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New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers)

26. Synthesis of α-Phenyl-ω-*t*-Chloropolyisobutylene by the *M*onofunctional *Inifer* (Minifer) Method

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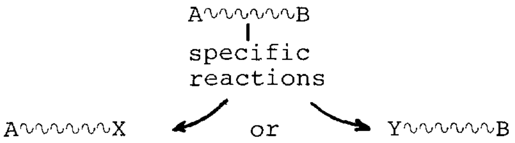
Summary

The synthesis of α-phenyl-ω-t-chloropolyisobutylene Ph-PIB-Cl^{t} by the use of the cumyl chloride/BCl_3/isobutylene minifer system has been accomplished. This asymmetric telechelic prepolymer possesses exactly one phenyl head group and one t-chloro end group. The molecular weight of Ph-PIB-Cl^{t} can be readily controlled by the $[I]_0/[M]_0$ ratio in a refluxing system. Experiments with other minifers, i.e., p-methylcumyl chloride, p-chlorocumyl chloride, α-methylbenzyl chloride and benzyl chloride have also been carried out and the results discussed in terms of carbenium ion stabilities.

Introduction

While a large number of publications concern symmetric linear and three-arm star telechelic polyisobutylenes (i.e., prepolymers carrying the same terminal functional group) (see previous papers in this series), only one asymmetric telechelic polyisobutylene (i.e., prepolymer capped by dissimilar terminal functions) has been described (1). The great advantage of asymmetric telechelics over symmetric telechelics is that the end groups A and B of the formers can be derivatized independent of each other and thus unique new materials can be prepared:



where X and Y are small groups or polymer sequences.

In the course of our fundamental studies on the mechanism of inifer reactions, recently it occurred to us that monofunctional initiator-chain transfer agents (minifers) would be eminently suitable for the synthesis of well-defined asymmetric telechelic polyisobutylene. Specifically, we postulated that α-phenyl-ω-t-chloropolyisobutylene Ph-PIB-Cl^{t} could be prepared with the cumyl chloride/BCl_3/isobutylene system by the following mechanism (this mechanism has been discussed in some detail elsewhere (2)):

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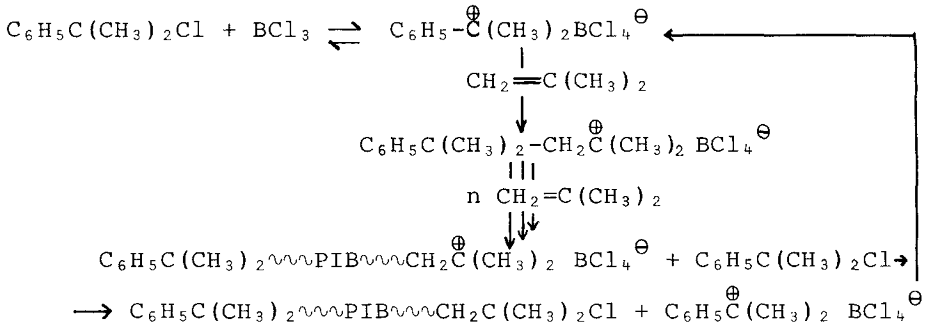

$$C_6H_5C(CH_3)_2Cl + BCl_3 \rightleftharpoons C_6H_5\text{-}\overset{\oplus}{C}(CH_3)_2BCl_4^{\ominus}$$

$$CH_2{=}C(CH_3)_2$$

$$\downarrow$$

$$C_6H_5C(CH_3)_2\text{-}CH_2\overset{\oplus}{C}(CH_3)_2\,BCl_4^{\ominus}$$

$$n\ CH_2{=}C(CH_3)_2$$

$$\downarrow\downarrow\downarrow$$

$$C_6H_5C(CH_3)_2{\sim\sim}PIB{\sim\sim}CH_2\overset{\oplus}{C}(CH_3)_2\ BCl_4^{\ominus} + C_6H_5C(CH_3)_2Cl \rightarrow$$

$$\rightarrow C_6H_5C(CH_3)_2{\sim\sim}PIB{\sim\sim}CH_2C(CH_3)_2Cl + C_6H_5\overset{\oplus}{C}(CH_3)_2\ BCl_4^{\ominus}$$

Both terminal functions, the α-phenyl and ω-t-chloro groups, can be used for a variety of transformations. This paper concerns the convenient synthesis and characterization of Ph-PIB-Cl$^{\underline{t}}$, proof that the number average terminal functionalities are close to theoretical, a method of molecular weight control, and supporting experiments with various potential minifers.

