Photochemical degradation of polyepichlorohydrin and its cleavage with n-butyl lithium

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The photochemical stability and degradation of polyepichlorohydrin, freed from antioxidant, have been investigated under various conditions, with the polymer in the solid state, in solution, stored in the dark, and exposed to bright sunlight or u.v. light from a medium pressure mercury discharge lamp. The solid polymer maintained in the dark was found to be relatively stable without added antioxidant for at least three months. The polymer in the solid state or in solution exposed to sunlight or u.v. light underwent degradation involving cleavage and possible cross-linking with formation of carbonyl and hydroxyl groups in the degraded polymer. A relatively slow cross-linking reaction occurred with polyepichlorohydrin in solution in the dark. Base cleavage of polyepichlorohydrin with n-butyl lithium has been investigated at room temperature. The polymer underwent a relatively fast cleavage reaction, resulting in a sharp decrease both in molecular weight and limiting viscosity number. Various groups in the degraded polymer such as –OH, –C≡CH, α,β-unsaturated carbonyl, for example, were identified by infra-red spectroscopy.

Keywords Polyepichlorohydrin; degradation; photochemistry; n-butyl lithium; cleavage

INTRODUCTION

Epichlorohydrin (ECH) based elastomers including the homopolymer, polyepichlorohydrin, PECH, and the 1:1 molar ratio copolymer with ethylene oxide, designated P(ECH–co–EO), are notable for their good balance of physical and chemical properties[1,2]. Their commercial importance has motivated several studies of their stability, and stabilization by various additives. The polymers have been found to be relatively stable towards heat up to a temperature of 150°C[3-5]. The rubbers in their compounded and uncompounded forms decompose slowly above 150°C and rapidly above 200°C, with evolution of HCl, both in air and in an inert atmosphere[3,4]. With suitable formulations and cure, the compounded polymers present no serious problems with respect to HCl evolution up to temperatures of 175°C[3]. In order to increase the service temperatures of the elastomers, the effect of various additives, including acceptors of HCl[4] and other metal salts[5] on the thermal stability of the polymers has been investigated. However, the photochemical stability of the ECH elastomers has not been studied extensively. It has been shown that ECH elastomers and other polyethers, mixed with suitable antioxidants, are relatively stable photochemically. However, during the synthesis of poly(epichlorohydrin-g-styrene) copolymers[6,7], it was noticed that purified amorphous polyepichlorohydrin, free from antioxidant, underwent photochemical degradation in sunlight. More extensive results of such degradation are reported in the present paper.

It has also been observed that epichlorohydrin polymers undergo degradative cleavage in the presence of strong bases[6,8]. The degradation of PECH induced by n-butyl lithium was studied primarily to compare and contrast this type of degradation with that induced by polystyryl lithium, which had previously been examined[6]. Data relating in particular to the molecular weight decrease of PECH induced by n-BuLi are reported in this paper.

EXPERIMENTAL

Reagents

Polyepichlorohydrin, PECH, used in these studies, designated PECH-2 and PECH-3, consisted of samples, freed from antioxidant obtained by a double precipitation of 'Herchlor H' (Hercules Inc.) from a 2% w/v benzene solution into excess methanol (BDH, Tech, grade). Samples of PECH synthesized in this laboratory were also used, designated PECH-1, following the procedure described elsewhere[9]. Polymer samples dried to a constant weight in a vacuum oven at 50°C, were stored in the dark in stoppered bottles, wrapped in Al-foil, until required.

Benzene C_6H_6 and toluene, Ph-CH_3 (Koch-Light Lab. Ltd.), were distilled and the middle fractions used as required. n-Butyl lithium, n-BuLi (Alpha Products), was diluted, stored and handled as described previously[6].

Chloroform $CHCl_3$ (BDH, spectroscopic grade) used for spectroscopic analysis of the polymer samples in solution, was eluted through activated alumina, Al_2O_3, to ensure that the solvent was free from stabilizer, ethanol.

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Silver nitrate $AgNO_3$ (BDH, 'AnalaR' grade) was used in some gravimetric analyses being converted into AgCl by free chloride ions. 2,6-Di-terbutyl-*p*-cresol (BDH) was used as an antioxidant in some experiments.

Characterization techniques

Viscometry: Reduced viscosities, $[\eta_{sp}/c]$, and limiting viscosity numbers, $[\eta]$, of the initial and degraded polymer samples, were measured in toluene, at various temperatures stated in the text using a modified Ubbelohde suspended level viscometer.

