Cyclopentadienylation of Polychloroprene

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ABSTRACT

Polychloroprenes CR containing pendant cyclopenta-
diene Cp functions have been synthesized by treating
the rubbers with dimethylcyclopentadienyl-aluminum
Me_2CpAl. Optimum reaction conditions have been deter-
mined. Cyclopentadienylated polychloroprenes CR-Cp
gelled on drying, however, the products became soluble
upon treatment with strong dienophiles, e.g., maleic
anhydride or dimethyl acetylenedicarboxylate. Evidently
gelation is due to Diels-Alder addition of pendant Cp
groups and may lead to thermally reversible networks.

INTRODUCTION

Carbocationic cyclopentadienylation with Me_2CpAl
of polymers containing labile (allylic, tertiary) chlor-
ines, e.g., chlorinated butyl rubber, ethylene-propylene
copolymer (KENNEDY and CASTNER 1979 a,b,c), PVC (IVÁN
et al. 1979 a,b, 1980 a) has been shown to produce a
series of unique materials. For example, cyclopenta-
dienylated butyl rubbers have been demonstrated (KENNEDY
and CASTNER 1979 a,b,c) to yield thermally reversible
(remoldable) networks by Diels-Alder/retro-Diels-Alder
reactions. As a continuation of these studies CR's have
been cyclopentadienylated, cyclopentadienylation condi-
tions have been optimized, and some crosslinking studies
have been carried out to demonstrate the possibility of
reversible Diels-Alder network formation with CR-Cp.

EXPERIMENTAL
    A. Materials
    Two polychloroprene samples have been used. CR(D)
is an experimental sample (No. 15894-79-2, obtained
from E. I. DuPont de Nemours and Co.) having a Mooney
viscosity $ML_{100}^{2.5} \approx 25$ and $\bar{M}_n = 1.03 \times 10^5$ by osmometry.
Details of preparation have been described (IVÁN et al.
1980 b). CR(R) is a commercial polychloroprene, MC(30),

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from Rhone-Poulenc S.A.

Pure CR's are oxygen and light sensitive. Thus, purification of CR samples has been carried out under a dry nitrogen atmosphere in a stainless steel enclosure in glasswares covered by aluminum-foil. Samples were purified by repeated precipitations from dry methylene chloride into dry n-pentane.

The synthesis and purification of dimethylcyclopentadienylaluminum (Me$_2$CpAl) has been described (KENNEDY and CASTNER 1979 b). Maleic anhydryde (MA) (Aldrich) and dimethyl acetylenedicarboxylate (DMADC) (Aldrich) were used as received. Solvents were thoroughly dried and distilled before use.

B. Procedures

Cyclopentadienylation experiments were carried out by adding Me$_2$CpAl dissolved in dry methylene chloride to CR in dry methylene chloride solution (2-3%CR by weight) under vigorous stirring in a stainless-steel enclosure under a dry nitrogen atmosphere. Reactions were quenched by prechilled methanol. Solid aluminum-containing residues were removed by filtration soon after quenching with methanol the cyclopentadienylation experiments.
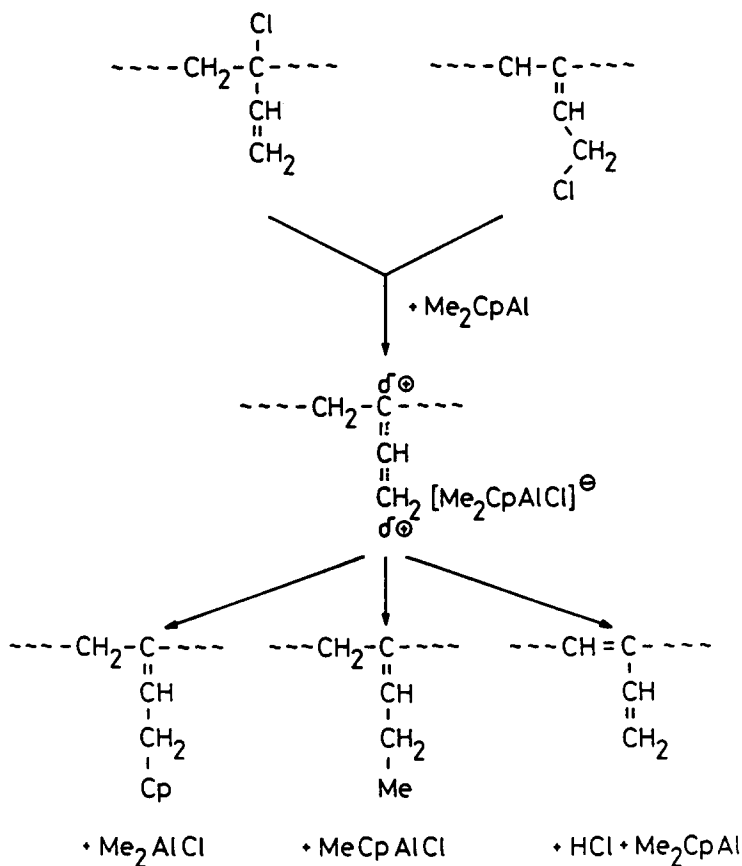
Cyclopentadienylated CR's (~1% polymer solution in THF or chlorobenzene) were refluxed with excess maleic anhydride or dimethyl acetylenedicarboxylate overnight under a dry nitrogen atmosphere.

