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Styryl-Telechelic Polyisobutylenes. I. Synthesis of Linear and Tri-Arm Star Styryl-Telechelic Polyisobutylenes

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ABSTRACT

New linear and three-arm star polyisobutylenes carrying two and three terminal styryl endgroups, i.e., $\bar{F}_n = 2.0$ and 3.0, respectively, have been prepared. The synthesis of these styryl-telechelic polyisobutylenes involved Friedel-Crafts alkylation by linear and/or three-arm star polyisobutylenes carrying tertiary chlorine endgroups of (2-bromoethyl)benzene or β-bromoisopropylbenzene followed by dehydrobromination. According to model studies, ^{1}H-NMR, and UV spectroscopy, the conversions are essentially quantitative. These new terminally di- and tri-styrenated polyisobutylenes may be useful for the preparation of block copolymers and as cross-linking materials.

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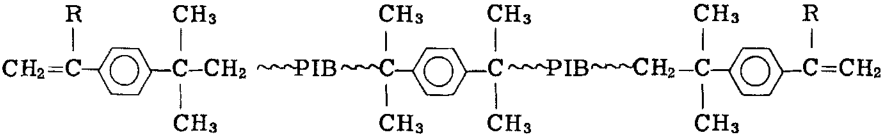
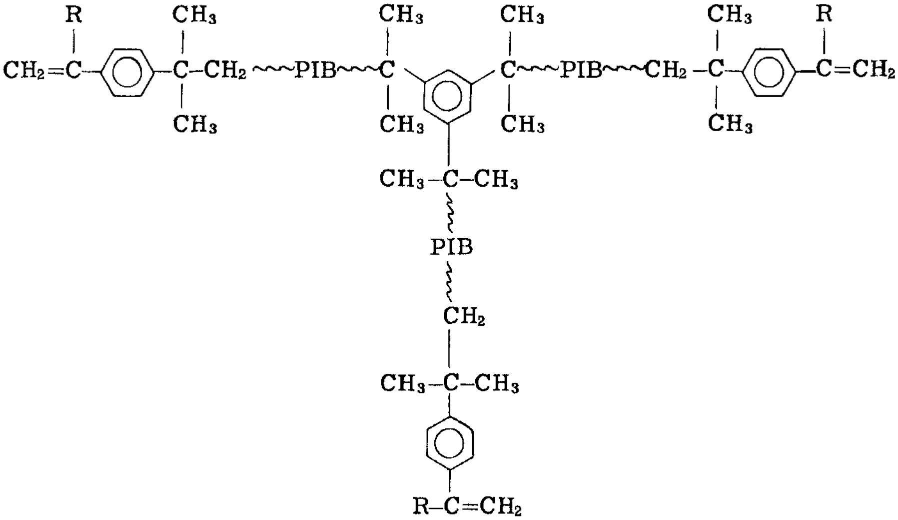
INTRODUCTION

Polymers carrying reactive endgroups are of interest for block and/or graft copolymer syntheses, endgroup derivatization, chain extension, and cross-linking. Previous papers in this series concerned the synthesis of linear and three-arm star polyisobutylenes carrying tertiary chlorine endgroups [1, 2] and their derivatization [2-5]. As an extension of these investigations, tertiary chlorine-telechelic polyisobutylenes have been converted quantitatively into styryl-telechelic polyisobutylenes. These prepolymers may be potentially useful in many applications, e.g., cross-linking agents and telechelic macromers for the preparation of new copolymers.

This paper concerns the synthesis and characterization of the following linear and three-arm star styryl-telechelic polyisobutylenes:



where R = H or CH_3



where R = H or CH_3.

EXPERIMENTAL

Materials

The syntheses and purification of linear and three-arm star PIB's carrying tertchlorine endgroups have been described [1, 2]. n-Hexane (Fisher Scientific) was treated with fuming sulfuric acid at refluxing temperature overnight, washed with water, and distilled over calcium hydride under dry nitrogen before use. Tetrahydrofuran and methylene chloride (Fisher Scientific) were refluxed over calcium hydride under nitrogen overnight and distilled before use. 2-Chloro-2,4,4-trimethylpentane (ClTMP) was prepared by hydrochlorination of the 2,4,4-trimethyl-1-pentene (Aldrich). (2-Bromoethyl)benzene (BrEBz) and β-bromoisopropylbenzene (BrPBz) (Aldrich) were stored over 3Å Molecular Sieves and used as received. Aluminum chloride and potassium t-butoxide (Aldrich) were used as received.

