New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-transfer Agents (Inifers)
15. Synthesis and Characterization of Telechelic Acid-ester Polyisobutylenes

Tung-Ping Liao and Joseph P. Kennedy

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

Summary
        New carboxyl terminated linear polyisobutylenes,
$HOOCRCOOCH_2$-PIB-$CH_2OOCRCOOH$ where R = p-C_6H_4- or
-$(CH_2)_4$- have been prepared. The synthesis involved
reactions between α,ω-di(hydroxy)polyisobutylene,
$HOCH_2$-PIB-CH_2OH, and excess dicarboxylic acid chlorides,
i.e., terephthaloyl chloride and adipoyl chloride, fol-
lowed by hydrolysis. According to model studies and
IR, H^1-NMR and UV spectroscopy the yields of the tar-
get α,ω-acid-ester polyisobutylenes are essentially
quantitative. These telechelic dicarboxylic prepoly-
mers open new avenues toward the synthesis of many new
materials, e.g., cross-linked carboxylic elastomers.
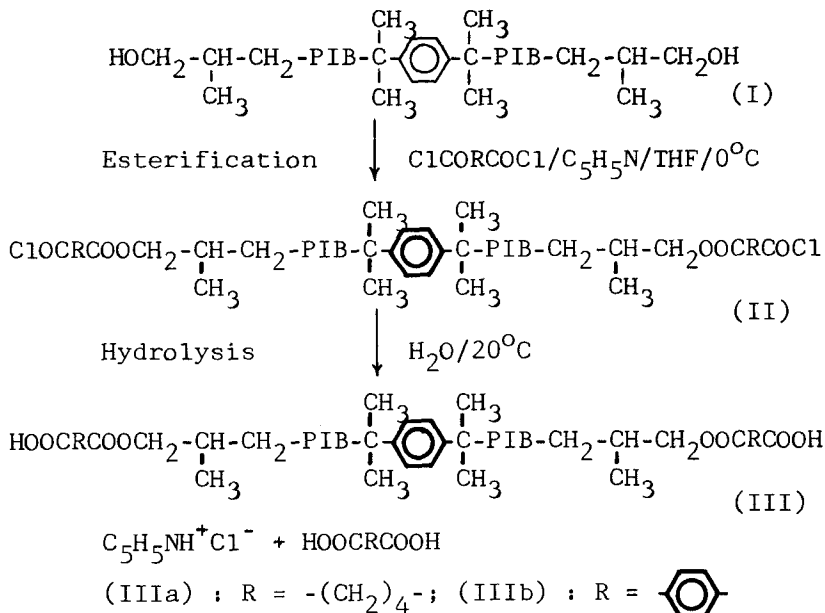
Introduction
        One aim of our continuing investigation with
telechelic polyisobutylenes (PIB's) (KENNEDY, SMITH
1980, KENNEDY et al., 1979, IVAN et. al. 1980) has
been the preparation of perfectly telechelic carboxyl-
terminated PIB's. Incentive for these studies is
provided by the many potential applications for such
materials in liquid rubbers, adhesives, coatings,
elastic fibers, etc. An effort toward this objective
was made by earlier authors (BALDWIN et al. 1967,
1979) who ozonized isobutylene-piperylene copolymers,
however, obtained only partially telechelic products
(terminal functionality $\sim$ 1.8). Also, these products
may have contained some in-chain (non-terminal) func-
tional groups due to the ozonolysis of pendant un-
saturations of 4,3-piperylene units in the copolymer.
        This paper concerns the synthesis and character-
ization of carboxy-telechelic PIB's obtained by ester-
ification of hydroxy-telechelic PIB with excess adi-
poyl and terephthaloyl chlorides followed by hydroly-
sis. The synthesis route is shown in Scheme I.