Gel permeation chromatography: g.p.c. measurements of the undegraded and degraded polymer samples were carried out by the Polymer Supply and Characterization Centre, RAPRA, Shawbury, Shrewsbury, using 0.2% w/v solutions of the polymers in THF at 20°C.

Infra-red, i.r. spectroscopy: i.r. measurements of the initial and degraded polymer samples were made using a Perkin-Elmer 157G grating spectrophotometer. Thin films of the polymers directly cast onto NaCl plates from $CHCl_3$ solutions, or $CHCl_3$ solutions of the polymers in a variable path length cell were examined.

Photochemical degradation of PECH

A sample of polyepichlorohydrin freed from antioxidant, PECH-1, synthesized in these laboratories as described elsewhere[9], was studied under different experimental conditions. Thus a portion of solid PECH-1, placed in a stoppered Pyrex bottle wrapped in Al-foil, was stored in a dark cupboard. Fresh solutions were made using this solid PECH-1 in toluene ($4.0\ g\ dm^{-3}$) from time to time, and reduced viscosities, (η_{sp}/c), were measured at 25°C. Another portion of solid PECH-1 was placed in a stoppered Pyrex bottle but now exposed to bright sunlight. Fresh solutions were made using this solid PECH-1 sample in toluene ($4.0\ g\ dm^{-3}$) from time to time and reduced viscosities were measured at 25°C.

In three further experiments, the degradation of a solution of polyepichlorohydrin in toluene ($4.0\ g\ dm^{-3}$) at room temperature ($\sim$20°C) was followed. Thus, one solution of PECH-1 was stored in a stoppered Pyrex bottle covered in Al-foil, inside a dark cupboard, while a second solution of PECH-1 was stored in an uncovered stoppered Pyrex bottle and exposed to bright sunlight. A third toluene solution of another polyepichlorohydrin, PECH-2 of the same initial concentration as above was stored in a stoppered uncovered Pyrex bottle and exposed to u.v. light from a medium pressure mercury discharge lamp with its envelope removed. The reduced viscosities of these three solutions were measured at 25°C as a function of time.

The i.r. spectrum of a solid sample of PECH-2 exposed to sunlight for one month was also recorded, as was that of a sample of solid PECH-2 exposed to u.v. light from a high pressure mercury lamp for 4 h.

Butyl lithium cleavage of PECH

A sample of polyepichlorohydrin, PECH-3, freed from antioxidant, was dissolved in C_6H_6, 1% w/v, which was carefully flushed with purified argon. n-BuLi in n-hexane was then added and the mixture was stirred at room temperature (approx. 20°C) for 6 h. The reaction was then short-stopped by addition of degassed distilled water. A small amount of antioxidant, 2,6-di-tert-butyl-*p*-cresol, dissolved in C_6H_6 was added to give a final concentration of 0.05% w/v of the antioxidant in the total dissolved solid. Four similar experiments were performed under otherwise identical experimental conditions, but with different values of the ratio R, defined as (number of moles of n-BuLi/number of moles of Cl in PECH).

The mixture from a cleavage experiment was rotary evaporated at room temperature, to remove benzene and water. The polymer was redissolved in benzene, filtered through a porosity 3 sintered crucible and this solution was rotary evaporated to dryness to recover the degraded and previously soluble polymer. The polymer was further dried for a week in a vacuum desiccator in the dark before characterization.

The solid retained in the sintered crucible, insoluble in C_6H_6, consisting of LiCl, LiOH, and possibly other lithium compounds, was dried and then dissolved in dilute HNO_3. The total amount of chloride ions in each acidic solution was determined as AgCl by gravimetric analysis[10].

In this paper, the % chlorine loss from the PECH was defined:

$$\%\ \text{Chlorine loss} = \left(\frac{\text{mass of Cl displaced from PECH}}{\text{mass of Cl in original PECH}}\right) \times 100$$

The relative amounts of various groups produced from PECH by cleavage were determined as a function of the ratio (number of moles of n-BuLi/number of moles of Cl in original PECH sample), designated as *R*, by analysis of their i.r. spectra recorded in $CHCl_3$ solutions. Due corrections were made for absorptions due to the solvent.

