Polymer Bulletin 1, 575-580 (1979)

Polymer Bulletin

New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers)

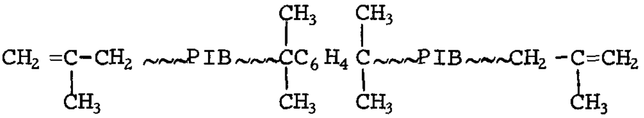
V. Synthesis of α-tert.-Butyl-ω-isopropenylpolyisobutylene and α, ω-Di(isopropenyl)polyisobutylene

Joseph P. Kennedy, Victor S. C. Chang, Robert Alan Smith* and Béla Iván**

Institute of Polymer Science, University of Akron, Akron, Ohio 44325, USA

Summary

Polyisobutylenes carrying one or two terminal isopropenyl unsaturations have been obtained by complete dehydrochlorination of α-tert.-butyl-ω-tert.-chloropolyisobutylene and α,ω-di(tert.-chloro)polyisobutylene, respectively. By the use of t-BuOK in refluxing THF only 1-olefin formed leading to a new macromer and a symmetrical telechelic diolefin. According to H^1 NMR spectroscopy the structure of this new telechelic polymer is:



$$CH_2{=}\underset{CH_3}{C}-CH_2\sim\sim PIB\sim\sim\overset{CH_3}{\underset{CH_3}{C}}C_6H_4\overset{CH_3}{\underset{CH_3}{C}}\sim\sim PIB\sim\sim CH_2-\underset{CH_3}{C}{=}CH_2$$

Introduction

We have shown in earlier publications of this series (FEHERVARI et al. 1979; KENNEDY, SMITH 1979a, 1979b, 1979c) that α,ω-di(tert.-chloro)polyisobutylenes (Cl-PIB-Cl) can be readily prepared by bifunctional initiator-transfer agents (inifers). The synthesis and characterization of Cl-PIB-Cl has been described (KENNEDY, SMITH 1979a, 1979b). The thought occurred to us that valuable telechelic diolefins could be obtained from Cl-PIB-Cl by exhaustive (100%) dehydrochlorination.

A research of the literature provided important clues as to the dehydrochlorination method to be used. According to BROWN et al.(1953; 1956a, 1956b) $(CH_3)_3$-$CCH_2(CH_3)_2Br$ can be readily dehydrobrominated by

---

* Present address: The Goodyear Tire and Rubber Co., Akron, Ohio 44316, USA; **Visiting Scientist, permanent address: Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, POB 17, Hungary

0170-0839/79/0001/0575/$01.20

t-BuOK in t-BuOH solvent and the product is essentially pure 1-olefin. In our hands dehydrochlorination by t-BuOK in refluxing THF proved to be eminently suitable for dehydrochlorination of polyisobutylenes carrying one (PIB-Cl) or two (Cl-PIB-Cl) tert.-chlorine termini. This paper concerns the synthesis of a polyisobutylene macromer i.e., a polyisobutylene carrying one $-CH_2-C(CH_3)=CH_2$ endgroup, and an olefin-telechelic polyisobutylene i.e., a polyisobutylene carrying an $-CH_2-C(CH_3)=CH_2$ group on either terminus, by dehydrochlorination of PIB-Cl and Cl-PIB-Cl, respectively. These olefins are most valuable intermediates for subsequent derivatizations.

Experimental

Materials

The synthesis and purification of PIB-Cl and Cl-PIB-Cl have been described (KENNEDY, SMITH 1979a, 1979b). Potassium t-butoxide (Aldrich Chemical Co.) and t-butyl alcohol (Mallinckrodt, Inc.) were used as received without further purification. Tetrahydrofuran (Fisher Scientific Co.) was refluxed overnight under nitrogen in the presence of lithium aluminum hydride and distilled before use.

Dehydrohalogenation

Dehydrohalogenations were carried out in three-neck flasks equipped with stirrer, condenser and dropping funnel under a dry nitrogen atmosphere. A representative experiment was as follows: To a refluxing solution of polyisobutylene containing one or two tert.-chlorine termini in THF (3.0g/100ml) was added dropwise a solution of t-BuOK in THF (2.0g/30ml) over a period of 10 minutes, stirred for 20 hours and then cooled to room temperature. Subsequently, 50 ml n-hexane was added, stirred for a few minutes, 50 ml distilled water was introduced, stirred for 10 minutes; the organic layer was then washed three times with 150 ml distilled water each, separated and dried with anhydrous magnesium sulfate. Finally the product was filtered, the solvent removed by evaporation and dried in vacuo at 75°C overnight.

H^1 NMR Analysis

H^1 NMR spectroscopy was performed by a Varian Associates T-60 NMR spectrometer at room temperature. Solutions of 10-15% polymer in CCl_4 with a few percent TMS standard were employed.