Samples for thermal dehydrochlorination were prepared in form of thin films deposited on U-shaped glass tubes (6 mm id). The films were prepared by filling the tubes with CH$_2$Cl$_2$ solutions of samples in the dry box, evaporating the solvent, and drying to constant weight (~0.02-0.03 g) under vacuum in the dark. The extent of dehydrochlorination was determined by using conventional conductivity measurements (TÜDÖS and KELEN 1973) of HCl solutions. The technique has been described in detail (IVÁN et al. 1980 b).

RESULTS AND DISCUSSION

A. Cyclopentadienylations

CR contains two types of allylic chlorines -CH$_2$C(Cl)(CH=CH$_2$) and -CH$_2$C=CHCH$_2$Cl, and two types of vinylic chlorines -CH$_2$C(Cl)=CHCH$_2$- and -CH$_2$-CH(CCl=CH$_2$) (COLEMAN et al. 1977, COLEMAN and BRAME 1978). On the basis of experience with similar systems (KENNEDY and CASTNER 1979 a,b,c,) we expected only the allylic chlorines to react with Me$_2$CpAl. The scheme below shows the proposed path of cyclopentadienylation of CR with Me$_2$CpAl.

$$
\begin{array}{ccc}
\text{----CH}_2\text{--}\overset{\displaystyle Cl}{\underset{\displaystyle\underset{\displaystyle CH_2}{\overset{\|}{CH}}}{\underset{|}{C}}}\text{----} & \qquad & \text{----CH--}\underset{\displaystyle\underset{\displaystyle\underset{\displaystyle Cl}{CH_2}}{\overset{\|}{CH}}}{C}\text{----}
\end{array}
$$

$$\downarrow \ \text{+ Me}_2\text{CpAl}$$

$$
\text{----CH}_2\text{--}\underset{\displaystyle\underset{\displaystyle\underset{\displaystyle\overset{\displaystyle d\oplus}{CH_2}}{\overset{\|}{CH}}}{\overset{d\oplus}{\underset{\|}{C}}}\text{----}\ \ [\text{Me}_2\text{CpAlCl}]^{\ominus}
$$

$$
\begin{array}{ccc}
\text{----CH}_2\text{--}\underset{\displaystyle\underset{\displaystyle\underset{\displaystyle Cp}{CH_2}}{\overset{|}{CH}}}{\overset{\|}{C}}\text{----} &
\text{---CH}_2\text{--}\underset{\displaystyle\underset{\displaystyle\underset{\displaystyle Me}{CH_2}}{\overset{|}{CH}}}{\overset{\|}{C}}\text{----} &
\text{---CH}=\underset{\displaystyle\underset{\displaystyle CH_2}{\overset{\|}{CH}}}{\overset{|}{C}}\text{----}\\[4ex]
\text{+ Me}_2\text{AlCl} & \text{+ MeCpAlCl} & \text{+ HCl + Me}_2\text{CpAl}
\end{array}
$$

Detailed experiments have been carried out to determine the extent of cyclopentadienylation and optimum cyclopentadienylation conditions.

