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Living carbocationic polymerization
XIX. Synthesis of four-arm star polyisobutylenes capped by *t*-chlorine and isopropylidene groups

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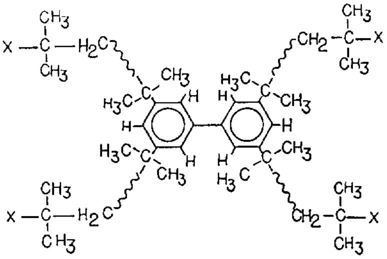
Summary

The synthesis of the first four-arm star polyisobutylenes (PIB) capped by t-chlorine and isopropylidene groups has been accomplished by the 3,3',5,5'-tetra(2-acetoxy-isopropyl)biphenyl/BCl_3 initiating system. The polymerizations yield tert-chlorine capped arms which have been quantitatively dehydrochlorinated to isopropylidene end-groups. Homogeneous polymerization conditions seem to be mandatory for the synthesis of well-defined products. The polymers were characterized by GPC and ^1H NMR spectroscopy and product homogeneity was demonstrated by KSN plots. The number average end functionality was found to be $F_n = 4.06 \pm 0.4$.

Introduction

In the course of our fundamental investigations on well-defined telechelic prepolymers by living carbocationic polymerizations (1,2), we have synthesized four-arm star polyisobutylenes (PIB) capped by chloro or isopropylidene end groups:



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where the wiggly lines are isobutylene units ($-CH_2C(CH_3)_2-$), and X = $-Cl$ or $-CH_2-C(CH_3)=CH_2$. The synthetic strategy was similar to that used earlier focusing on the preparation of linear (3) and three-arm star (4) telechelic PIBs. According to previous findings (1-5) cumyl acetates and/or ethers are efficient initiators in conjunction with BCl_3 or $TiCl_4$ for the living polymerization of isobutylene for the synthesis of well-defined telechelics. In line with these facts we have now used the 3,3',5,5'-tetra(2-acetoxy isopropyl)biphenyl/BCl_3 initiating system for the preparation of four-arm star tert-chlorine capped PIB:

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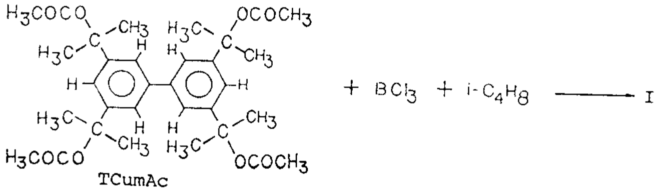
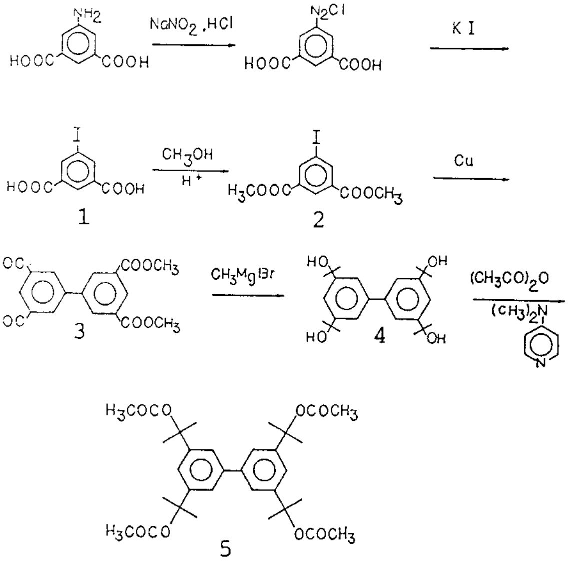


TCumAc

This communication concerns the synthesis and characterization of the above new four-arm star telechelic PIB (I) and the synthesis of TCumAc, a new compound, as the initiator. The polymer-chemical challenge was to find conditions for the synthesis of the four-arm star telechelic PIB and its characterization.

