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Synthesis, Characterization and Diels-Alder Extension of Cyclopentadiene Telechelic Polyisobutylene

2. α-Dicyclopentadienyl-ω-*t*-Chloropolyisobutylene*, **

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Abstract

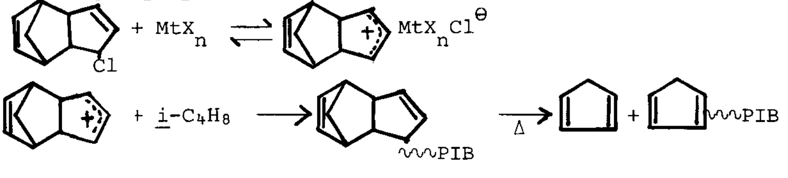
The use of 1-chlorodicyclopentadiene (DCp-Cl) as a minifer for the polymerization of isobutylene leading to asymmetric telechelic polymers having dicyclopentadienyl head groups and t-chloro tail groups, has been investigated. BCl_3 is ineffective, however, diethylaluminum chloride was found to be a suitable coinitiator for the polymerization. According to kinetic investigations chain transfer to monomer is absent and DCp-Cl is an efficient minifer. Polymer characterization indicated a DCp functionality close to 1.0. The t-chloro functionality was 0.27, probably due to side reactions of the t-chloro group with the strong Lewis acids formed during the polymerization.

Introduction

The use of binifers has led to the synthesis of α,ω-di(t-chloro)-polyisobutylene[1], ^{t}Cl-PIB-Cl^{t} whose derivatization has led to numerous novel telechelic polyisobutylenes carrying various useful end groups, e.g., isopropenyl[2], hydroxyl[3], dimethylsilylchloride[4]. These polymers are symmetrically substituted, i.e., they carry the same functions at each terminus. This symmetry is due to the symmetrical binifer, p-dicumyl chloride, used for the synthesis of the parent compound ^{t}Cl-PIB-Cl^{t}.

Recently experimentation has also been extended to the preparation of asymmetric telechelic prepolymer A∿∿B, i.e., telechelics carrying different functional groups A and B at either chain end, by the use of minifers. The principles governing the synthesis with minifers have been discussed and the preparation of α-phenyl-ω-t-chloropolyisobutylene by the cumyl chloride/BCl_3/isobutylene minifer system was described[5,6]. This paper concerns an extension of research on minifers, in particular the synthesis and characterization of α-dicyclopentadienyl-ω-t-chloropolyisobutylene DCp-PIB-Cl^{t}, a new asymmetric telechelic prepolymer.

It was theorized that DCp-PIB-Cl^{t} could be prepared by 1-chlorodicyclopentadiene, DCp-Cl, as the minifer in conjunction with a suitable Friedel-Crafts acid coinitiator. DCp-Cl is in fact an allylic chloride and as such was visualized to lead to controlled initiation (head group control). Further the DCp head group was thought to lead to the versatile cyclopentadiene, Cp, head group upon thermal cracking:



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* Part XXXII of the series "New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers)".

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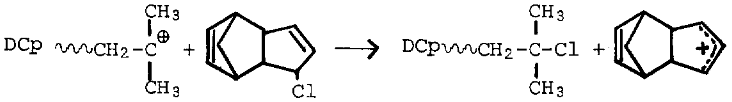
DCp-Cl should also act as a chain transfer agent yielding a new growing chain and a PIB chain having a *t*-chloro tail group:



The resulting polymer (DCp-PIB-Cl$^{\underline{t}}$) would have a DCp head group formed during initiation or chain transfer to DCp-Cl and a Cl$^{\underline{t}}$ tail group. Since PIB's having Cl$^{\underline{t}}$ termini have been shown to initiate α-methylstyrene polymerization[7], the synthesis of poly(isobutylene-*b*-α-methylstyrene) was envisioned. Thermal cracking of the DCp head group would yield α-cyclopentadienyl-ω-poly(isobutylene-*b*-α-methylstyrene) and Diels-Alder dimerization of this diblock would give a most intriguing A-B-A triblock copolymer.