RESULTS AND DISCUSSION

Photochemical degradation

Viscosity results show that the amorphous solid polyepichlorohydrin sample PECH-1, free from antioxidant, remained stable in the dark (*Figure 1*, curve I) during a period of investigation of 110 days. The same

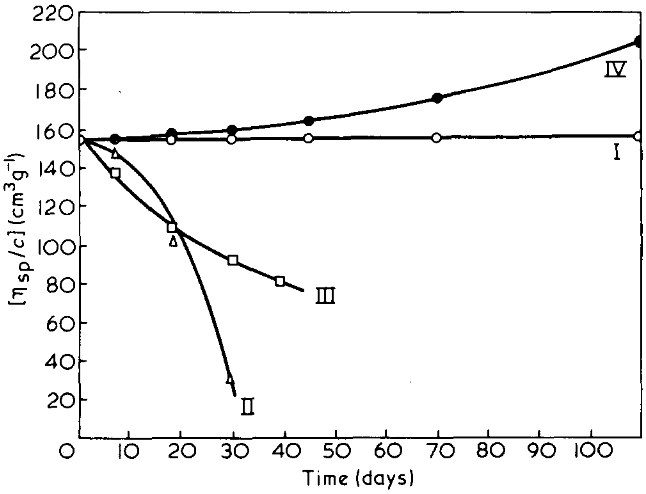


Figure 1 Reduced viscosities of amorphous polyepichlorohydrin, sample PECH-1, free of antioxidant, in toluene at 25°C. Curves: I, ○ solid sample kept in the dark; II, △ solid sample exposed to sunlight; III, □ sample in solution exposed to sunlight; IV, ● sample in solution kept in the dark. (Concentration of all solutions at 25°C was $4.00\ g\ dm^{-3}$)

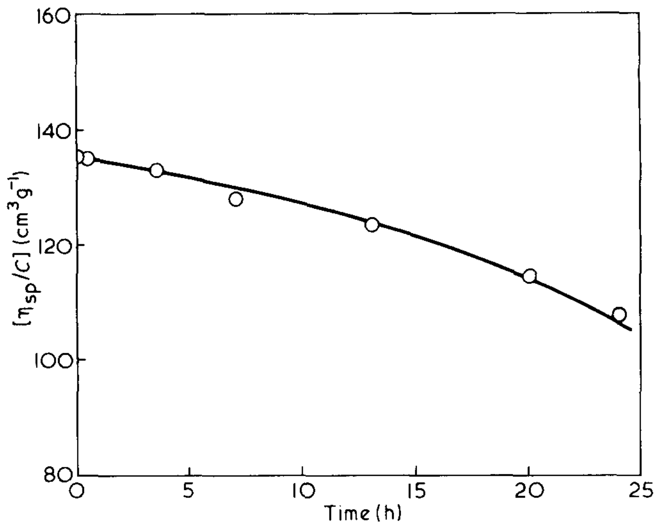


Figure 2 Reduced viscosities of amorphous polyepichlorohydrin, sample PECH-2, in toluene solution, exposed to u.v. light. (Concentration, 4.00 g dm^{-3}; temp. of viscosity measurement, 25°C, type of lamp, medium pressure mercury discharge lamp with envelope removed; solution in Pyrex bottle 35 cm away from the lamp.)

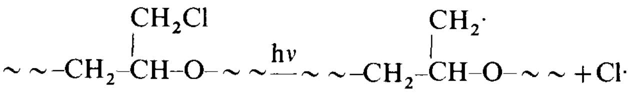
sample, when exposed to bright sunlight continuously underwent chain cleavage (*Figure 1*, curve II), initially at a slow rate, but later at an accelerated rate. Similar cleavage was observed in further experiments using other purified solid commercial samples, freed of antioxidant. Other experiments also revealed that the rate of degradation depended markedly upon the extent to which the polymer was free from antioxidant, the intensity of sunlight and the presence of traces of solvents, trapped in the solid polymer. The polymer was found to become progressively brownish following exposure to sunlight and gave off pungent fumes in air, which were assumed to be HCl. Polyepichlorohydrin, sample PECH-1, in toluene solution also underwent chain cleavage in the presence of sunlight, but the rate of decrease of (η_{sp}/c) with time was gradually reduced (*Figure 1*, curve III). Possibly some cross-linking occurred as well as cleavage. PECH in toluene solution stored in the dark showed no marked change in reduced viscosity for about two weeks, but then the reduced viscosity increased slowly (*Figure 1*, curve IV). Here the cross-linking reaction was presumably predominant. Sample PECH-2 in toluene solution on exposure to a u.v. lamp emitting wavelengths of about 365 nm but subject to intensity reduction by the Pyrex bottle, also underwent cleavage resulting in a continual decrease in reduced viscosity as shown in *Figure 2*. The rate of degradation of PECH in u.v. light under the conditions corresponding to *Figure 2* is much more rapid than in sunlight, corresponding to *Figure 1*, curve III.