The extent of cyclopentadienylation was obtained by determining by thermal dehydrochlorination the difference of the extent of HCl evolved from virgin and Me_2CpAl treated CR's. If dehydrochlorination is carried out to a sufficient extent, this difference is a quantitative measure of allylic chlorines reacted during Me_2CpAl-treatment. It is assumed that Me_2CpAl cyclopentadienylates only allylic chlorines, and that side reactions such as methylation and/or deprotonation shown in the Scheme are absent, thus the difference is also a measure of the extent of cyclopentadienylation.

Figure 1 shows the results of two dehydrochlorination experiments. The control curve reflects ξ_{HCl} as a function of time of purified virgin CR, whereas curves 1 and 2 show the same for CR's treated with Me_2CpAl ($R=\text{Me}_2\text{CpAl}/CR=0.06$, where CR = number of repeat

units in CR) at -40° for 5 and 30 mins, respectively. The
kinetics of CR dehydrochlorination as revealed by the
shape of these curves has been analyzed (IVÁN et al.
1980 b, KENNEDY et al. 1980) and according to these
studies the first rapid phase of HCl loss is due exclu-
sively to the presence of allylic chlorines whereas the
later relatively slower steady HCl loss phase mainly
reflects the rate of dehydrochlorination due to vinylic
chlorines in CR. Importantly, the slopes of the slow
HCl loss phases are parallel for the control and
Me_2CpAl-treated samples indicating identical HCl loss
kinetics during the later stages of these experiments.
Thus the labile allylic chlorines consumed by Me_2CpAl
may be obtained by determining the difference in ξ_{HCl}
versus time plots, $\Delta\xi_{HCl}$, between control and Me_2CpAl-
treated samples:

$$\Delta\xi_{HCl} = \xi_{HCl, \text{ untreated}} - \xi_{HCl, Me_2CpAl\text{-treated}}.$$

At longer dehydrochlorination times $\Delta\xi_{HCl}$ becomes hori-
zontal and the concentration of allylic chlorines lost
by cyclopentadienylation Δ can be obtained by extra-
polation to the ordinate (dotted lines) as shown by
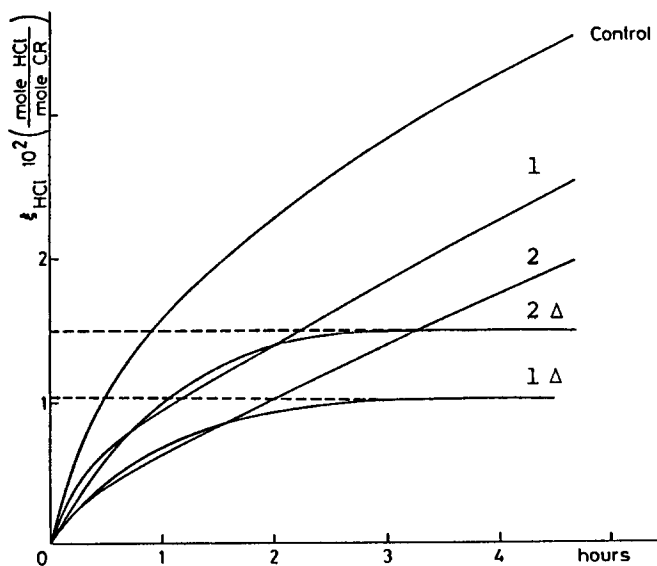lines 1Δ and 2Δ in Figure 1.

Figure 1.   Extent of HCl loss as a function of time for
untreated CR, $Me_2CpAl/6/-40/30$ (2) and
$Me_2CpAl/6/-40/5$ (1) samples, and the differ-
ences.

By the use of this dehydrochlorination method recently we determined that the labile chlorine concentration in CR(D) $[Cl_L]$ is 1.59 mole % (IVÁN et al. 1980 c).