Experimental

Materials

Materials, purification and handling techniques have been described (1-7). DCp-Cl was synthesized by the method of Dilling *et al.*[8]

Polymer Synthesis

Equipment and procedures have been described (1-7). Typically the reactors were charged with solvent followed by condensed isobutylene, DCp-Cl, and finally Et$_2$AlCl or BCl$_3$. Polymerizations began immediately. Precooled methanol was added to quench. The polymers were dissolved in *n*-hexane and washed with aqueous sodium potassium tartrate to remove aluminum oxide residues.

Polymer samples were analyzed using a Waters Associates 6000 A High Pressure Gel Permeation Chromatograph equipped with ultraviolet (UV) and refractive index (RI) detectors and Microstyragel columns of 10^5, 10^4, 10^3, and 500 Å. Approximately 0.2 ml of a 0.2% polymer in tetrahydrofuran solution was used at a flow rate of 2 ml/min. Fractionated samples of polyisobutylene having narrow molecular weight distributions were used as standards to contruct a calibration curve.

The DCp head group was analyzed using a Perkin-Elmer 559-A UV/Vis Spectrophotometer. A sample of DCp-PIB-Cl$^{\underline{t}}$ was heated to 160°C at 0.5 mm to crack the DCp head group. The polymer was dissolved in spectrograde *n*-hexane and the UV absorbance determined using a path length of 1 cm. Using *n*-propyl cyclopentadiene as a model compound for the cyclopentadiene absorbance, it was possible to determine the DCp functionality of the polymer.

The Cl$^{\underline{t}}$ end group concentration was determined by quantitative thermal dehydrochlorination[9]. A thin polymer film was coated on the inner surface of a U-shaped glass tube and heated to 180°C while dry nitrogen was passed through this tube. The evolved HCl was swept into water whose conductivity was measured.

Results and Discussion

1. Orienting Experiments with the DCp-Cl/BCl$_3$ System

Initially BCl$_3$ was examined as a coinitiator. BCl$_3$ is preferred for the synthesis of *t*-chloro telechelic polymers because this end group is formed during termination as well as during chain transfer[1]. Results are shown in Table I. DCp-Cl did not produce increased conversions beyond those obtained in control runs. Evidently the polymer arises via initiation due to protogenic impurities i.e., water. Conversions increased with decreasing temperature in the control experiments as well as in those containing DCp-Cl because termination is frozen out by lowering the temperature. This phenomenon has been observed and discussed previously[10].

The inability of DCp-Cl to initiate isobutylene polymerization in the presence of BCl_3 can be explained by Kennedy et al.'s observation[11] that allylic halides, which lead to secondary-secondary carbenium ions such as DCp-Cl, do not initiate (or initiate only very slowly) isobutylene polymerization. For initiation to occur it is necessary that the allylic chloride yields secondary-tertiary allylic carbenium ions.

While DCp-Cl is unable to initiate isobutylene polymerization in conjunction with BCl_3, it is able to act as a chain transfer agent. Thus according to the molecular weight data in Table I, DCp-Cl reduces molecular weights, presumably by chloride transfer.

The inability of BCl_3 to act as a coinitiator with DCp-Cl made it necessary to use other, less desirable initiators. Conventional Lewis acids such as BF_3, $AlCl_3$, $AlBr_3$, $TiCl_4$, $SnCl_4$, were not taken into consideration because they would not lead to controlled initiation (i.e., head group control would be impossible because they initiate with ubiquitous protic impurities). It was decided to use diethylaluminum chloride, Et_2AlCl, because it readily coinitiates the polymerization of isobutylene in the presence of allylic chlorides, such as DCp-Cl, and because it is known to lead to controlled initiation (head group control). Termination in Et_2AlCl coinitiated polymerizations lead to undesirable saturated end groups[10]. It was hoped that termination can be minimized in favor of chain transfer by DCp-Cl, an event that would yield the desired Cl^{t} terminus.