Experimental

1. Materials. The source and purity of most chemicals have been published (5). The synthesis of the 3,3'5,5'-tetra(2-acetoxy isopropyl)biphenyl initiator 5 followed the following route:



5-Iodophtalic acid.(1) was prepared by Grahl's procedure (6) and the dimethyl ester 2 was obtained with CH_3OH in the presence of H_2SO_4 catalyst. The crude product was recrystallized from CH_3OH; mp. 103.5-104.5°C (uncorr.) (lit. (7) 104-105°C). ^{1}H NMR ($CDCl_3$) = δ 3.91 (6H,s), 8.49 (3H,s). 3,3',5,5'-tetra(methyl carboxylate)biphenyl,(3) was obtained by Kornblum and Kendall (8). Thus a solution of 30 g 2 in 150 mL DMF in a 300 mL 3 neck flask equipped with stirrer and reflux condenser was heated to reflux and 30 g Cu powder was added. After 36 hrs at reflux 30 g more Cu powder was added and refluxing was continued for an additional 36 hours. After cooling to ambient, the charge was poured into 3L water, the solids were filtered off, and the solution was extracted with 3L refluxing benzene. After removing the benzene (rotovap), 10.2 g (28%) white crystals were obtained; mp. 213-215°C (lit. (8) 209°). ^{1}H NMR ($CDCl_3$) $\delta = 4.04$ (12H,s), 8.55 (6H,s). To prepare <u>3,3',5,5'-tetra(2-hydroxyl isopropyl)biphenyl</u>,(4) 6.3 g (0.016 mole) <u>3</u> in 260 mL anhydrous THF were stirred in a 500 mL 3-neck flask equipped with stirrer, pressure equalizer addition funnel and gas-inlet tube at 0°C under dry N_2. To this solution were added 84 mL (0.254 mole) CH_3MgBr in diethyl ether and after agitating at 0°C for 8 hrs the system was poured over a mixture of 180 g ice and 23 g ammonium chloride while stirring. The product was extracted with ether, the solution dried with anhydrous $MgSO_4$, filtered, and the ether removed under reduced pressure. The crude product was recrystallized from methanol and gave 4.9 g (78%) white crystals, mp. 218-220°C (uncorr.); ^{1}H NMR ($CD_3OD + CDCl_3$) $\delta = 1.64$ (24H,s), 7.62 (6H,s). <u>The final product</u> <u>5</u> was obtained by acetylation of <u>4</u> according to Hofle and Steglich (9). Products <u>4</u> and <u>5</u> seem to be new, they have not been described in the scientific literature. Thus into a 100 mL 2 neck flask equipped with a magnetic stirring bar and reflux condenser were placed 1.7 g (0.0044 mole) <u>4</u>, 10 mL (0.072 mole) Et_3N, 3 g (0.029 mole) 4-N,N'-dimethylamino pyridine and 40 mL Et_2O, and then under stirring 3 mL (0.032 mole) acetic anhydride were added. The system was stirred for 16 hrs at ambient and then at reflux for 8 hrs. The excess anhydride was quenched with water, the mixture suspended in ether, and treated successively with 2N HCl and aqueous $NaHCO_3$. The ether layer was separated, dried with anhydrous $MgSO_4$, and the solvent was removed (rotovap). The crude yellow product treated with charcoal and recrystallized from n-hexane gave yellowish crystals, 1.6 g (66%) mp. 123-125°C (uncorr.). IR = 1737 cm^{-1} (C=O), 1245 cm^{-1} (COC). ^{1}H NMR ($CDCl_3$) $\delta = 2.01$ (24H,s), 2.13 (12H,s), 7.64 (6H,s). Figure 1 shows the ^{1}H NMR spectrum of the TCumAc used as initiator in these studies.

2. Polymerization

Polymerizations were carried out in a dry box under dry nitrogen (5). IR spectra were obtained by a Beckman 2100 FTIR instrument and ^{1}H NMR spectra were recorded by Varian T-60 and 300 MHz NMR spectrometers (5). Molecular weights were determined by a Waters high pressure GPC instrument; operational details have been described (5).

The $\overline{M}_n$s obtained by GPC are approximations since the calibration curve was obtained with linear (i.e., "two-arm star") PIBs. In this context it is of interest that the calibration plot constructed with narrow molecular weight distribution linear PIBs gives acceptable $\overline{M}_n$ values for three-arm, star PIBs (10). The $\overline{M}_w/\overline{M}_n$ data generated by GPC are meaningful for four-arm star PIBs.