Techniques

^{1}H-NMR analyses were carried out using a Varian Associates T-60 NMR Spectrometer. Solutions of approximately 10% polymer and 5% small compounds in CCl_4 were employed.

Molecular weights were determined by a Waters Associates 6000A high pressure GPC equipped with dual UV and RI detectors and μ-Styragel columns of 100, 500, 10^4, 10^5, and 10^5 Å. Approximately 0.2 mL of 0.2% polymer in THF was used. The flow rate was 1 mL/min. The calibration was effected with well-fractionated PIB samples.

IR spectra were obtained by the use of a Perkin-Elmer 521 Grafting Infrared Spectrophotometer.

UV spectra were recorded on a Perkin-Elmer 550 A UV/VIS Spectrophotometer. Solutions of 0.5-5 × 10^{-5} M p-t-butylstyrene and IV in cyclohexane were used to construct the UV calibration curves.

Model Compound Syntheses

(a) p-(2-Bromoethyl)(2,2,4,4-tetramethylbutyl)benzene (I) and p-(β-Bromoisopropyl)(2,2,4,4-tetramethylbutyl)benzene (II)

A three-necked flask equipped with stirrer was charged with 1.48 g ClTMP (10^{-2} mol), 5.46 mL BrEBz (4 × 10^{-2} mol), 4 mL n-hexane, and 2 mL CH_2Cl_2. The solution was cooled to -50 to -55°C, then 0.13 g $AlCl_3$ (10^{-3} mol) in 1 mL CH_2Cl_2 was added and stirred for 2 h. The reaction was stopped by adding precooled methanol. Subsequently, the mixture was washed with distilled water, dried with $MgSO_4$, stripped of solvents, and analyzed by ^{1}H-NMR. The same procedure was employed for the synthesis of II.

(b) 4-(2,2,4,4-Tetramethylbutyl)styrene (III) and 4-(2,2,4,4-Tetramethylbutyl)-α-methylstyrene (IV)

To a solution of ~ 3.0 g I in 10 mL THF in a 100-mL three-necked flask equipped with stirrer, dropping funnel, and gas inlet tube was added 5.6 g t-BuOK (5×10^{-2} mol) in 30 mL THF over 10 min while stirring. After 30 additional minutes of stirring, the solution was poured into 100 mL n-hexane. Subsequently, the mixture was washed with distilled water, dried with $MgSO_4$, and fractionally distilled over CaH_2 to give 1.2 g III (bp 95°C, 0.1 mmHg). The same procedure was employed for the synthesis of IV, and it yielded 3.7 g IV (bp 101°C, 0.1 mmHg).

Styryl-Telechelic Polyisobutylene Synthesis

(a) α,ω-Di[(2-bromoethyl)phenyl]polyisobutylene (Va) and α,ω-Di[β-bromoisopropyl)phenyl]polyisobutylene (Vb)

Friedel-Crafts alkylation reactions were carried out in three-necked flasks equipped with stirrer and dry nitrogen inlet tube. A representative reaction is described: A flask was charged with 16 g α,ω-di(tert-chlorine)polyisobutylene ($\overline{M}_n$ = 3100), 32 mL n-hexane, 15 mL CH_2Cl_2, and 42 mL (2-bromoethyl)benzene (~60 times molar excess of Cl-PIB-Cl). The solution was stirred and cooled to -50 to -55°C, then 5.2 g $AlCl_3$ (~8 times molar excess of Cl-PIB-Cl) in 5 mL n-hexane were added under a dry nitrogen atmosphere. The mixture was allowed to react under vigorous stirring for 5 h, then the reaction was quenched by adding 20-mL prechilled methanol. To remove the excess of (2-bromoethyl)benzene, the polymer was precipitated three times into methanol, dissolved in n-hexane, washed with distilled water, and dried with anhydrous $MgSO_4$. After filtration the solvent was evaporated and the Va product was further dried under vacuum at ambient temperature. The same procedure was used for the preparation of Vb except p-(β-bromoisopropyl)benzene was employed.