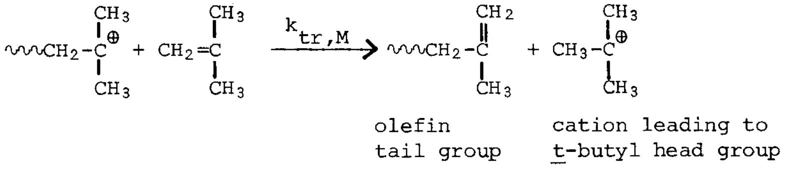
TABLE I

Polymerization of Isobutylene with the DCp-Cl/BCl Minifer System [IB] = 1 M; [DCp-Cl] = 0.005 M; [BCl] = 0.005 M; Total Volume = 20 ml CH_2Cl_2 Solvent

Temp. °C	[DCp-Cl] M x 10^3	Conv. %	$\bar{M}_n$ x 10^{-4}
-40	-	11.8	4.8
-40	5	8.8	2.6
-50	-	17.2	5.5
-50	5	13.0	3.4
-60	-	23.5	6.5
-60	5	20.7	3.6
-70	-	28.1	7.9
-70	5	22.1	5.0

2. Anticipated Reaction Scheme

Figure 1 is a scheme of isobutylene polymerization by the DCp-Cl/Et_2AlCl system. The nature of the end groups is determined by the relative rates of the individual reactions. The DCp head group is formed during initiation and chain transfer to minifer. Chain transfer to monomer results in an olefin tail group (and a sterile t-butyl head group) rather than the desired Cl^{t} tail group:

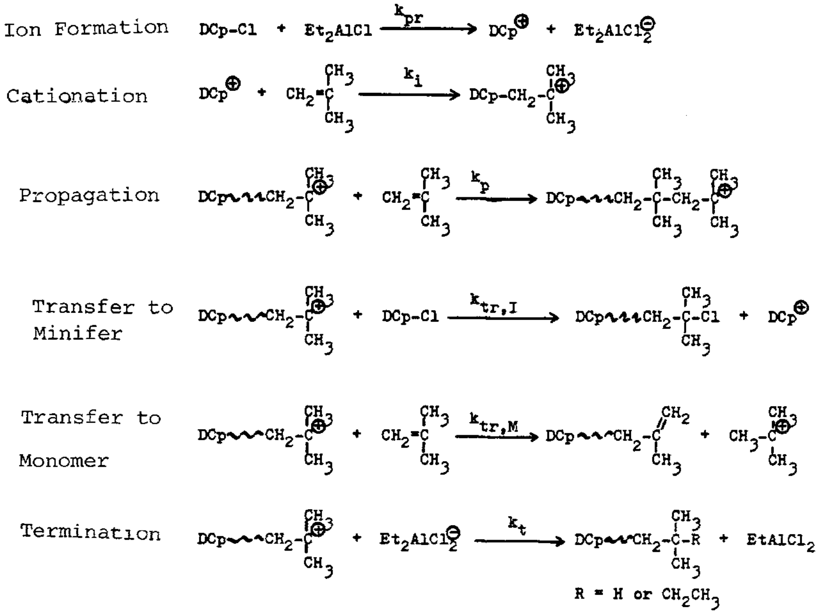


$$\sim\sim CH_2-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} + CH_2=\underset{CH_3}{\overset{CH_3}{C}} \xrightarrow{k_{tr,M}} \sim\sim CH_2-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}} + CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}}$$

For the DCp headed polymer to form quantitatively, $k_{tr,M}$ must be zero. Thus, the first priority was to develop conditions under which $k_{tr,M} = 0$.

The Cl^{t} tail group concentration is determined by the relative rates of various chain transfer and termination steps. It has been shown that the polymerization of isobutylene in the presence of Et_2AlCl proceeds in the absence of chain transfer to monomer, i.e., $k_{tr,M} = 0$. Thus in such systems the nature of end groups will be controlled by the relative rates of chain transfer to initiator (giving rise to the desirable Cl^{t} terminus) and termination (giving rise to undesirable saturated termini) as shown by the last equation in Figure 1.