Polyepichlorohydrin was found to absorb u.v. light, slightly at wavelengths above 243 nm and had a maximum absorbance at 252–268 nm. The specific extinction coefficient at 252–268 nm was 0.06 dm^3 g^{-1} cm^{-1}. In the region 300–400 nm, the absorbance of PECH was a little lower with specific extinction coefficients <0.04 dm^3 g^{-1} cm^{-1}. Light absorption may be due to oxygen-containing groups introduced into the polymer during preparation or purification, or due to C–Cl bonds probably absorbing at less than 300 nm.

The i.r. spectra of solid PECH, degraded in strong sunlight for one month, showed a strong peak at 1730 cm^{-1} due to non-conjugated $>$C=O groups. A broad peak in the region 3600–3300 cm^{-1} was due to hydrogen bonded OH and possibly also from OH of hydroperoxide groups. A thin film of the polymer exposed to u.v. light of 365 nm also showed similar but relatively stronger i.r. peaks.

Consideration of the results reported in *Figures 1* and *2* together with the i.r. results suggests that while solid PECH in the dark is relatively stable, it degrades thermally at 20°C in toluene solution due to a cross-linking reaction.

This could be due, for example, to reaction between a Cl-atom on one chain with a tertiary H-atom on a neighbouring chain, or to a radical combination process. In the presence of sunlight or u.v. light, two main degradative processes may occur, one being the cross-linking reaction as above and the other being a photochemically induced oxidative cleavage reaction giving $>$C=O, –OH and/or –OOH groups in the degraded polymer. The production of these groups in the photochemical oxidation of polymers both in the solid and solution states is now well established[11] and the initiation step could involve the process:



$$\sim\sim\text{-}\mathrm{CH_2}\text{-}\overset{\mathrm{CH_2Cl}}{\overset{|}{\mathrm{CH}}}\text{-O-}\sim\sim \xrightarrow{h\nu} \sim\sim\text{-}\mathrm{CH_2}\text{-}\overset{\mathrm{CH_2\cdot}}{\overset{|}{\mathrm{CH}}}\text{-O-}\sim\sim + \mathrm{Cl}\cdot$$

or for example, cleavage of the tertiary C–H bond.

n-BuLi cleavage

n-BuLi causes extensive cleavage of PECH as evident from the drop in number average molecular weights obtained by g.p.c. (*Figure 3*) and in limiting viscosity

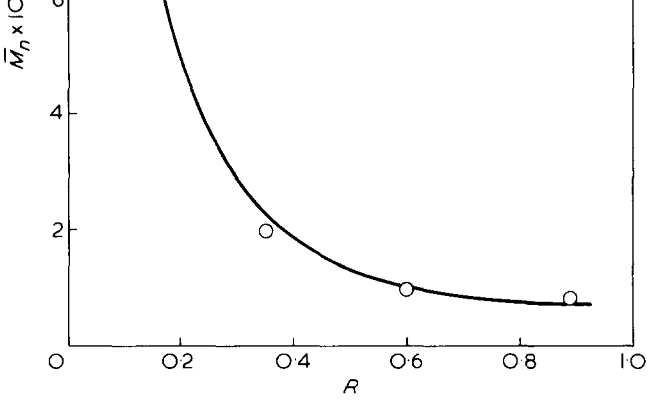


Figure 3 Molecular weights of the n-BuLi-cleavage products from PECH as a function of molar ratio *R*. [*R* = (moles of n-BuLi/moles of Cl in initial PECH) used in a cleavage experiment]. Temp. of cleavage experiments ≃ 20°C