Experimental
A. Materials
        The synthesis and purification of hydroxy-
telechelic PIB, $HOCH_2$-PIB-CH_2OH (Formula I in Scheme I)

Scheme I

Synthesis of Telechelic Acid-Ester Polyisobutylenes

$$HOCH_2\text{-}CH\text{-}CH_2\text{-}PIB\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\langle\bigcirc\rangle\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}PIB\text{-}CH_2\text{-}CH\text{-}CH_2OH$$

with CH_3 groups on the CH positions. (I)

Esterification $\quad\downarrow\quad$ ClCORCOCl/C_5H_5N/THF/$0°C$

$$ClCORCOOCH_2\text{-}CH\text{-}CH_2\text{-}PIB\text{-}\underset{CH_3}{\overset{CH_3}{C}}\langle\bigcirc\rangle\underset{CH_3}{\overset{CH_3}{C}}\text{-}PIB\text{-}CH_2\text{-}CH\text{-}CH_2OOCRCOCl$$

(II)

Hydrolysis $\quad\downarrow\quad$ $H_2O/20°C$

$$HOOCRCOOCH_2\text{-}CH\text{-}CH_2\text{-}PIB\text{-}\underset{CH_3}{\overset{CH_3}{C}}\langle\bigcirc\rangle\underset{CH_3}{\overset{CH_3}{C}}\text{-}PIB\text{-}CH_2\text{-}CH\text{-}CH_2OOCRCOOH$$

(III)

$$C_5H_5NH^+Cl^- + HOOCRCOOH$$

(IIIa) : R = $-(CH_2)_4-$; (IIIb) : R = $\langle\bigcirc\rangle$

has been described (IVAN et. al. 1980). The diol used in this research had $\overline{M}_n=4,900$ and $\overline{F}_n=1.95\pm0.07$ (number average terminal functionality). THF was treated with KOH and further purified by distillation from LiAlH₄. Adipoyl chloride (Aldrich) was purified by vacuum distillation. Terephthaloyl chloride (Aldrich) was recrystallyzed from hexanes. Pyridine was treated with KOH then refluxed over BaO and distilled. 2,4,4-Trimethyl-1-pentanol (Aldrich) was used as received. n-Pentane (Eastman) was stirred with sulfuric acid overnight, dried with $CaCl_2$ and further distilled from CaH_2.

B. Techniques

Esterifications with adipoyl chloride and terephthaloyl chloride were carried out in three-neck flasks equipped with stirrer and dropping funnel under dry N_2 at $0°C$. A solution of HOCH₂-PIB-CH₂OH (1 wt% in THF) was added dropwise to charges of $\sim$ 20 fold excess adipoyl chloride or terephthaloyl chloride. Subsequently, pyridine (three-fold excess on the acid chlorides) was added dropwise over a period of $\sim$ 30 mins. After five hours of stirring at room temperature, water (half of THF) was added and the mixture

was hydrolyzed for five hours. The experiments with
adipoyl chloride gave homogeneous solutions whereas
those with terephthalic acid yielded precipitates.
After removing the precipitate by filtration, n-
pentane was added and stirred for a few mins. The
products were washed several times with distilled
water, separated, and dried with $MgSO_4$. After filtra-
tion the solvent was removed by evaporation and the
products were dried under vacuum at 50°C overnight.
     H^1 NMR analysis was carried out by using a
Varian Associates T-60 NMR and 5 -30% polymer solu-
tions in CCl_4 and $CDCl_3$. Infrared spectra were re-
corded on a Perkin-Elmer 521 grating IR spectrometer
by using 0.55 mm KBr cells and 5-25 mM polymer solu-
tions in CCl_4. Ultraviolet spectra were recorded on
a Perkin-Elmer 552 A microcomputer controlled spectro-
photometer by using 0.01-1 mM polymer solutions in
THF. $\bar{M}_n$'s were determined by a Mechrolab vaporphase
osmometer.