Experimental

The synthesis and purification of terminally functional polyisobutylenes has been described(3,4). Benzyl chloride was distilled before use. α-Methylbenzyl chloride, cumyl chloride, p-methylcumyl chloride and p-chlorocumyl chloride were prepared from corresponding olefins by hydrochlorination (3). α,p-Dimethylstyrene was synthesized by the Wittig reaction as reported (5).

General experimental procedures involving the use of a dry box have been described (3). Polymerizations in refluxing methyl chloride were carried out in a 2000 ml three-neck round bottom flask equipped with stirring bar, thermometer, dropping funnel cooled with Dry Ice-i-PrOH, and Dewar-condenser cooled with Dry Ice-i-PrOH under dry N_2 atmosphere. Measured amounts of isobutylene and cumyl chloride were added to the flask containing methyl chloride through the dropping funnel. Polymerizations were initiated by carefully introducing BCl_3-CH_2Cl_2 (0.5 M) solutions to isobutylene-minifer-solvent charges so as to prevent run-away reactions. Polymerizations were extremely rapid and heterogeneous in nature, i.e., the polyisobutylene precipitated as soon as it formed. Reactions were killed by adding methanol at desired intervals and the methyl chloride was evaporated. Purification consisted of dissolving the product in benzene, washing with water to remove boron containing residues, precipitating into methanol, storing overnight, decanting the solvents, redissolving in hexanes, drying over $MgSO_4$, filtering, evaporating the hexanes, and drying the final product at room temperature in vacuum. The methanol soluble low molecular weight fraction of the product was lost by this procedure.

Structures and molecular weights were determined by ^1H-NMR (Varian Associates, T-60 NMR) and GPC (Waters Associates 600 High Pressure GPC, refractive index detector, μ-Styragel columns of 10^5, 10^4, 10^3, 500 and 10^2 Å). The determination of number average functionality $\overline{F}_n$ by ^1H-NMR spectroscopy has been described (2). The method involves dehydrochlorination of Ph-PIB-Cl$^{\underline{t}}$ and ^{1}H-NMR quantitation of protons associated with the terminal $CH_2{=}C(CH_3)$- and C_6H_5- groups. Inifer efficiency I_{eff} (fraction of inifer consumed during polymerization) was calculated by I_{eff}=[inifer consumed]/[inifer charged] = $([M]_o-[M])/(\overline{DP}_n\cdot[I]_o)$ where $[M]_o$ and [M] are the initial and final monomer concentrations, and $[I]_o$ is the initial inifer concentration.

Results and Discussion

1. Comparison of Benzylic Chloride Minifers

According to Kennedy et al. (6) the cumyl chloride/BCl_3 system efficiently initiates the polymerization of isobutylene. This lead was extended by examining further benzylic derivatives as potential minifers. Table I shows representative data. Importantly, cumyl chloride, *p*-methylcumyl chloride and *p*-chlorocumyl chloride yielded number average terminal functionalities $\overline{F}_n$'s close to theoretical ($\overline{F}_n$=1.0 signifies that each macromolecule contains one phenyl and one *t*-chloro terminus). The $\overline{F}_n$ values of the polymers harvested in the benzyl chloride and α-methylbenzyl chloride experiments could not be determined because the high $\overline{M}_n$ prevented end-group quantitation.

Since conversions were very high, the molecular weights are useful only as qualitative signposts which in conjunction with I_{eff} data may suggest some trends. Thus the relatively high $\overline{M}_n$'s and very low I_{eff}'s obtained with benzyl chloride and α-methylbenzyl chloride indicate rather low inifer activity. Cumyl chloride is a better chain transfer agent (lower $\overline{M}_n$), however, its I_{eff} is still only 0.38. *p*-Methylcumyl chloride is an excellent minifer as it yields the lowest $\overline{M}_n$ and its I_{eff} is maximum (unity). *p*-Chlorocumyl chloride is a much less reactive chain transfer agent as indicated by the relatively high $\overline{M}_n$ and low I_{eff}.

TABLE I. Effect of Minifer Structure on the Polymerization of Isobutylene with BCl_3 Coinitiator. ($[M]_o$=1.0 *M*, $[I]_o$=$[BCl_3]$=0.01 *M*, methyl chloride solvent, total volume = 250 ml., -60°C, 15 min.)

Minifer structure	Conv.[a] (%)	$\overline{F}_n$	$\overline{M}_n$ (g/mole)	I_{eff}
$C_6H_5CH_2Cl$	44		78,700	0.03[b]
$C_6H_5CH(CH_3)Cl$	42		77,400	0.03[b]
$C_6H_5C(CH_3)_2Cl$	100	1.02	14,900	0.38
p-$CH_3C_6H_4C(CH_3)_2Cl$	40	1.00	2,100[c]	1.07
p-$ClC_6H_4C(CH_3)_2Cl$	81	1.02	20,300	0.22

[a] Based on the amounts of isobutylene charged and products

[b] $\overline{F}_n$ was assumed to be unity

[c] Cloudy system, may be close to homogeneous

Evidently the electron donating *p*-methyl substituent greatly facilitates ion generation and chain transfer activity ("iniferíng"). In contrast, the electron withdrawing *p*-chloro substituent leads to a much less reactive though still acceptable minifer. The reactivity of the cumyl chloride parent compound falls inbetween the *p*-Me and *p*-Cl derivatives.