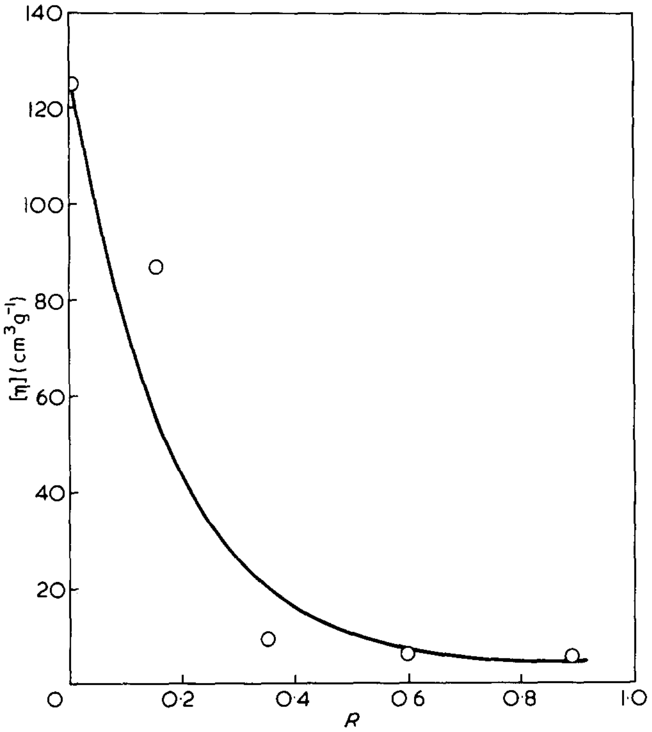


Figure 4 Limiting viscosity numbers of the n-BuLi cleavage products from PECH as a function of molar ratio *R*. (Temp. of cleavage experiments 20°C; limiting viscosity numbers measured in toluene at 30°C)

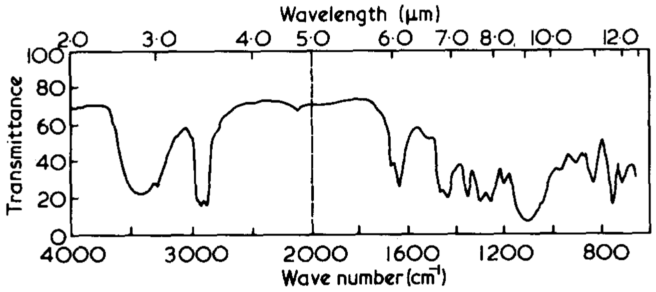


Figure 5 Infra-red spectrum of a thin film of a n-BuLi cleavage product from PECH

numbers (*Figure 4*). Both sets of measurements approached a limiting value with a value of *R* greater than 0.5. It is possible that during isolation of the polymer samples are degradation, much of the lower molecular weight fractions would be lost during rotary evaporation and drying.

The degradation of PECH by n-BuLi followed by subsequent treatment with water resulted in the formation of different end-groups identified by i.r. spectra. Thus, the spectra recorded in $CHCl_3$ solution of samples of PECH cleaved by n-BuLi showed peaks, apart from those due to PECH and solvent, at 3460 cm^{-1} (broad, strong) due to OH, at 3305 cm^{-1} due to $-C\equiv CH$, at 1730 cm^{-1} (weak) due to normal aldehyde, $-CHO$ or ketone, $>C=O$, at 1670 cm^{-1} (sharp, strong) due to α,β-unsaturated aldehyde or ketone, $>\underset{|}{C}=\underset{|}{C}-C=O$, at 1630 cm^{-1} (sharp, strong) due to $>C=C<$ conjugated to etheral oxygen as in a vinyl ether, or to a carbonyl group, as in an α,β-unsaturated aldehyde or ketone. Also peaks occurred at 1605 cm^{-1} and 1580 cm^{-1}. These two peaks are probably characteristic of $>=C<$ conjugated to a carbonyl group.

The i.r. spectra of the films also showed peaks at approximately the above wave numbers, with the exception that a weak but distinct peak due to $-C\equiv CH$ appeared at 2120 cm^{-1} and the peaks at 1605 cm^{-1} and 1580 cm^{-1} were not observed (*Figure 5*). Formation of similar types of group has also been observed previously during the preparation of poly(epichlorohydrin-g-styrene) by coupling of PECH and living PS^-Li^+ though it occurred then to a lesser extent. It may be assumed that the nature of the degradation and cleavage reactions of PECH, induced by PS^-Li^+ is similar to that of PECH induced by n-BuLi. The formation of various end-groups induced by attack of PS^-Li^+ on PECH has been discussed elsewhere[6].

The basicity order of organolithium compounds is n-$BuLi > C_6H_5Li > C_6H_5CH_2Li$[12] and PS^-Li^+ would be expected to be less basic than $C_6H_5CH_2Li$ and much less basic than n-BuLi, partly because of its greater size and ionic character.

