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New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer-Agents (Inifers)

42. Telechelic Polyisobutylenes by Brominated Inifers

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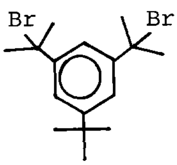
Summary

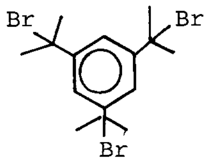
Linear and three-arm star telechelic polyisobutylenes PIB's with perfect end-functionalities ($\bar{F}_n$ = 2.0±0.1 or 3.0±0.1) have been synthesized by the use of 1,3-di(2-bromo-2-propyl)5-tert-butylbenzene (m-tBuDCB) binifer or 1,3,5-tri(2-bromo-2-propyl)benzene (TCB) trinifer/BCl_3 systems. The counter anion is most likely $BCl_3Br^{\ominus}$ in these polymerizations. The inifer efficiencies of these brominated inifers are lower than those of the chlorinated analogues, probably because of side reactions during the polymerization. The rate of chain transfer to inifer is similar for both the chlorinated or brominated inifer/BCl_3 systems but that of termination is faster in the former system. Elementary analysis shows that the PIB's obtained with m-tBuDCB carry 90% bromine and 10% chlorine end groups.

Introduction

The syntheses of linear or three arm star tert-chlorine telechelic PIB's have been repeatedly demonstrated by the use of chlorinated inifers[1,2]. In the course of investigations concerning telechelic PIB's by the inifer technique we became interested in exploring the use of bromine-containing inifers. This paper concerns the synthesis of linear and three-arm star PIB's by the use of the m-tBuDCB binifer and TCB trinifer, respectively,



m-tBuDCB



TCB

with special regard to the study of chain transfer to inifer and termination processes. In the presence of these inifers indanyl ring formation cannot occur during the polymerization and perfectly telechelic products are obtained. The effect of the bulky t-Bu substituent in the chlorinated analogue of m-tBuDCB, a "sterically hindered" inifer, in preventing intramolecular cyclization by steric compression, has been discussed in detail[3].

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Experimental

Inifer Syntheses

The synthesis of m-*t*BuDCC has been described[3] . The TCB has been synthesized by benzylic bromination of 1,3,5-triisopropylbenzene with N-bromosuccinimide (NBS). A 3000 ml 3 neck flask equipped with a reflux condenser and a stirrer was charged with 800 ml CCl_4, 0.17 mole (41 ml) 1,3,5-triisopropylbenzene (Aldrich Chemical Co.), 0.56 mole (100 g) NBS (Aldrich Chemical Co.), and 0.056 mole (13.56 g) benzoyl peroxide (Fisher Scientific Co.). After 5 minutes of refluxing and stirring the mixture was cooled to 0°C. The benzoic acid by-product was removed by filtration and the solvent evaporated (rotovap) at room temperature. The TCB was recrystallized from *n*-hexane and then from *n*-pentane yielding colorless crystals, Mp = 70-71°C. ^1H NMR in CCl :δ(ppm) = 7.6 (aromatic, s, 3H), 2.0 (methyl, s, 18H).

Polymerization

The syntheses of linear and three-arm star telechelic PIB's in the presence of m-*t*BuDCC and TCB were identical to the techniques used in conjunction with the chlorinated inifers[1,2].

Characterization

^1H NMR spectroscopy was carried out by using a Varian Associates T-60 NMR Spectrometer. $\bar{M}_n$ was determined by a Waters Associates 6000A high pressure GPC equipped with dual ultraviolet and refractive index detector and μ-Styragel columns (10^6, 10^5, 10^4, 10^3 and 500Å). Solutions of 0.25% by weight in THF were used and the flow rate was 1 ml/min. The calibration curve was constructed with well fractionated PIB samples of known molecular weight. Elemental analysis was done by Galbraith Laboratories.

Results and Discussion

A. Polymerization of Isobutylene by the m-*t*BuDCB/BCl_3 Binifer System

The synthesis of tert-chlorine telechelic PIB's has been repeatedly demonstrated by the use of chlorinated inifers[1,2]. The effect of halogen (bromine versus chlorine) in the inifer on the polymerization details has been investigated by the use of m-*t*BuDCB/BCl_3 and TCB/BCl_3 combinations.

Table I compares representative results obtained with the brominated and chlorinated binifer but otherwise under identical conditions. A variety of conclusions can be drawn. First of all, conversions, molecular weights and inifer efficiencies all increase by increasing the time of polymerization from 5 to 30 min, however the effect appears to be more pronounced with the brominated system. Evidently, after a period of very rapid growth followed by termination, slow reinitiation and growth may proceed as first suggested by Nuyken et al[4].