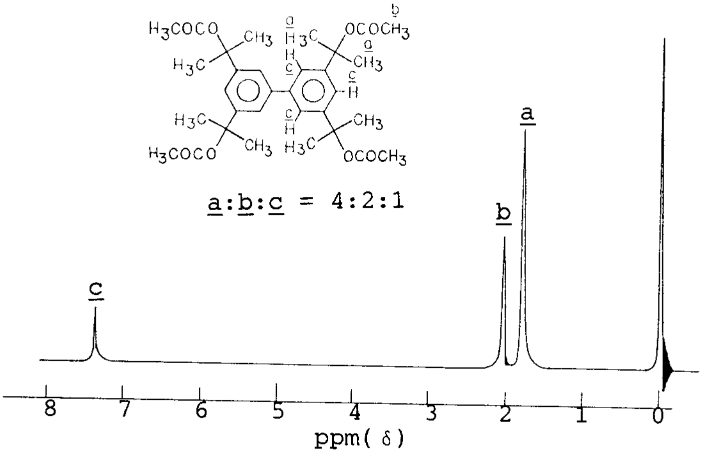


Figure 1. ^{1}H NMR Spectrum of 3,3'5,5'-tetra(2-acetoxy-isopropyl) biphenyl

Results and Discussion

Orienting experiments have shown that the TCumAc/BCl$_3$ initiating system readily polymerizes isobutylene in dilute solutions in the -35 to -80°C range. Polymerizations were induced by the addition of liquefied BCl$_3$ to TCumAc/IB systems. TCumAc is soluble in IB/solvent systems, however, the solubility of the initiating TCumAc·BCl$_3$ complex is very low. Except in highly dilute systems (see below), the addition of BCl$_3$ to premixed TCumAc/IB solutions instantaneously gave heavy white precipitates (ostensibly the polar TCumAc·BCl$_3$ complex). Precipitation due to rapid polymer formation is readily distinguishable with a little experience from the precipitation of the small-molecular complex.

Representative results are shown compiled in Table I. Conditions for the synthesis of well-defined four-star arm telechelic PIB have been found (Expt. No. 8, Table I). The route toward this synthesis is now analyzed.

The polymerization of IB initiated by cumyl derivatives (3,5), and particularly by 1,3-dicumyl derivatives similar to those in TCumAc (12,13), tends to give undesirable indanyl skeletons. This unacceptable side reaction can be avoided by the use of relatively nonpolar media (i.e. by the use of a 40/60 CH$_3$Cl/n-C$_6$H$_{14}$ solvent mixture) at low temperatures (i.e., at -80°C) (3). Experiments carried out with the TCumAc·BCl$_3$ system under such conditions (cf. Expt. 1-6 in Table I), however, yielded very low conversions and ill-defined products. In these experiments immediate copious white precipitation occurred upon BCl$_3$ addition to TCumAc/IB/40-60 CH$_3$Cl-C$_6$H$_{14}$ charges at -80°C. These unsatisfactory results are due to the low solubility of the relatively polar TCumAc·BCl$_3$ in the relatively nonpolar medium. The polarity of the solvent system is further reduced by the presence of IB monomer.

TABLE I

Polymerization of Isobutylene with the 3,3',5,5'-tetra-(2-acetoxy-isopropyl)biphenyl/BCl_3 Initiating System ($[BCl_3]$ = 0.2 M/L, $[I_o]$ = 2.10^{-3} M/L, 30 mins -80°C, 25 mL)

	$CH_3Cl/n\text{-}C_6H_{14}$ %		[IB] M/L	Conversion %	$\overline{M}_n{}^e$	$\overline{M}_w/\overline{M}_n$
1^a	40	60	0.257	2.0	-	-
2^d	40	60	0.257	3.8	-	-
3^d	40	60	0.514	2.8	-	-
4^d	40	60	0.771	3.6	-	-
5^d	40	60	1.029	3.0	-	-
6^d	40	60	1.286	3.0	-	-
7^a	100	-	0.257	1.8	-	-
8^b	100	-	0.129	24	3350	1.86
$9^{b,c}$	100	-	0.129	95	3750	1.97
10^d	100	-	0.257	72	4850	1.94
11^d	100	-	0.514	42	6400	2.47
12^d	100	-	0.771	35	11770	2.10
13^d	100	-	1.029	29	19700	2.07
14^d	100	-	1.286	27	28700	2.03