The relative absorbances due to different groups in i.r. spectra taken in $CHCl_3$ solution plotted against values of *R* used in the cleavage reactions, suggest that the concentrations of these groups were directly proportional to the relative amounts of n-BuLi used. (*Figure 6*).

The results of the PECH–n-BuLi experiments are broadly in agreement with the type of reactions suggested previously by Vandenburg[8]. The decrease in $[\eta]$ and $\bar{M}_n$

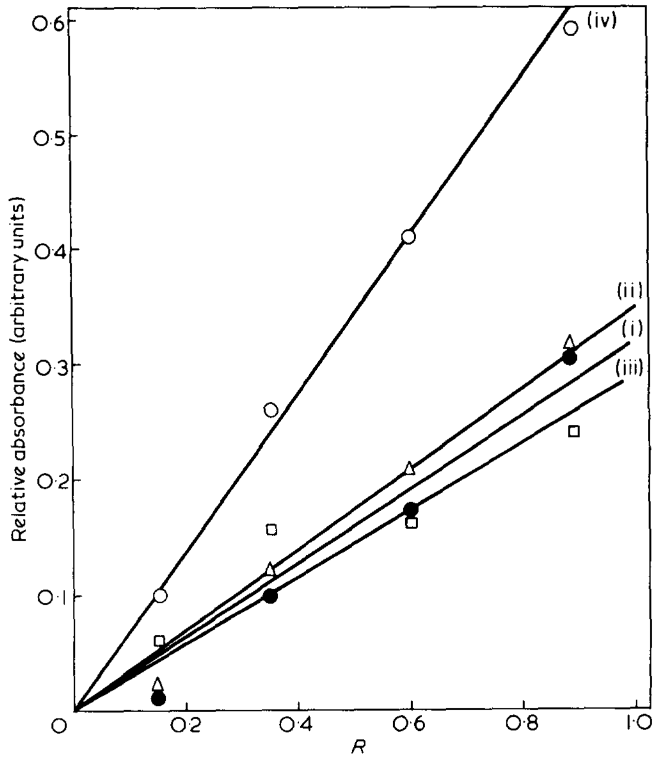


Figure 6 Relative absorbance of different groups formed in the n-BuLi cleavage products from PECH as a function of *R*. Groups: (i) (□) OH; (ii) (△) $-C\equiv CH$; (iii) (●) $-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=O$; (iv) (○) $-\underset{|}{C}=\underset{|}{C}-O-$

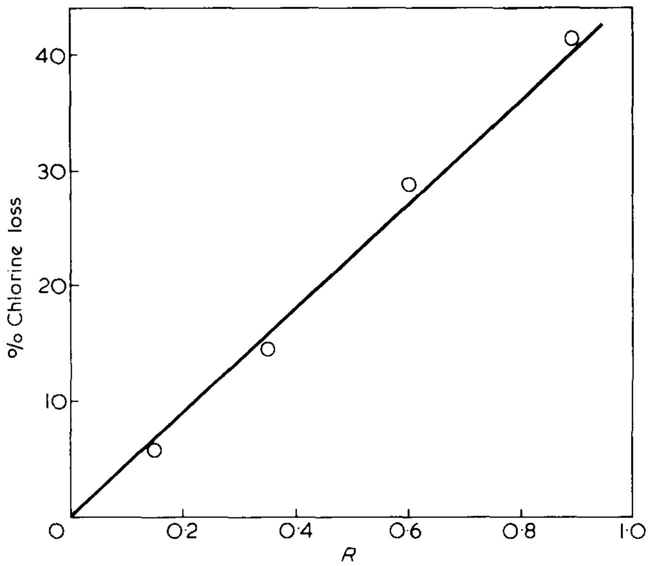


Figure 7 Percentage chlorine loss from PECH on cleavage with n-BuLi, as a function of molar ratio *R*. [% Chlorine loss = (mass of Cl displaced from PECH/mass of Cl in original PECH) x 100; temp. of cleavage reactions 20°C; time of reaction = 6 h]

with increase in values of *R* are also consistent with the existence of cleavage reactions, some of which may liberate Cl^-. Other reactions may liberate Cl^- without backbone cleavage, but a % weight of chlorine displaced from PECH vs. *R* plot, shown in *Figure 7* remains linear.

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