Results and Discussion

Table I summarizes representative data. Dehydrochlorination with KOH/EtOH and EtONa/EtOH in heterogeneous systems, or with *t*-BuOK/THF:*n*-hexane (50:50) in homogenous medium gave unsatisfactory results. In contrast, complete dehydrochlorination of PIB-Cl and Cl-PIB-Cl was readily obtained by using *t*-BuOK in refluxing THF (see last three rows in Table I). The best conditions for elimination to 1-olefin are believed to exist by the use of refluxing THF. In the presence of THF/*t*-BuOH mixtures the danger of elimination to 1- and 2-olefin mixture exist (BROWN et al. 1953; 1956a, 1956b).

TABLE I

Dehydrochlorination of Polyisobutylene Chlorides

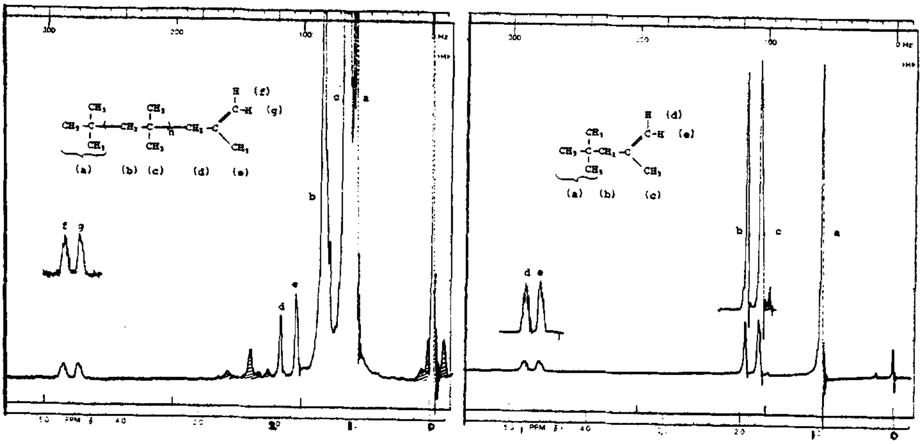
Polymer	Reaction Conditions	Observations
PIB-Cl	KOH/EtOH	heterogeneous system, partial elimination
PIB-Cl	NaOEt/EtOH	heterogeneous system, partial elimination
PIB-Cl	*t*-BuOK/THF:*n*-hexane(50:50) reflux, 20 hrs.	~50% elimination
PIB-Cl	*t*-BuOK/THF, reflux, 20 hrs.	100% elimination (see Figure 1 a)
Cl-PIB-Cl	*t*-BuOK/*t*-BuOH:THF(10:100) reflux, 16 hrs.	100% elimination
Cl-PIB-Cl	*t*-BuOK/THF, reflux, 20 hrs.	100% elimination (see Figure 2)

Direct evidence for dehydrochlorination was obtained by H^1 NMR spectroscopy.

Figure 1a shows the H^1 NMR spectrum of the product obtained by HCl elimination from PIB-Cl ($\overline{M}n \simeq$ 650-700) and indicates 100% dehydrochlorination to 1-olefin. Resonances at 4.58 and 4.78 ppm are assigned to $-CH_2-C(CH_3)=\underline{CH_2}$. Identical resonances appear in 2,4,4-trimethyl-1-pentene model compound (Figure 1). These resonances are also very close to those observed by MANATT et al.(1977) and FRANCIS and ARCHER (1963). Resonances at 1.75 and 1.93 ppm are associated with

Figure 1

^{1}H NMR Spectra of PIB-CH_2-$C(CH_3)=CH_2$ (Mn $\simeq$ 650-700)(a) and 2,4,4-Trimethyl-1-pentene (b)

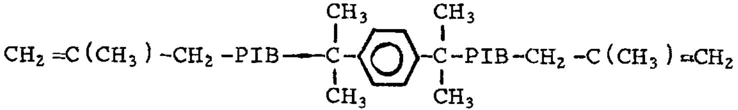


1 a

1 b

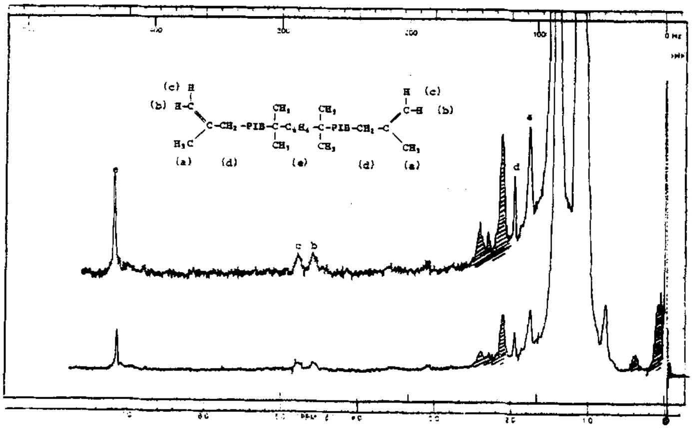
Figure 2

^{1}H NMR Spectrum of

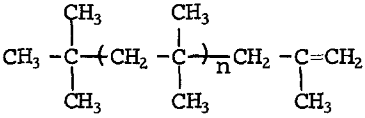


$$CH_2=C(CH_3)-CH_2-PIB-C(CH_3)_2-C_6H_4-C(CH_3)_2-PIB-CH_2-C(CH_3)=CH_2$$

(Mn $\simeq$ 4,500)