TABLE I

Isobutylene Polymerization by the m-tBuDCB and m-tBuDCC/BCl_3 Systems at -50°C

Binifer	Solvent	Time min	conv. %	$\bar{M}_w$ g/mole	$\bar{M}_w$ g/mole	$\bar{M}_w\bar{M}_n$	I_{eff} %	$\bar{F}_n$**
m-tBuDCB	CH_3Cl	5	81.4	5300	12100	2.27	72	2.0±0.1
m-tBuDCB	CH_3Cl	30	100	6300	13100	2.08	74	2.0±0.1
m-tBuDCB	CH_3Cl/ n-hexane	5	69.5	6300	13400	2.14	53	2.0±0.1
m-tBuDCB	CH_3Cl/ n-hexane	30	90.9	7300	16000	2.18	58	2.0±0.1
m-tBuDCC*	CH_3Cl	5	71.4	1800	3700	2.1	99	2.0±0.1
m-tBuDCC	CH_3Cl	30	75.2	3700	7600	2.03	∿100	2.0±0.1
m-tBuDCC	CH_3Cl/ n-hexane	5	70.9	3000	9300	3.14	∿100	2.0±0.1
m-tBuDCC	CH_3Cl/ n-hexane	30	76.1	4200	11800	2.8	93	2.0±0.1

[Binifer] = 4.9×10^{-3}M, [IB] = 0.41M, [BCl_3] = 2.45×10^{-2}M, CH_3Cl/n-hexane 76/17 v/v, -50°C

*[Binifer] = 6.72×10^{-3}M, IB = 0.3M

**Obtained by ^1H NMR after dehydrohalogenation

Inifer efficiencies, I_{eff}, are consistently higher in the experiments with chlorinated binifer, indeed I_{eff} ∿100% in the latter system. An unidentified inifer-consuming side-reaction may account for low I_{eff} values in the brominated binifer systems. To gain insight into this possibility experiments have been conducted in which BCl_3 was added to binifers in the absence of isobutylene. Thus BCl_3 was added to a solution of m-tBuDCC in CH_3Cl/n-hexane at -30°C and after 10 minutes methanol was added to quench the reaction. Figure 1 shows the ^1H NMR of the product. New resonances appeared at 7.45, 7.2, 5.3, 5.0, 3.0 and 1.45 ppm. Two of the three original resonances of m-tBuDCC(3) are still visible at 1.95 ppm ($-C(CH_3)_2Cl$) and 1.35 ppm ($-C(CH_3)_3$), however, the third resonance at 7.35 ppm characteristic of the 2,4,6 aromatic protons has split into two resonances appearing at 7.45 and 7.2 ppm. The appearance of the resonances at 5.3 and 5.0 ppm suggests dehydrochlorination to the corresponding olefin ($-C(CH_3)-C{=}CH_2$). The new resonances and shifts observed may be due to a dimerization (oligomerization?) of m-tBuDCC under the influence of BCl_3 involving the cation formed from m-tBuDCC + BCl_3 and the dehydrochlorinated product.

Figure 2 shows a representative ^1H NMR spectrum of a PIB obtained in the m-tBuDCB/BCl_3/CH_3Cl-nC_6H_{14} system at -50°C. Comparison of these spectra shows that the resonance at 3.0 ppm in the PIB spectrum is at the same position as the one observed in Figure 1. This resonance was not observed in ^1H NMR spectra of PIB's when the chlorinated binifer was used. The appearance

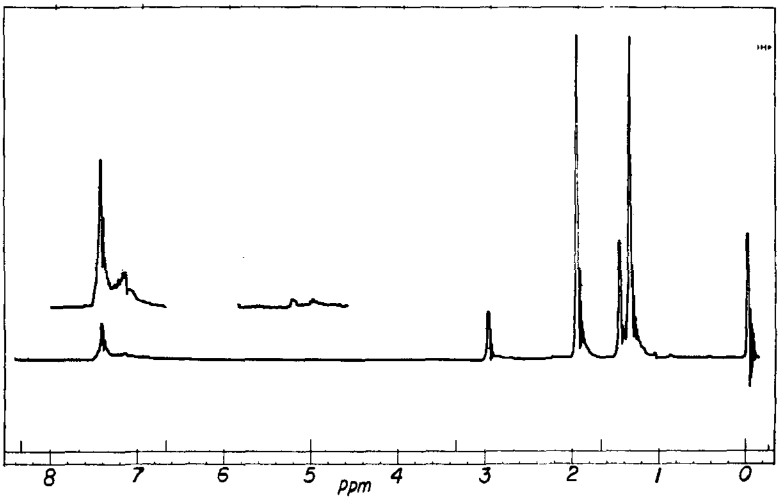

Figure 1. ^1H NMR Spectrum of the Product Obtained in the m-tBuDCC/BCl_3/CH_3Cl + n-C_6H_{14} (70/20) System at -30°C. (10 min).