According to these data the rates of initiation (ionization) and chain transfer to minifer are accelerated by increasing the stability of the intermediate carbenium ion. Most importantly, these minifers give rise to well-defined phenyl head and *t*-chloro end groups, and neither chain transfer to monomer resulting in an olefinic terminus plus a CH_3-head group, nor indane-skeleton formation by intramolecular alkylation, nor ring alkylation (polybenzyl formation) occur (see later). In view of its modest cost, ease of handling, storage stability, availability and ease of preparation (from α-methylstyrene plus HCl) it was decided to use cumyl chloride in further investigations.

2. The Effect of Temperature

The effect of temperature on polymerization details in the cumyl chloride/BCl_3/isobutylene/CH_3Cl system has been investigated. Table II shows the findings. $\overline{F}_n$'s were close to theoretical in the -60° to -17.5°C temperature range. Surprisingly, $\overline{F}_n \approx 1.0$ even in a refluxing system! A slight tendency of decreasing $\overline{M}_n$'s and increasing I_{eff}'s with decreasing temperature is noticeable. The parallel temperature-$\overline{M}_n$ trend has also been observed in the similar binifer system (3). These trends can be explained by assuming that both the rate of ionization and chain transfer increase by increasing the polarity of the medium (i.e., by decreasing the temperature).

Figure 1 shows the ^{1}H-NMR spectra together with assignments of Ph-PIB-Cl$^{\underline{t}}$ prepared at -17.5 ± 0.5°C (first row Table II) and the monoolefin obtained from it upon dehydrochlorination with *t*-BuOK (4). The absence of terminal olefinic protons in spectrum *a* indicates the absence of proton elimination, i.e., chain transfer to monomer. Since the aromatic/olefinic proton ratio is close to theoretical, i.e., 5/2=2.5, indane-skeleton formation or polybenzylation can also be neglected

TABLE II. Effect of Temperature on the Polymerization of Isobutylene with the Cumyl Chloride/BCl_3 Minifer System ([M] = 1.0 *M*, [I] = [BCl_3] = 0.01 *M*, Methyl Chloride Solvent, 15 min.)

Temperature (°C)	Conv.^{b} (%)	$\overline{F}_n$	$\overline{M}_n$ (g/mole)	$\overline{M}_w/\overline{M}_n$	I_{eff}
-17.5 ± 0.5^{a}	100	0.98	19,000	1.6	0.29
-40	100	1.02	16,600	1.6	0.34
-60	100	1.02	14,900	1.7	0.38

a. Refluxing system

b. Based on the amounts of isobutylene charged and products

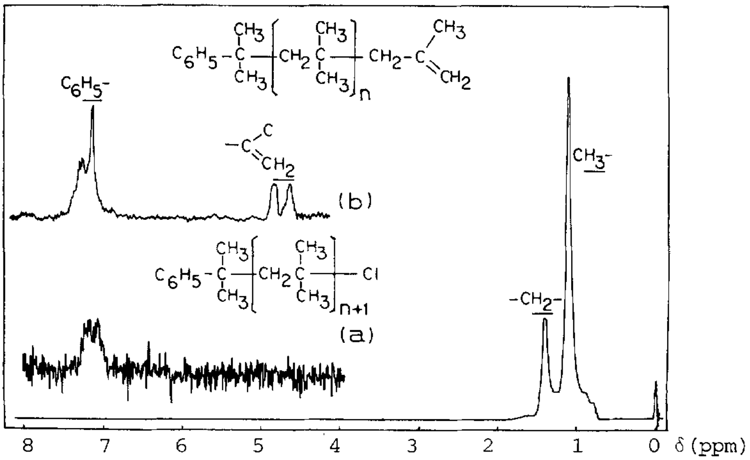

Fig. 1 ^{1}H-NMR spectra of Ph-PIB-Cl^t(a) formed at -17.5 ± 0.5°C and the dehydrochlorinated product (b)

3. The Effect of Monomer and Minifer Concentration

Having established that well-defined asymmetric telechelic prepolymers can be obtained under reflux conditions, a series of experiments designed to control molecular weights have been carried out at different monomer and inifer concentrations, $[M]_o$ and $[I]_o$. Table III shows the data. $\overline{F}_n$ values were consistently unity within what is considered to be experimental error. As anticipated by the similar results obtained in the binifer system (3), the molecular weights are strongly affected by $[M]_o$ and $[I]_o$.