$-CH_2-C(C\underline{H}_3)=CH_2$ and $-C\underline{H}_2-C(CH_3)=CH_2$ protons, respectively, while those at 1.00 and 1.03 ppm are assigned to the $(C\underline{H}_3)_3C-$ protons at the α terminus and the $-C(C\underline{H}_3)_2-CH_2-C(CH_3)=CH_2$ protons at the ω endgroup. According to these results the product obtained by dehydrochlorination of PIB-Cl leads to a new macromer (macromolecular monomer) with the following structure:



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}\left(CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right)_n CH_2-\underset{CH_3}{C}=CH_2$$

Figure 2 shows the H^1 NMR spectrum of the product obtained by dehydrochlorination of Cl-PIB-Cl (Mn ≃ 4,500). The synthesis of the starting material has been described (KENNEDY, SMITH 1979a, 1979b). Three areas have been analyzed: The region from 1.0 to 2.0 ppm contains protons associated with the various methyl and methylene groups. Thus the resonances at 1.75 and 1.93 ppm are identical to those discussed above and indicate the presence of $-C\underline{H}_2-C(C\underline{H}_3)=CH_2$ protons. The two large resonances at 1.1 and 1.4 ppm are associated respectively with $-C\underline{H}_3$ and $-C\underline{H}_2-$ protons in isobutylene units along the PIB backbone excluding those at chain ends.

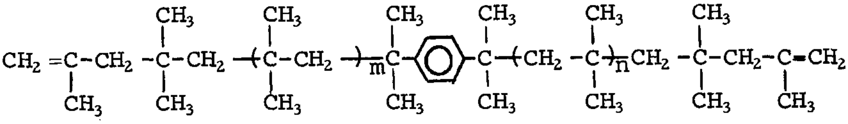
The region from 4.5 to 5.0 ppm contains two important resonances at 4.58 and 4.78 ppm associated with $-CH_2-C(CH_3)=C\underline{H}_2$ protons (see also above).

The third region from 7.0 to 7.5 ppm contains only one sharp resonance at 7.15 ppm indicating aromatic protons. Integration of this area and that between 4.5 to 5.0 ppm show the presence of an equal number of protons in these regions. This is expected since the 7.15 ppm resonance represents four aromatic protons and the resonances at 4.58 and 4.78 represent four vinylene protons. This result is consistent with 100% dehydrochlorination, and indicates a functionality of 2.0, i.e., two olefinic endgroups per PIB chain.

Complete (100%) dehydrochlorination of Cl-PIB-Cl also indicates 100% inifer efficiency during synthesis. The aromatic/vinylene proton ratio can be 1.0 only if dehydrochlorination is complete, which can occur only if inifer efficiency is 100% i.e., chain transfer to monomer is absent during synthesis.

On the basis of these observations and taking into account synthesis and characterization details of

Cl-PIB-Cl (KENNEDY, SMITH 1979) we propose the following structure for the new telechelic polymer:



These dehydrochlorination products of PIB-Cl and Cl-PIB-Cl yielding exclusively α-tert.-butyl-ω-isopropenylpolyisobutylene and α,ω-di(isopropenyl)polyisobutylene substantiate BROWN et al.'s views on dehydrohalogenation (1953, 1956a, 1956b) according to which sterically hindered alkyl halides with hindered base preferentially produce 1-olefins.

Acknowledgements

The authors are grateful for financial assistance by the NSF (Grant DMR-77-27618) and one of us (B. Ivan) to the Institute for Cultural Relations, Hungary.

References

BROWN, H.C. and MORITANI, I.: J. Am. Chem. Soc. 75, 4112 (1953)

BROWN, H.C., MORITANI, I. and OKAMOTO, Y.: J. Am. Chem. Soc. 78, 2193 (1956a)

BROWN, H.C. and MORITANI, I.: J. Am. Chem. Soc. 78, 2203 (1956b)

FEHERVARI, A., KENNEDY, J.P. and TUDOS, F.: Polymer Preprints, in press (1979)

FRANCIS, S.A. and ARCHER, E.D.: Anal. Chem. 35, 1363 (1963)

KENNEDY, J.P. and SMITH, R.A.: Polymer Preprints, in press (1979a)

KENNEDY, J.P. and SMITH, R.A.: J. Macromol. Sci., Chem., in press (1979b)

KENNEDY, J.P. and SMITH, R.A.: J. Macromol. Sci., Chem., in press (1979c)

MANATT, S.L., INGHAM, J.D. and MILLER, J.A. Jr.: Org. Mag. Res. 10, 198 (1977)

Received May 25, 1979