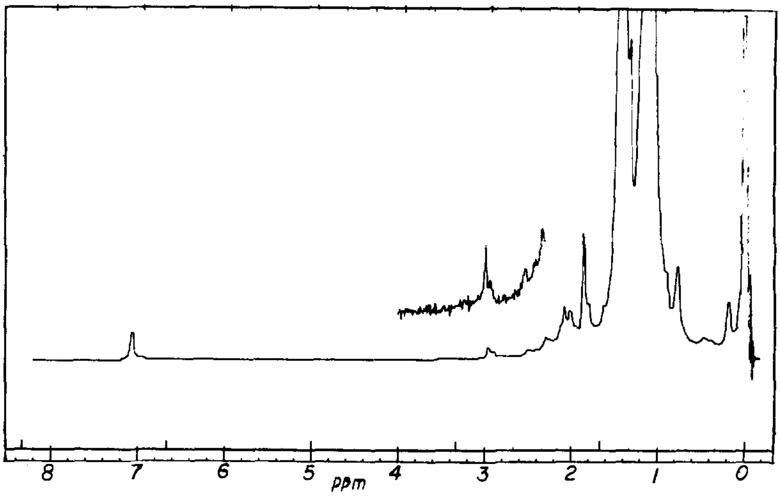

Figure 2. ^1H NMR Spectrum of PIB Obtained in the m-tBuDCB/BCl_3/isobutylene/CH_3Cl + n-C_6H_{14} (76/17)/-50°C System (5 min).

of this signal may indicate the presence of side reactions during the polymerization, and evidently they are more likely to occur with the brominated binifer as also indicated by the relatively low I_{eff} values obtained (cf Table I).

The $\overline{M}_w/\overline{M}_n$ values are not too far from the theoretical value of 1.5.[5] Reasons for this discrepancy may lay in the conventional manner these polymerizations have been conducted. Under semicontinuous conditions theoretical $\overline{M}_w/\overline{M}_n$ values have been consistently obtained[6]. The molecular weights obtained in the presence of the m-tBuDCB/BCl_3 system are higher than those with the m-tBuDCC/BCl_3 system possibly because part of the inifer in the former system might have been consumed by side reactions.

The number average degree of end group, $\overline{F}_n$, was obtained from ^1H NMR spectroscopy. The analytical procedure involved dehydrohalogenation of the products by tBuOK and quantitatively determining the terminal $-C(CH_3)=CH_2$ protons[7]. The $\overline{F}_n$ values were consistently 2.0±0.1 indicating that perfectly telechelic tert-halogen ended PIB's can be prepared by the use of the m-tBuDCB/BCl_3 binifer system.

B. Kinetic Studies Using the m-tBuDCB/BCl_3 Binifer System

The purpose of these investigations was to determine and compare $k_{tr,I}/k_p$ (abbreviated by C_I) and k_t/k_p values for brominated and chlorinated binifers. These parameters can be obtained from the slope and intercept of the integrated form of the inifer equation[5]:

$$[M]_o-[M](\ln[M]_o/[M])^{-1}\overline{DP}_n^{-1} = 1/2(C_I[\overline{I}] + k_t/k_p)$$

where $[\overline{I}]$ is the arithmetic mean of the initial and final inifer concentrations.

Table II shows the data obtained in two series of polymerization experiments and Figure 3 is the corresponding inifer plot. The $[\overline{I}]$ values were calculated by averaging the amount of binifer consumed i.e., $([I]_o-[I])/2$, where $[I]_o$ and $[I]$ are the initial and final inifer concentrations, respectively. The latter was calculated from I_{eff}. The C_I values for the brominated and chlorinated binifers are quite similar, 2.39 and 2.54, respectively, however, k_t/k_p of the brominated binifer is just about half of that of the chlorinated reagent, 1.34×10^{-3} and 2.76×10^{-3}, respectively. According to these results the rates of chain transfer to binifer for the brominated and chlorinated compounds are about the same. In contrast, termination, i.e., $\sim C^{\oplus} + BX_4^{\ominus} \longrightarrow \sim CX + BX_3$, seems to be slower with the brominated binifer than with that of the chlorinated system. It could be that halogen loss is slower from the $BCl_3Br^{\ominus}$ than $BCl_4^{\ominus}$ counter ion, or that charge separation is larger with the bromine-containing counter ion which then results in retardation of termination.

According to elemental analysis, a PIB obtained by the m-tBuDCB binifer contained 90 mole% Br and 10 mole% Cl end groups. Interestingly, ten percent of the end groups contained chlorine, although the binifer was a bromine-containing species. The most likely source of the Cl end groups is the $BCl_3Br^{\ominus}$

counter anion (the intervention of CH_3Cl diluent is considered much less likely). Chlorine incorporation may also arise during quenching: The HCl formed during the decomposition of excess BCl_3 in the system may displace the bromine in the end groups.