TABLE III. Effect of Reaction Conditions on the Polymerization of Isobutylene with the Cumyl Chloride/BCl_3 Minifer System($[I]_o$ = $[BCl_3]$, Methyl Chloride Solvent, 20 min., conv. = 100%)

$[M]_o$ M	$[I]_o$ M	$\frac{[I]_o}{[M]_o}$	Temperature (°C)	$\overline{F}_n$	$\overline{M}_n$ (g/mole)	$\overline{M}_w/\overline{M}_n$	I_{eff}
1.0	0.01	0.01	-17.5±0.5	0.98	19,000	1.6	0.29
0.5	0.01	0.02	-17.7±0.5	0.96	14,800	1.6	0.19
0.2	0.01	0.05	-19.5±1.5	0.96	8,800	1.7	0.13
1.0	0.05	0.05	-16.5±1.5	0.97	9,000	1.5	0.12
1.0	0.10	0.1	-16.5±0.5	0.96	5,300	1.6	0.11

The inifer plot ($[M]/\overline{DP}_n$ versus $[I]$) shown in Figure 2 constructed with the data in Table III ($[M]$= 1 M) gave a straight line whose slope and intercept yielded $k_{tr,I}/k_p$ = 0.08 and k_t/k_p = 1.0 x 10^{-3}M. Evidently cumyl chloride is a less reactive inifer than p-dicumyl chloride (for the latter $k_{tr,I}/k_p$ = 2.0 and k_t/k_p = 3.6 x 10^{-3}M*(3)). Evidently the p-$C(CH_3)_2Cl$ and/or p-$C(CH_3)_2$-PIB substituents are net electron

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*Footnote: recalculation of the data in ref. 3 by using $[M]$ = $([M]_o + [M])/2$ instead of $[M] = [M]_o$ as done by the original authors yields k_t/k_p = 3.6 x 10^{-3} (and not 1 x 10^{-2}).

donors that increase the stability of the carbenium ion intermediate, i.e., enhance the rate of infering. This also explains the much higher $k_{tr,I}/k_p$ value found in the binifer system (3). As to the k_t/k_p values, this ratio is 3.6×10^{-3} for the binifer system and 1.0×10^{-3} for the minifer case; this discrepancy may be due to experimental variation and/or to the different temperatures used i.e., -60° here and -70°C in ref. 3.

Figure 3 shows a different version of the inifer plot. According to this presentation a straight relationship exists between $1/\overline{DP}_n$ and $[I]_o/[M]_o$. By the use of this relationship the molecular weight of Ph-PIB-Cl^t can be controlled within very wide limits.

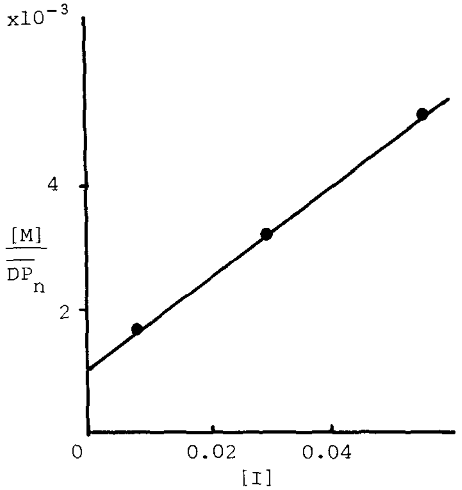

Fig. 2 Inifer Plots (data from Table III, $[M]_o$ = 1.0 M)

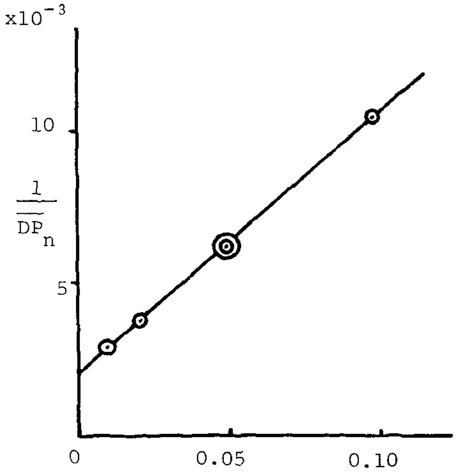

Fig. 3 Reciprocal Molecular Wts. vs Feed Ratios (data Table III)

Conclusion

Experimental conditions have been worked out for the convenient inexpensive quantitative preparation of Ph-PIB-Cl^t, i.e., an asymmetric telechelic polyisobutylene possessing exactly one phenyl and one t-chloro end group over a wide molecular weight range and relatively narrow molecular weight distribution.

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