(b) α,ω-Di(styryl)polyisobutylene (VIa) and α,ω-Di(α-methylstyryl)polyisobutylene (VIb)

A 5% (w/w) solution of 15 g Va in 300 mL dry THF was charged into a three-necked flask equipped with stirrer and condenser under dry nitrogen, then 3.36 g t-BuOK (~6 times molar excess of Va) in 15 mL THF was added. After stirring 24 h at room temperature, 300 mL n-hexane was added. Subsequently, the solution was washed with distilled water several times, dried with $MgSO_4$, and filtered. Finally, the solvent was evaporated and the product was further dried under vacuum at ambient temperature to give VIa. The synthesis of VIb was carried out by the same procedure.

RESULTS AND DISCUSSION

Model Experiments

Preparatory to the derivatizations of tertiary chlorine-telechelic polyisobutylene (Cl-PIB-Cl), model Friedel-Crafts alkylations were carried out using ClTMP, which exactly mimics the endgroup structure of Cl-PIB-Cl. Figure 1(a) shows the ^{1}H-NMR spectrum of the ClTMP plus BrEBz charge. After $AlCl_3$ addition, the product was dehydrobrominated and the spectrum shown in Fig. 1(b) was obtained. The singlets at 1.0, 1.57, and 1.8 ppm associated, respectively, with the $-C(CH_3)_3$, $-CH_2(\underline{CH_3})_2Cl$, and $-\underline{CH_2}(CH_3)_2Cl$ protons of the ClTMP disappeared and new resonances appeared at 0.68, 1.38 and 1.68 ppm,

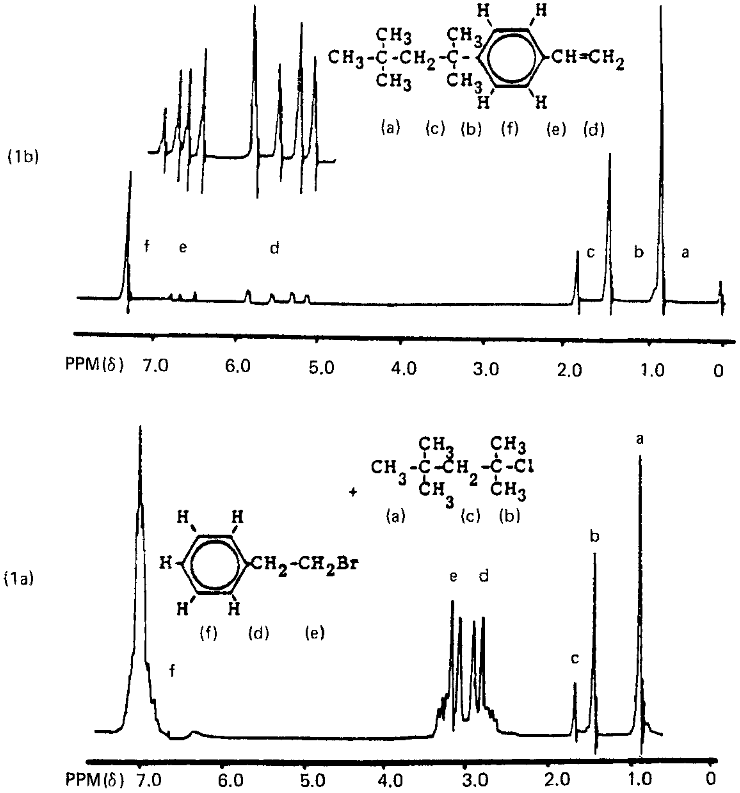


FIG. 1. ^{1}H-NMR spectra of (1a) (2-bromoethyl)benzene plus 2-chloro-2,4,4-trimethylpentane; and (1b) 4-(2,4,4,4-tetramethylbutyl)-styrene.