[a] Control experiments in the absence of TCumAc (I_o = 0)

[b] Total volume 100 mL (to facilitate the addition of low amounts of IB)

[c] Yield after 180 mins (independent experiment)

[d] Immediate precipitate formation upon BCl_3 addition; see comments in text

[e] Approximations by GPC; see comments in Experimental

In view of these difficulties experiments have been carried out using CH_3Cl. While precipitation occurred even under these conditions, the extent of precipitation diminished by decreasing the IB concentration and homogeneous systems were obtained, with [IB] = 0.129 mole/L (Expt. 8). The conversions increase and the molecular weights decrease with decreasing monomer concentrations. Evidently, a fraction of TCumAc·BCl_3 is dissolved in CH_3Cl which induces polymerization, however, the concentration of TCumAC·BCl_3 in the solution is less than that of the TCumAc employed, which results in higher than theoretical $\overline{M}_n$ values. The closer the concentration of TCumAc·BCl_3 approaches that of the TCumAc input, the better the agreement between the actual and theoretical $\overline{M}_n$s (i.e., $\overline{M}_n = [M]_o 56/[I_o]$, where $[M_o]$ and $[I_o]$ are the initial concentrations of IB and TCumAc). The inverse relationship between monomer concentration and conversions, also reflects the extent of TCumAc·BCl_3 depletion by precipitation.

At low monomer concentrations, i.e., at [IB] = 0.514 and 0.257 mole/L, (Expts. 10 and 11) the observed $\overline{M}_n$s are close to theoretical taking into consideration the less than 100% conversions (e.g., (0.514/0.002)x56x0.42 = 6050). At higher monomer concentrations the $\overline{M}_n$s are much higher than calculated indicating relatively slow initiation, most likely due to slow dissolution of the complex in the medium.

The polymers formed in Expts 10-14 have been examined by ^{1}H NMR spectroscopy and were found to contain appreciable amounts of "once fired' arms. Figure 2 shows a representative ^{1}H NMR spectrum and assignments. The characterization method of once-fired arms emanating from cumyl groups has been developed in conjunction with the synthesis of three-arm telechelic PIBs (11). To facilitate spectroscopic characterization, the original $-CH_2C(CH_3)Cl$ capped product was quantitatively dehydrochlorinated to the $-CH_2C(CH_3)=CH_2$ capped material (11,14).

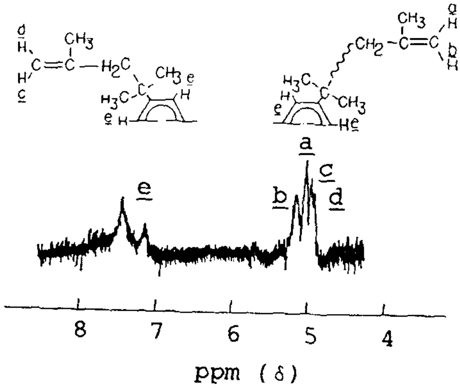


Figure 2. Part of the H^1 NMR Spectrum of Four-Arm Star PIB after Dehydrochlorination (Exp. 8, $CDCl_3$ solution, 60 MHz)

Led by these experiments, homogeneous (precipitation-free) polymerizations that yielded satisfactorily-defined four-arm star PIBs have been carried out with [IB] = 0.129 mole/L. Evidently in the presence of low IB concentrations increasing amounts of TCumAc·BCl_3 gradually dissolve in the medium. Conversions increased from 24% in 30 mins to ∿95% in 180 mins (Expts. 8 and 9).