The ratio $\Delta/[Cl_L]$ i.e., the labile allylic chlorines consumed by Me_2CpAl treatment over the total quantity of labile chlorines in CR, is a valuable measure of the extent of cyclopentadienylation. Series of detailed experiments have been carried out to determine the effect of Me_2CpAl concentration, temperature and time on $\Delta/[Cl_L]$. Figures 2-4 show the results.
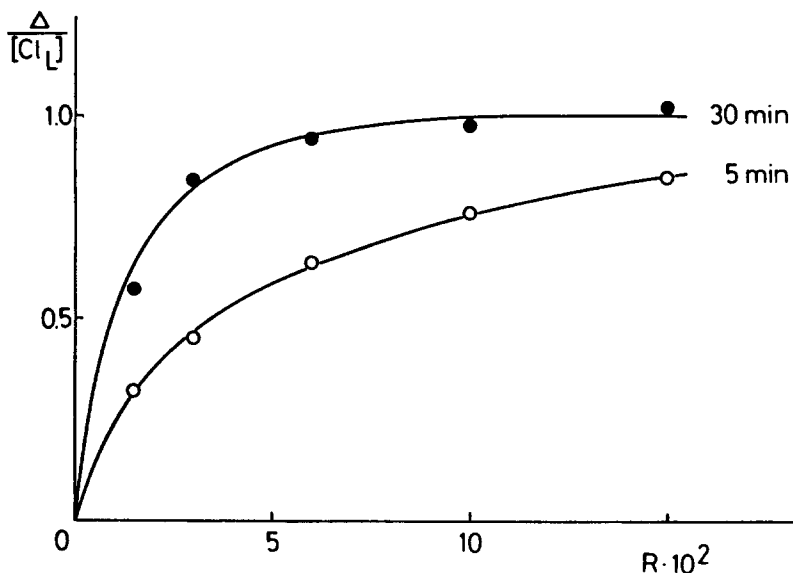
Figure 2. $\Delta/[Cl_L]$ as a function of Me_2CpAl/CR ratio for CR's treated for 5 and 30 minutes at $-40^{\circ}C$.

According to the data in Figure 2 increasing Me_2CpAl/CR increases the extent of cyclopentadienylation and the reaction is complete with $Me_2CpAl/CR = 0.10$ after 30 mins at $-40^{\circ}C$. Evidently, cyclopentadienylation is incomplete even with $Me_2CpAl/CR = 0.15$ when the reaction time is reduced to 5 mins.

According to the data in Figure 3, increasing the temperature increases the cyclopentadienylation extent in experiments carried out for 30 and 5 mins ($Me_2CpAl/CR = 0.10$). Cyclopentadienylation is essentially complete at or above $\sim -40^{\circ}C$ for samples treated for 30 mins. However, the yield is < 90% even at -10° after only 5 mins of treatment with Me_2CpAl.