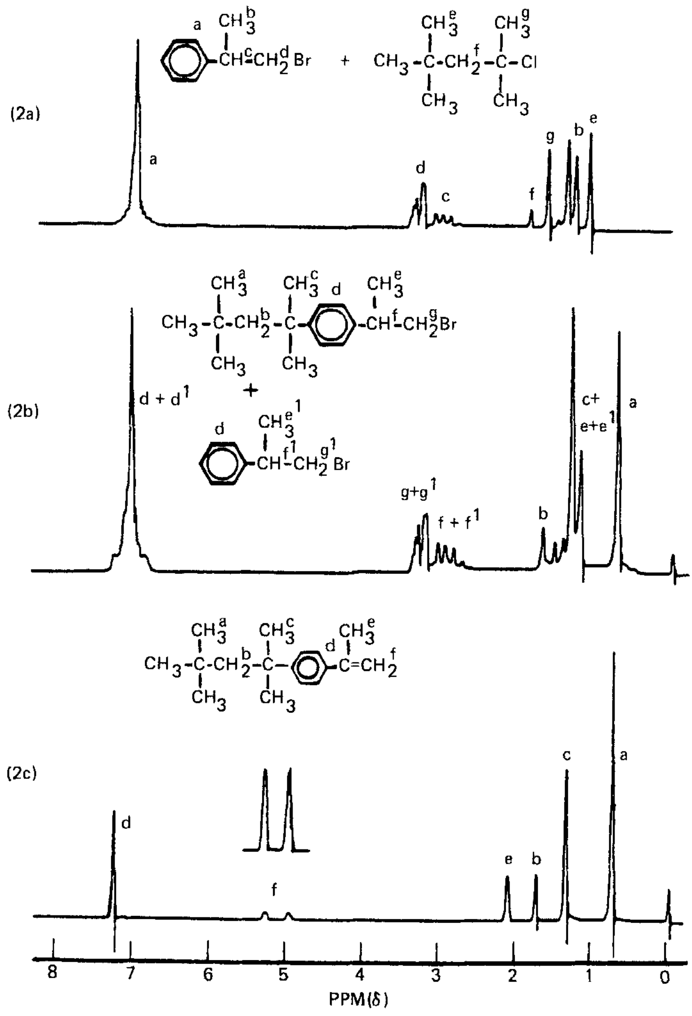


FIG. 2. ^{1}H-NMR spectra of (2a) β-bromoisopropylbenzene and 2-chloro-2,4,4-trimethylpentane; (2b) β-bromoisopropylbenzene plus p-(β-bromoisopropyl) (2,2,4,4-trimethylbutyl)benzene; and (2c) 4-(2,2,4,4-tetramethylbutyl)α-methylstyrene.

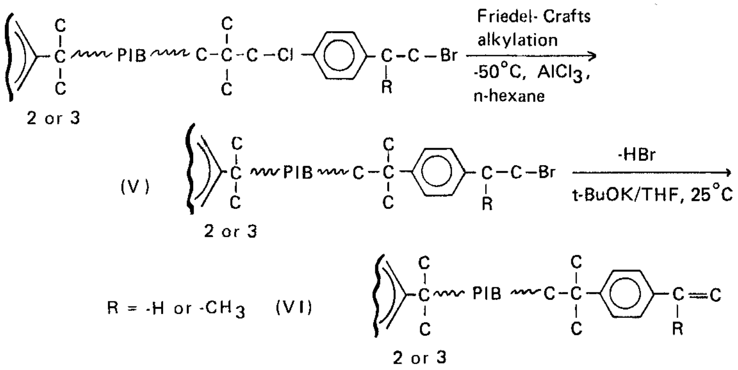
corresponding, respectively, to the $-C(C\underline{H}_3)_3$, $-C(C\underline{H}_3)_2-$, and $-C\underline{H}_2-$ groups of III. Further, after dehydrobromination, two quartets appeared at 5.0-5.8 and 6.4-6.7 ppm, which are respectively associated with the $-\phi-CH=C\underline{H}_2$ and $-\phi-C\underline{H}=CH_2$ groups of III. According to the singlet resonance observed at 7.24 ppm, only monosubstitution at the para position occurred.

Similarly, Fig. 2(a) shows the ^{1}H-NMR spectrum of the ClTMP plus BrPBz charge. Figure 2(b) shows the ^{1}H-NMR spectrum of the crude product of II and unreacted BrPBz; the spectrum does not indicate the presence of by-products. Figure 2(c) shows the ^{1}H-NMR spectrum of IV; the resonances associated with the ClTMP disappeared and new resonances appeared at 0.68, 1.38, and 1.68 ppm, corresponding, respectively, to $-CH(C\underline{H}_3)_2$, $-C(C\underline{H}_3)_2-$, and $-C\underline{H}_2-$ groups of IV. The resonances at 2.1 and 4.9-5.3 ppm were assigned to the $-\phi-C(C\underline{H}_3)=CH_2$ and $-\phi-C(CH_3)=C\underline{H}_2$ protons of IV, respectively.