Figure 1. Scheme for IB Polymerization by the DCp-Cl/Et_2AlCl Initiating System



The ratio of Cl^{t} tail groups to undesirable tail groups R (where R is H or ethyl) is given by

$$[Cl^{t}]/[R] = k_{tr,I}[DCp\text{-}Cl]/k_t \qquad (1)$$

Thus an increase in [DCp-Cl] will result in higher number average Cl^{t} functionality, $\overline{F}_n$(Cl^{t}). Increased [DCp-Cl] will also result in lower molecular weights, Table I and II. Since termination cannot be avoided, k_t 0, perfect Cl^{t} functionality cannot be achieved. Polymers having $\overline{F}_n$ (Cl^{t}) close to 1.0 would still be desirable. Cl^{t} functionality may be controlled by selecting reaction conditions e.g., solvent polarity, that effect $k_{tr,I}$ or k_t.

At low conversions the number average degree of polymerization ($\overline{DP}_n$) is given by

$$\overline{DP}_n = k_p[M]/k_{tr,M}[M] + k_{tr,I}[DCp\text{-}Cl] + k_t \qquad (2)$$

or

$$\frac{1}{\overline{DP}_n} = \frac{k_t + k_{tr,I}[DCp\text{-}Cl]}{k_p} \cdot \frac{1}{[M]} + \frac{k_{tr,M}}{k_p} \qquad (3)$$

By keeping [DCp-Cl] constant, the intercept of a plot of $1/\overline{DP}_n$ versus $1/[M]$ will give $k_{tr,M}/k_p$. If $k_{tr,M} = 0$, equation 3 simplifies to

$$[M]/\overline{DP}_n = k_{tr,I}/k_p + k_t/k_p \qquad (4)$$

Thus a plot of $[M]/\overline{DP}_n$ against [DCp-Cl] (inifer plot) should give a straight line with a slope of $k_{tr,I}/k_p$ and intercept k_t/k_p. Dividing the slope by the intercept gives $k_{tr,I}/k_t$ so that the ratio $[Cl^{t}]/[R]$ in Equation 1 can be calculated.

3. Verification of $k_{tr,M} = 0$.

The t-BuCl/Et_2AlCl and Cl_2/Et_2AlCl/isobutylene systems were found to be free of chain transfer to monomer[10,15]. The growing ion pair in these systems is the same as that present in the DCp-Cl/Et_2AlCl/isobutylene system so that chain transfer to monomer would be expected to be absent in this case also.

A series of experiments have been carried out to ascertain that $k_{tr,M} = 0$. A nonpolar solvent, methylcyclohexane, MeCH, was added so that the total volume of nonpolar solvents, isobutylene and MeCH should remain constant. The $1/\overline{DP}_n$ versus $1/[M]$ plot, shown in Figure 2, gives a straight line with a slope of 1.80 $\underline{M}^{-1}$ and zero intercept within experimental error. Evidently chain transfer to monomer is indeed absent and every polymer molecule should have a DCp head group.

4. Determination of $k_{tr,I}$

To obtain high yields of DCp-PIB-Cl^{t} it is necessary to find conditions where $k_{tr,I}/k_t$ is maximum. Thus a series of polymerizations have been carried out by varying [DCp-Cl] at two different solvent compositions at -50°C. Increased [DCp-Cl] was found to depress polymer molecular weights. Figure 3 shows the data. Both plots give the same intercept. The intercepts, k_t/k_p by equation 4, are 4.9×10^{-3}.

The data obtained by the use of the less polar solvent system (i.e., 22.5% MeCH)gives rise to a steeper slope. For the less polar solvent k_{tr}/k_p is 1.43 and for the more polar solvent $k_{tr,I}/k_p$ is 1.14. Dividing the slope by the intercept vies $k_{tr,I}/k_t$. For the less polar solvent system $k_{tr,I}/k_t$ is 300 while for the more polar solvent it is 230 l/mole. From Equation 1, the less polar solvent system will result in higher Cl^{t} functionality.

The fact that k_t/k_p is independent of solvent polarity indicates that the effect of solvent polarity on the transition state of termination and propagation is the same. A larger value for $k_{tr,I}/k_t$ for the lower solvent polarity can arise either by an increased $k_{tr,I}$ or by a decreased k_t value.