According to the data in Figure 4, cyclopentadienylation extent increases rapidly with the time and the reaction becomes essentially complete after $\sim$ 35 mins at $-40^{\circ}C$ with $Me_2CpAl/CR = 0.1$.
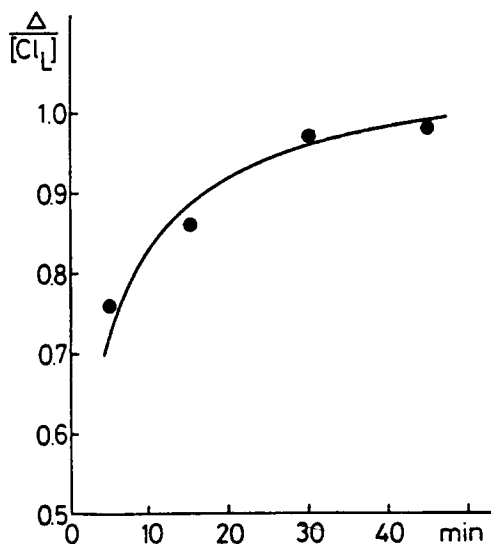
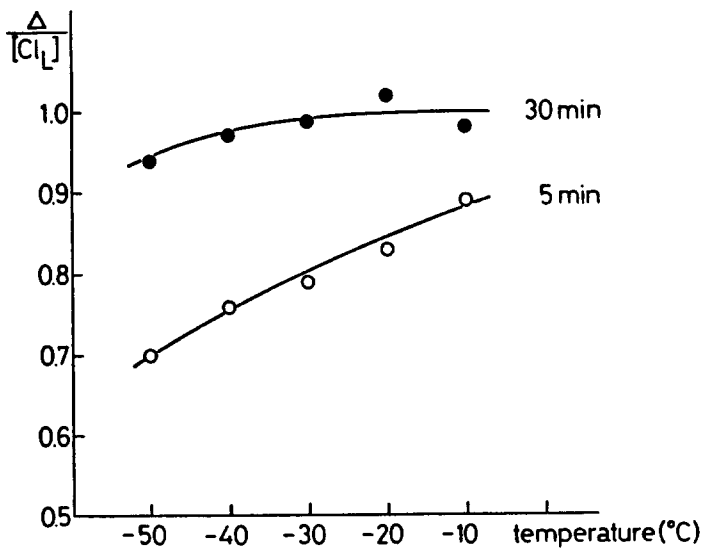Figure 3. $\Delta/[Cl_L]$ as a function of temperature for CR's treated with Me_2CpAl (R=0.1) for 5 and 30 minutes.

Figure 4. $\Delta/[Cl_L]$ as a function of time for CR's treated with Me_2CpAl (R=0.1) at $-40^\circ C$.

In sum, in line with these data allylic chlorines
in CR can be exhaustively cyclopentadienylated with
Me_2CpAl and essentially complete reactions can be read-
ily achieved by the use of $Me_2CpAl/CR \sim 0.1$, after ~ 35
mins at or above $-40^{O}C$.

B.   Diels-Alder Crosslinking of Cyclopentadienylated
     CR's

Guided by the above findings, larger amounts of
cyclopentadienylated CR's have been synthesized for
crosslinking (gelation) studies. Cyclopentadienylations
of CR(D) and CR(R) have been carried out at $Me_2CpAl/$
$CR = 0.1$ for 30 mins at $-40^{O}C$ as described in Experi-
mental.

Both CR's behaved quite similarly. The cyclopenta-
dienylated rubbers were soluble in CH_2Cl_2 immediately
after reactions. However, gelation occurred after stor-
age for 2-3 days at room temperature in vacuum in the
dark. None of the cyclopentadienylated CR samples dis-
solved completely in THF or benzene; the cyclopenta-
dienylated CR(D) and CR(R) gave 77 and 80% sol fraction
in THF, respectively. Similar phenomena have been ob-
served with cyclopentadienylated chlorobutyl rubber
(KENNEDY and CASTNER 1979 a,c).

Significantly, the gelled CR-Cp systems became
soluble upon the addition of strong dienophiles, such as
MA and DMADC. Thus dissolution ensued upon the addition
of excess amounts of MA and/or DMADC to swollen CR-Cp
gels in refluxing THF and/or chlorobenzene diluents.
Evidently gelation during the drying of these CR-Cp's
is not due to undesirable permanent network formation
but to Diels-Alder addition between pendant Cp groups.
Strong dienophiles capture the free Cp functions, per-
manently remove them from the Diels-Alder/retro-Diels-
Alder equilibrium and thus effect dissolution:
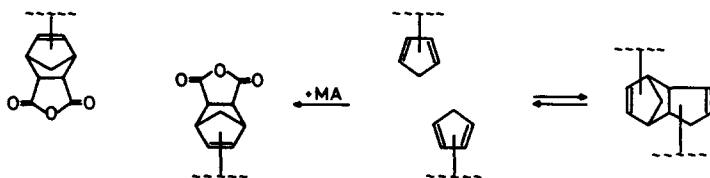
Cyclopentadienylated CR's may yield thermally
reversible networks and may lead to numerous other
valuable derivatives.

ACKNOWLEDGEMENT

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