According to these model experiments, side reactions are absent when carrying out the reactions at -50 to -55°C. At higher temperatures (> -50°C) some side reactions (e.g., fragmentation of ClTMP, carbocationation of BrEBz and BrPBz [6-9]) may occur.

Styryl-Telechelic Polyisobutylene Synthesis

Scheme 1 shows the steps involved in the synthesis of the new styryl-telechelic polyisobutylenes. Friedel-Crafts alkylations were carried out in the presence of excess BrEBz or BrPBz; undesirable side reactions (depolyalkylation, rearrangements, etc. [6-9]) were suppressed by working under conditions determined by model experiments (see



SCHEME 1. Syntheses of styryl-telechelic polyisobutylenes.

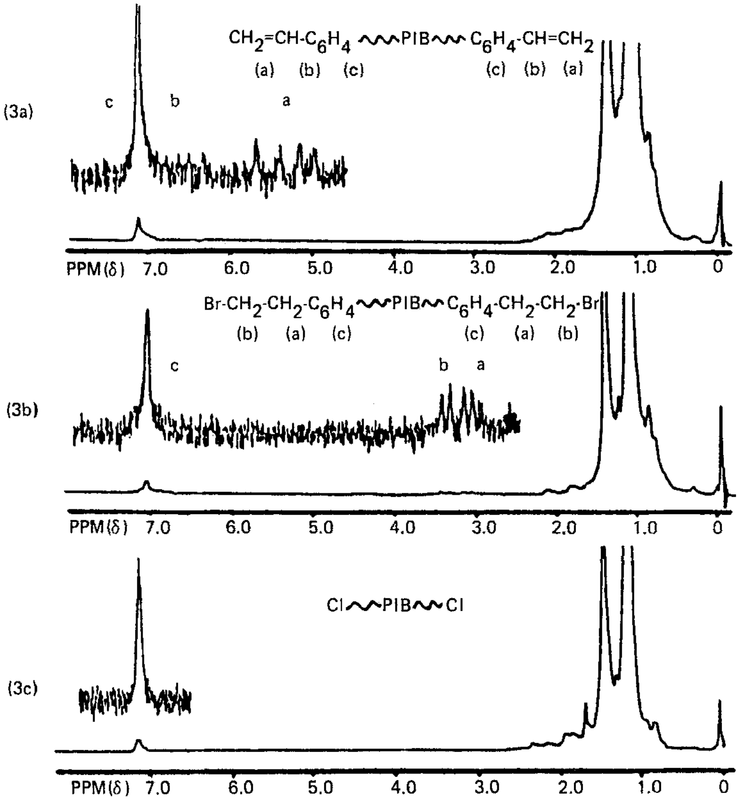


FIG. 3. ^{1}H-NMR spectra of (3a) α,ω-di(styryl)polyisobutylene; (3b) α,ω-di[(2-bromoethyl)phenyl] polyisobutylene; and (3c) α,ω-di(tert-chloro)polyisobutylene.

above). Dehydrobomination of Va or Vb to yield the target styryl-telechelic polyisobutylenes VIa or VIb proceeded rapidly in the absence of side reactions.

Figures 3(a), 3(b), and 3(c) show representative ^{1}H-NMR spectra of the starting Cl-PIB-Cl, the intermediate Va, and the final product VIa, respectively. Significantly, the resonance at 1.65 ppm (associated with the geminal methyl groups at the endgroups of Cl-PIB-Cl) disappeared upon alkylation, while two new multiplets appeared at 3.0-3.5 ppm, which are assigned to the terminal $-\phi-C\underline{H}_2CH_2Br$ groups in Va. According to the spectrum shown in Fig. 3(a), these multiplets disappeared upon dehydrobromination and two new quartets appeared at 6.4-6.7 and 5.0-5.8 ppm, which were assigned respectively to the terminal