Results and Discussion
1. Model Experiments with 2,4,4-Trimethyl-1-pentanol
   (TMP)
     Preparatory to experiments with $HOCH_2$-PIB-CH_2OH
model esterifications have been carried out with TMP.
Figures 1,2,3 and 4(a) show H^1-NMR, IR and UV spectra
of the products obtained by reacting TMP with excess
adipoyl and terephthaloyl chloride, respectively, fol-
lowed by hydrolysis. The resonances and absorptions
are identified and assigned as shown in Figures 1 and
2. According to this evidence conversion of the model
alcohol to the expected acids was complete.

2. Esterification of $HOCH_2$-PIB-CH_2OH with Diacid Chlo-
   rides and Hydrolysis to Telechelic Diacid-Esters
     Scheme I helps to visualize the synthesis steps
involved in the preparation of a representative ali-
phatic and aromatic diacid-ester. By-products could
be readily removed by washing with water or precipi-
tation. The rates of reactions were enhanced by the
use of pyridine (SONNTAG 1953, SMITH and BRYANT 1935)
and side reactions were minimized by working at rela-
tively low temperatures (0°C or 20°C). Due to low end
group concentrations the reaction time was long
(5 hrs.).
     Chain extension or ring formation during ester-
ification was minimized by the use of 20 fold excess
of acid chlorides. The $\bar{M}_n$ of IIIa was found to be es-
sentially the same as that of the starting diol ($\bar{M}_n$ =
4,900) indicating the absence of chain extension or
degradation. In contrast, the $\bar{M}_n$ of IIIb increased
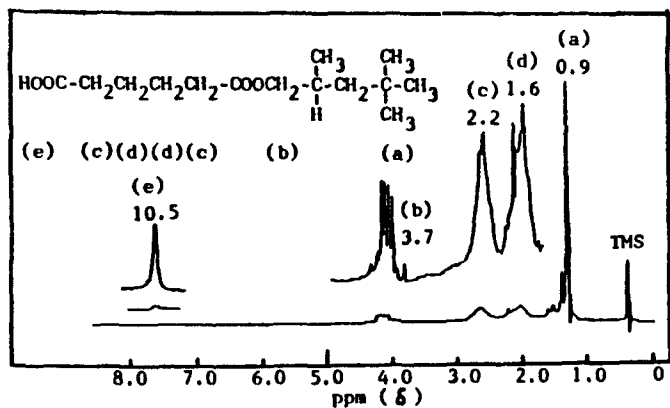to 5,400 which may be due to a small measure of chain
extension.

14

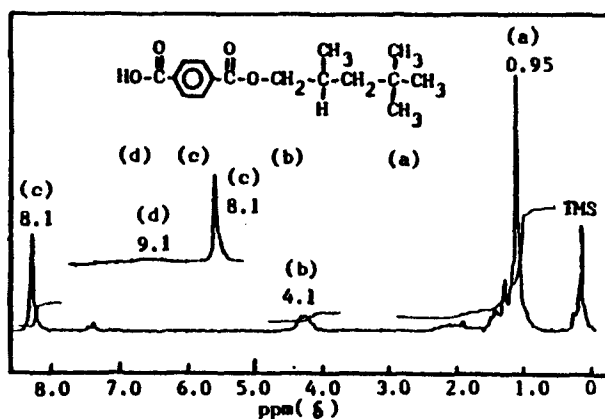Fig. 1: NMR spectrum of adipic acid mono-2,4,4-trimethyl-1-pentyl ester (30% in CCl₄).

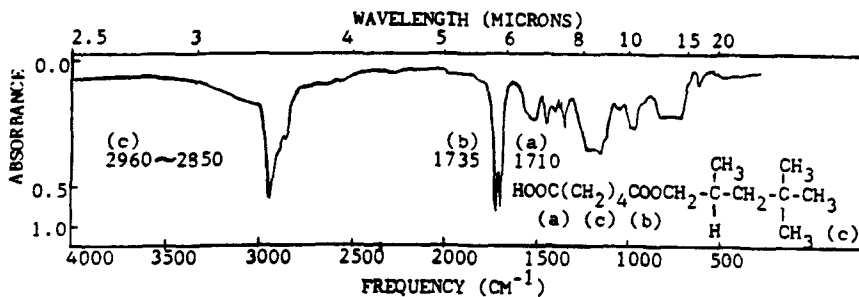Fig. 2: NMR spectrum of terephthalic acid mono-2,4,4-trimethyl-1-pentyl ester (5% in CDCl₃).