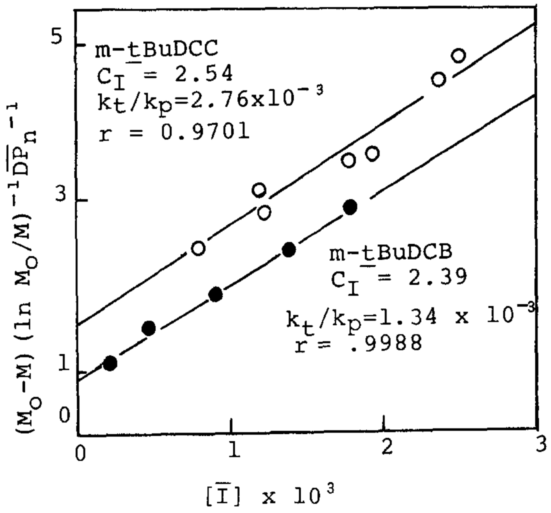

Figure 3. Determination of C_I and k_t/k_p for the m-tBuDCC (open circles) and m-tBuDCB/BCl_3/isobutylene/CH_3Cl + n-C_6H_{14}/-50°C (filled circles) system. Data in Table III

C. Polymerization of Isobutylene by the TCB/BCl_3 Trinifer System

Experiments have also been conducted with the brominated trinifer TCB. The purpose of these studies was to investigate the nature of the halogen (bromine or chlorine) in the synthesis of three-arm star telechelic PIB's. Extensive studies have already been carried out with the chlorinated analogue of TCB, 1,3,5-tri(2-chloro-2-propyl)benzene (TCC)[2,8].

Table III shows the data of isobutylene polymerization by the TCB and TCC/BCl_3 trinifer systems. As can be seen, $\overline{M}_n$'s in both systems increase as the trinifer concentration decreases. The I_{eff} seems to be smaller in the brominated than in the chlorinated system, probably due to similar side reactions as in the binifer system.

The number average degree of end groups, $\overline{F}_n$'s, was determined quantitatively by ^1H NMR spectroscopy[7] (after dehydrobrominating the polymers) combined with $\overline{M}_n$ measurement by GPC: All the values were found to be 3.0±0.1. Thus the TCB/BCl_3 trinifer system also produces PIB's with perfect end functionality.

TABLE II

Isobutylene Polymerization in the Presence of Brominated and Chlorinated Sterically Hindered Binifers*

[Binifer] M x 10^3	Conversion %	$\overline{M}_n$ g/mole	$\overline{M}_w$ g/mole	$\overline{M}_w/\overline{M}_n$	I_{eff} %
m-<u>t</u>BuDCB					
6.45	69.3	5100	11000	2.1	69.34
4.82	69.2	6300	14500	2.3	69.20
3.69	62.1	8900	16200	1.82	62.05
2.55	51.2	13400	23400	1.75	51.16
1.46	34.6	21100	30800	1.46	34.62
m-<u>t</u>BuDCC					
5.6	68.9	3300	9600	2.87	85.4
4.96	70.9	3000	9300	3.14	∿100
4.2	66.7	4100	10700	2.61	91.3
3.5	66.4	4400	11100	2.53	∿100
2.4	58.1	5200	12500	2.40	∿100
2.54	60.6	5700	13400	2.36	95.8
1.52	45.4	7600	16500	2.16	89.9

*[IB] = 0.41 M, [BCl_3]/[Binifer] = 5, CH_3Cl/<u>n</u>-hexane (76/17 v/v), 5 min., -50°C.

TABLE III

The Synthesis of Three-arm Star Telechelic PIB by the TCB and TCC/BCl_3 Trinifer Systems

[Trinifer] M x 10^2	Conversion %	$\overline{M}_n$ g/mole	I_{eff} %	$\overline{F}_n$
<u>TCB Experiments</u>	([IB] = 1.02M, [BCl_3]/[TCB] = 10, CH_3Cl, 30 min, -40°C)			
0.56	95	13500	70	3.0±0.1
1.11	98	9900	51	3.0±0.1
1.11	∿100	8900	58	3.0±0.1
1.42	∿100	7500	54	3.0±0.1
2.23	∿100	3200	80	3.0±0.1
*<u>TCC Experiments</u>	([IB] = 1.02M, [BCl_3]/[TCC] = 6-7, CH_3Cl, -50°C)			
0.048	42	50000	97	
0.070	40	37000	99	
0.090	38	35000	94	
0.22	59	27000	81	
0.5	62	14000	72	

*Data from ref. 8.

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