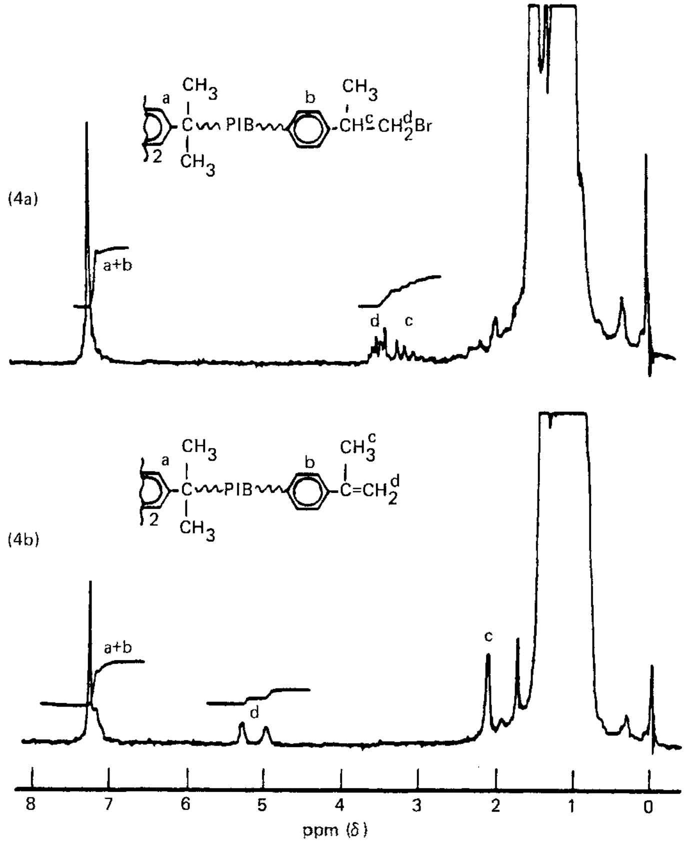


FIG. 4. ^{1}H-NMR spectra of (4a) α,ω-di[(p-bromoisopropyl)-phenyl]-polyisobutylene; and (4b) α,ω-di(α-methylstyryl)polyisobutylene.

$-\phi-\underline{CH}=CH_2$ and $-\phi-CH=\underline{CH_2}$ protons of VIa. Figures 4(a) and 4(b) show the ^{1}H-NMR spectra of the intermediate Vb and VIb, respectively. Figure 4(a) shows new multiplets at 2.6-3.5 ppm characteristic of the terminal $-\phi-\underline{CH}(CH_3)-\underline{CH_2}Br$ protons of Vb, and Fig. 4(b) shows a new doublet at 4.9-5.3 ppm associated with the terminal $-\phi-C(CH_3)=\underline{CH_2}$. All the assignments were confirmed by comparisons with model compounds.

Figures 5(a), 5(b), and 5(c) show IR spectra of Cl-PIB-Cl, Va, and VIa, respectively. The characteristic band of $-CH_2Br$ of Va at 1255 cm^{-1} in Fig. 5(b) disappeared upon dehydrobromination. New bands appeared at 1623 cm^{-1}, corresponding to the contribution of an olefinic

