synthesis conditions and characterization data, respectively. Experimentation started with "control" runs, i.e., runs in which $SnCl_4$ or BCl_3 solutions were added to αMeSt in the absence or presence of DtBP (Experiments 1, 1a, 2, 7, 7a, and 8 in Table 1).

The relatively large amounts of PαMeSt obtained in the absence of CR or Cl-IIR initiators (i.e., 20 and 100%, and 8 and 88% PαMeSt at 20 min and 5 h in Experiments 1, 1a, 7, and 7a) are most likely due to initiation by a small amount of unscavengable proton source (in spite of high vacuum drying) followed by continuous unabated chain transfer to monomer. Initiation must be slow since conversions are relatively low after 20 min. Independent polymerization experiments carried out under "conventional" conditions, i.e., in open systems in a dry box under nitrogen, resulted in 100% conversions within 2-3 min (not shown in Table 1). The above 100% conversion results also indicate that the polymerization of αMeSt under the conditions employed is "terminationless."

The results of Experiments 2 and 8 forcefully indicate the effect of DtBP: In the presence of proton trap, conversions remain negligible even after 5 h of reaction!

Grafting of αMeSt from CR or Cl-IIR with $SnCl_4$ or BCl_3 in the absence of DtBP occurs readily (Experiments 3, 5 and 9, 11) and polymerizations go to completion. This is not too surprising considering the relatively long reaction times (3-6 h), highly reactive coinitiators, and the propensity of αMeSt to undergo chain transfer. Since αMeSt conversions were invariably 100% in these runs, termination must have been absent. Grafting efficiencies, however, were much less than 100% (i.e., ~ 40% with Cl-IIR/$SnCl_4$, 48% with CR/ $SnCl_4$, 64% with Cl-IIR/BCl_3, and 58% with CR/BCl_3) which indicates the operational presence of chain transfer in these systems.

Graft characterization data are compiled in Table 2. The close agreement between the theoretical and experimental molecular weights of graft copolymers (Columns 5 and 6) strongly suggest the absence of undesirable side reactions, e.g., chain scission of the backbone, crosslinking, during graft copolymerization. This conclusion is further substantiated by the GPC traces shown in Figs. 4 and 5: After grafting, the traces remained monomodal and the position of their maxima shifted toward lower elution volumes (higher molecular weights).

The effect of DtBP on grafting efficiency G_{eff} is seen by comparing results of Experiments 3 with 4, 5 with 6, 9 with 10, and 11 with 12. While G_{eff}'s remain relatively low in experiments carried out in the absence of DtBP, G_{eff} approaches 100% in the presence of the proton trap. The fact that these results have been obtained after extremely long grafting times (3-6 h) should be emphasized: shorter grafting

times (<20 min) would have led to much larger differences in G_{eff} as seen from the αMeSt conversion data in Experiments 1a and 7a.

These results corroborate the basic proposition that DtBP intercepts the proton during chain transfer to monomer and thus prevents homopolymer generation.

At first glance the high αMeSt conversions obtained in the presence of DtBP (Experiments 4, 6, 10, and 12) may appear unusual. Evidently the branches grow until chain transfer to monomer occurs, and since this event seems to arise only about once per kinetic chain (G_{eff} values obtained in the presence of DtBP are about a factor of two higher than those obtained in the absence of proton trap), the number of actively growing branches, even in the presence of DtBP, suffices to consume the available low amount (~ 0.1-0.2 $\underline{M}$) of αMeSt.

Great circumspect must be exercised when intercomparing the analytical data shown in Table 2, since many of the grafting experiments had to be necessarily carried out under somewhat different conditions dictated by the nature of the two different backbones and Friedel-Crafts acid coinitiators used. Some cautious generalizations can, however, be made: Grafting experiments in the absence of DtBP (Nos. 3, 5, 9, and 11) resulted in relatively low G_{eff} of 40-64% with 25-40% PαMeSt incorporation whereas in the presence of DtBP, G_{eff} = 90-97.5% and 30-45% PαMeSt incorporation was obtained. The average b/B values for CR-g-PαMeSt were 4.7 and 7.0, and for IIR-g-PαMeSt 7.0 and 8.7 in the absence and presence of DtBP, respectively.

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