The structure of the products obtained under homogeneous conditions at short polymerization times has been investigated by 60 and 300 MHz ^{1}H NMR spectroscopy. The original $-C(CH_3)_2Cl$ end groups that arise in these polymerizations (2,3,4,5) have been quantitatively converted by our routine method (14) to $-CH_2C(CH_3)=CH_2$ groups to facilitate ^{1}H NMR spectroscopic quantitation. Figure 3 shows the aliphatic and aromatic proton region of a representative 60 MHz spectrum together with assignments (Expt. 8 in Table I). The six unsubstituted aromatic protons resonating in the 7.0-7.6 ppm region serve as internal standards for the eight $-C\underline{H}_2^{=}$ protons appering at 4.62 and 4.83 ppm. According to this evidence the number average end functionality $\bar{M}_n$ = 4.06 ± 0.4,i.e., all four arms are capped by a functional group. While the presence of the $-CH_2C(CH_3)_2Cl$ end groups have not been directly demonstrated, evidence for these termini in cumyl acetate induced polymerization exists (2-5) which together with the routine dehydrochlorination method (14), is viewed as proof positive for the presence of $-CH_2C(CH_3)_2Cl$ end groups in TCumAc·BCl_3 induced polymerization of IB.

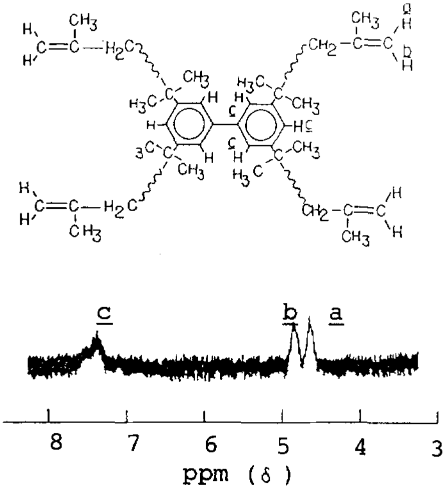


Figure 3. Part of the H^1 NMR Spectrum of Four-Arm Star PIB after Dehydrochlorination (Expt. 8, CCl_4 Solution, 60 MHz)

These conclusions have been substantiated by 300 MHz ^1H NMR spectroscopy. Figure 4 shows the aliphatic and aromatic proton regions of the product obtained in Expt. 8. There is no evidence for indanyl structures in the aromatic range (3) or of "non-fired" or "once-fired' sites in the olefinic range (11). The small resonances at ∿7.66 and 7.7 ppm are unidentified impurities. The product formed at longer reaction times (Expt. 14, Table I) contains once-fired arms, most likely because during the latter stages of the polymerization the TCumAc·BCl_3 that slowly dissolves into the charge encounters rather low IB concentrations (once-fired arm formation preferentially occurs in the presence of low IB concentrations (15)).

The homogeneity of the product formed in Expt. 8 has been established by the Kennedy-Smith-Nagy plot (16) shown in Figure 5. The unity slope of the plot indicates that the UV-active central biphenyl unit is uniformly distributed among the four-arm star PIB molecules.

Acknowledgement

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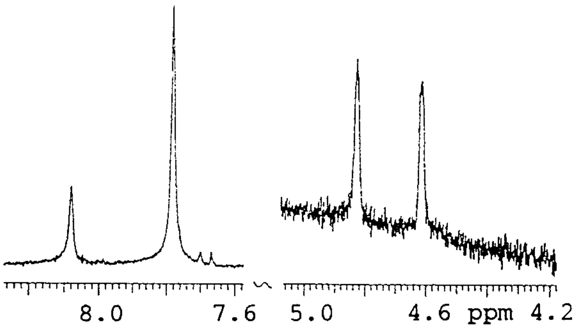

Fig. 4. Parts of the H^1 NMR Spectrum of Four-Arm Star PIB after Dehydrochlorination (Expt. 8, $CDCl_3$ Solution, 300 MHz)

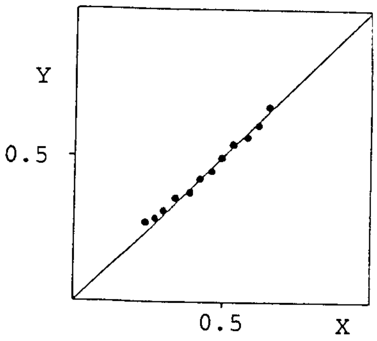

Fig. 5. The KSN Plot of Four-Arm Star PIB(Expt.8) $X=M_x/M_{peak} + M_x)$, $Y=(UV/RI)_{peak}/[(UV/RI)_{peak} + (UV/RI)_x)]$

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