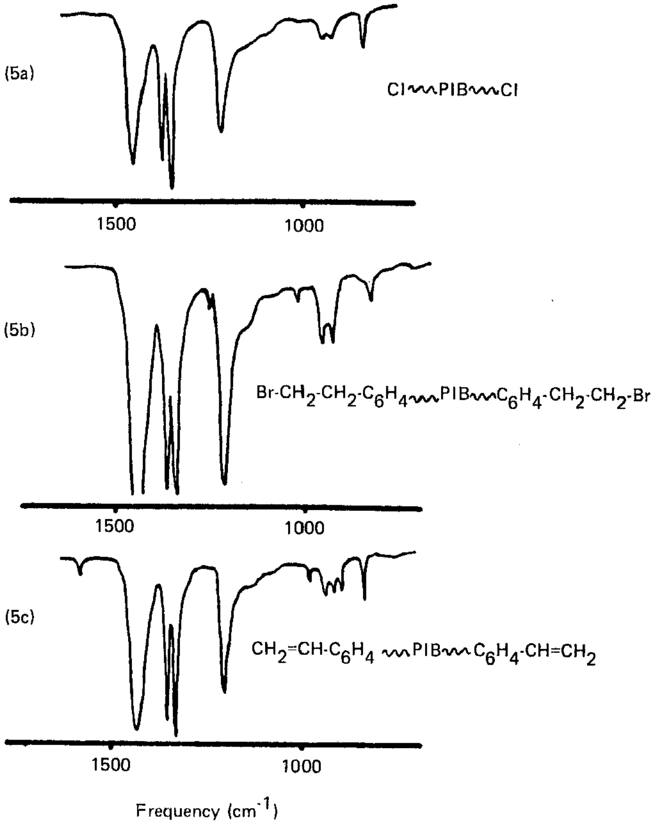


FIG. 5. IR spectra of (5a) α,δ-di(tert-chloro)polyisobutylene; (5b) α,ω-di[2-bromoethyl)phenyl]polyisobutylene; and (5c) α,ω-di(styryl)polyisobutylene.

double bond conjugated with an aromatic ring; the bands at 895 and 980 cm^{-1} were assigned to vinyl endgroups. A most informative band appears at 830 cm^{-1}: this band is due to two adjacent hydrogen atoms on one aromatic ring and indicates the presence of para-substituted rings. Figures 6(a) and 6(b) show IR spectra of Vb and VIb, respectively, and indicate the presence of characteristic bands similar to those exhibited by Va and VIa.

Quantitative Endgroup Characterization

Great care has been exercised to determine quantitatively the styryl endgroup concentration in these new linear and three-arm star tele-

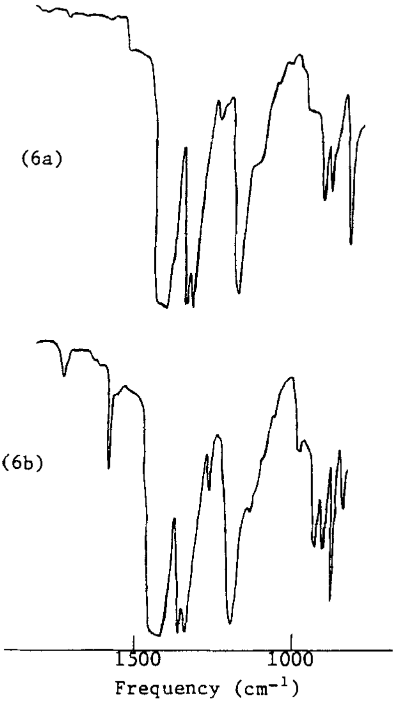


FIG. 6. IR spectra of (6a) α,δ-di[(β-bromoisopropyl)phenyl]-polyisobutylene; and (6b) α,ω-di(α-methylstyryl)polyisobutylene.

chelic products. Two independent methods were used: ^{1}H-NMR spectroscopy and UV spectroscopy in conjunction with $\overline{M}_n$ determination by GPC. Proton NMR spectroscopy provides reliable data by quantitatively correlating protons characteristic of the aromatic ring and olefin group $-C_6H_4-$ and $-C_6H_4-C(R)=CH_2$ in VI. The equation used to calculate the functionalities was $\overline{F}_n$ = olefinic proton x6/aromatic protons. Similarly, most reliable quantitative information has been obtained by determining the styryl- endgroup concentration of these strong UV chromophores at λ_{max} = 252 nm ($\pi \rightarrow \pi^*$ transition) and 250 nm of VIa and VIb, respectively, in conjunction with $\overline{M}_n$'s obtained from GPC determinations. The styryl endgroup concentration was measured by the use of a calibration plot constructed with p-t-butylstyrene and IV, the λ_{max}'s are 1.94×10^4 and 1.44×10^4, respectively.

Table 1 shows the data. The agreement between the data obtained by the ^{1}H-NMR and UV methods is good. According to these results,

TABLE 1. Number-Average Functionality of $CH_2=C(R)-Ph$~~~PIB~~ $Ph-C(R)=CH_2$

		Number-average functionality	
$\overline{M}_n$	R	^{1}H-NMR	UV
3,100	H	1.98 ± 0.05	1.95 ± 0.04
7,800	H	2.01 ± 0.07	1.96 ± 0.05
3,200[a]	H	3.03 ± 0.08	2.98 ± 0.07
15,200[a]	H	3.02 ± 0.04	2.96 ± 0.06
3,400	CH_3	1.96 ± 0.05	1.94 ± 0.05

[a] Three-arm star polymer.

the linear and the three-arm star styryl-telechelic polyisobutylenes carry exactly 2.0 and 3.0 styryl endgroups, respectively.

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