While lower solvent polarity is favorable for chain transfer to DCp-Cl, it is unfavorable for initiation. Charge separation necessary for initiation is stabilized by solvation with polar solvent. In our experiments initiation was very slow and the polymerizations were incomplete even after 30 minutes in solvents containing more than 22.5% methylcyclohexane.

5. Survival of DCp Head Group

The DCp head group contains two double bonds which may react with a growing polymer chain. To investigate this possibility a series of polymerizations were carried out in the presence of various amounts of DCp. According to the results shown in Table II, DCp has no effect on conversion, $\overline{M}_n$, of polydispersity of the PIB. The reaction with the DCp double bond probably does not occur because this would lead to a secondary carbenium ion which is of higher energy than the propagating tertiary carbenium ion. Thus decreased polymer molecular weights obtained in the presence of DCp-Cl are most likely due to chloride anion transfer from DCp-Cl to the growing polymer chain.

Figure 2

Plot of $1/\overline{DP}_n$ versus $1/[M]$ to Demonstrate $k_{tr,M} = 0$

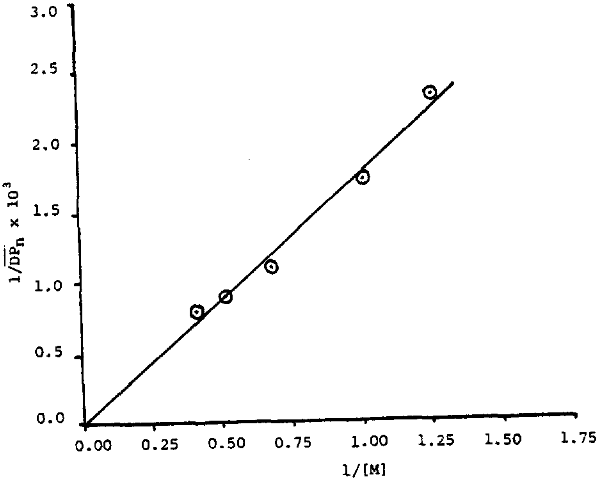


TABLE II

Effect of [DCp] on Molecular Weight of DCp-PIB-Cl$^{\pm}$

$[IB] = 1M$; $[Et_2AlCl] = 1 \times 10^{-2}M$; $[DCp\text{-}Cl] = 1 \times 10^{-3}M$ CH_2Cl_2; -50°C

Sample	DCp [M] x 10^3	Conv. %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
811-25	1.0	66.7	49,500	1.84
811-26	2.0	64.7	41,500	2.12
811-27	3.0	61.3	52,700	1.79
811-28	4.0	59.3	50,800	1.88
811-29	5.0	67.9	49,400	1.86

6. Synthesis and Characterization of DCp-PIB-Cl$^{\pm}$

DCp-PIB-Cl$^{\pm}$ of $\overline{M}_n \sim 20,000$ would be suitable for the synthesis of poly(isobutylene-b-α-methylstyrene) having a DCp head group. After cracking off of Cp, Diels-Alder dimerization of the Cp head group would lead to an A-B-A triblock copolymer having an elastomeric polyisobutylene middle segment of $\bar{M}_n$ = 40,000, i.e., a useful thermoplastic elastomer. According to the data shown in Figure 3, such a polymer could be obtained with [DCp-Cl] = 3 x 10^{-3}M in 22.5% MeCH/77.5% CH_2Cl_2.

According to Equation 1 $k_{tr,I}/k_t$ ≈ 300 and $[Cl^t]/R$ = 0.90: from this $\bar{F}_n(Cl^t)$ = 0.47, i.e., 47% of the chains will have Cl^t end groups and 53% either a hydrogen atom or an ethyl group. An increase in the [DCp-Cl] will result in a greater $\bar{F}_n(Cl^t)$ but will also decrease the $\bar{M}_n$ so that triblock copolymers having useful properties may not form.

According to these data a limited number of Cl^t tail groups can be incorporated into the polymer, however, it would be very difficult to find conditions where the functionality of Cl^t tail groups would be close to unity.

Figure 3. Plot of $M/\bar{DP}_n$ versus [I] to Determine $k_{tr,I}/k_p$

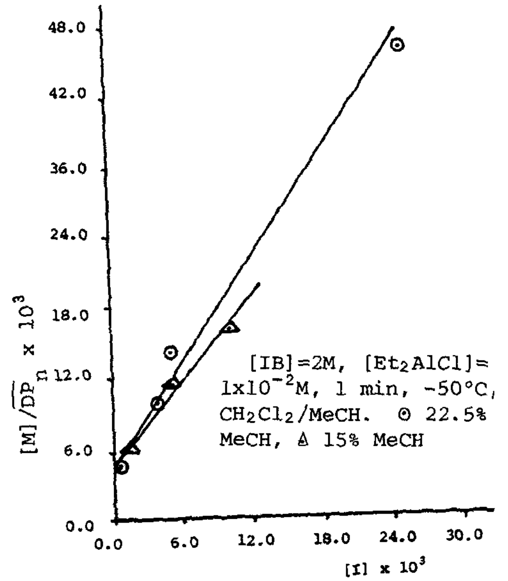
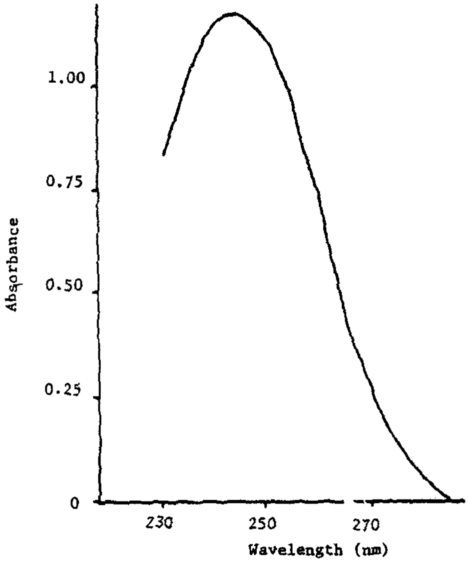


Figure 4. UV Spectrum of Cp-PIB-Cl^t



7. Quantitative Analysis of DCp Head Group and Cl^t Tail Group

The validity of the kinetic scheme has been examined by determining quantitatively the DCp head group and Cl^t tail group concentration in a sample of DCp-PIB-Cl^t. A polymer sample was prepared using [DCp-Cl] = 3 x 10^{-3}M, [IB] ≈ 1M, and [Et_2AlCl] = 2 x 10^{-3}M at -50°C in a solvent containing 22.5% MeCH and 77.5% CH_2Cl_2. $\bar{M}_n$ was 26,300 with $\bar{M}_w/\bar{M}_n$ = 2.30.

To crack the DCp head group the sample was heated to 160°C at 0.5 mm for 3 hours and then analyzed by UV spectroscopy. The spectrum shown in Figure 4 was obtained. Using n-propylcyclopentadiene as the model for the head group (ε_{max} - 3670 l/mol/cm), the number average functionality of Cp head group, $\bar{F}_n(Cp)$ was found to be 0.95. This value confirms the results of the kinetic analysis according to which the polymer carried one DCp head group per molecule.

According to quantitative thermal dehydrochlorination at 180°C the DCp-PIB-$\mathrm{Cl}^{\underline{t}}$ was found to contain $\overline{F}_n(\mathrm{Cl}^t)$ of 0.27 instead of 0.47 calculated from kinetic parameters. The discrepancy between the anticipated and the actual value is too large to be due to experimental error. It is believed that side reactions (i.e., reaction of Cl^t tail group with excess $\mathrm{Et_2AlCl}$ or $\mathrm{EtAlCl_2}$ formed in situ) destroy almost half of the $\mathrm{Cl}^{\underline{t}}$ functionality.

Although $\overline{F}_n(\mathrm{Cl}^{\underline{t}})$ is lower than expected, the presence of $\mathrm{Cl}^{\underline{t}}$ termini indicates chain transfer to minifer, i.e., transfer of a chloride anion from the DCp-Cl to the growing polymer chain.

Acknowledgement

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