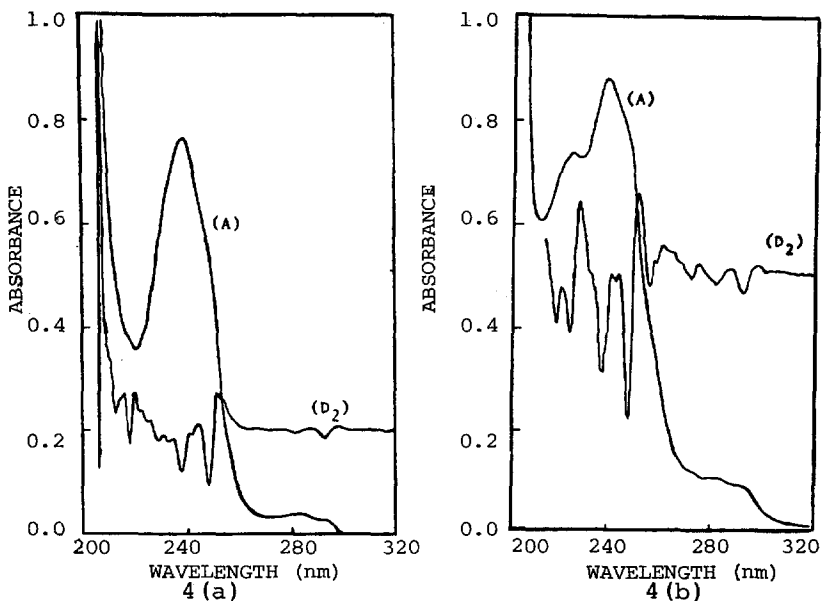Fig. 3: IR spectrum of adipic acid mono-2,4,4-trimethyl-1-pentyl ester (in CCl₄).

Fig. 4(a): UV spectrum of terephthalic acid mono-
2,4,4-trimethyl-1-pentyl ester, A and its
second derivative D_2 (in THF).

4(b): UV spectrum of IIIb, A and its second
derivative D_2 (in THF).

Figures 5 and 6 show H^1 NMR spectra of IIIa and
IIIb. The resonances are identified in the Figures.
The aromatic inifer fragment in the products is an in-
ternal standard for quantitative end group determina-
tion. Thus integration and correlation of the four
aromatic inifer protons (6.95-7.35 ppm) with the ter-
minal -CH$_2$- protons (3.5-3.9 ppm) in IIIa or the te-
rephthalic protons (7.9-8.3 ppm) in IIIb yields $\overline{F}_n$ =
1.95±0.18 for IIIa and 1.75±0.09 for IIIb, respective-
ly.

Figures 7,8, and 9 show IR spectra of the start-
ing diol and the two products, respectively, and Table
I contains major absorptions and corresponding struc-
tures. The characteristic absorptions of HOCH$_2$- ter-
mini at 3640 cm^{-1} (monomer) and 3480 cm^{-1} (dimer) dis-
appear after esterification and two strong peaks asso-
ciated with the ester and carboxyl groups appear in
the 1735-1690 cm^{-1} range. The somewhat lower than
theoretical functionality of the terephthaloyl deri-
vative may be due to anhydride formation (1795 cm^{-1}
peak in Figure 9) and/or to the relatively low reacti-
vity of terephthaloyl chloride toward HOCH$_2$- groups.

Figure 4(b) shows the UV absorption spectrum and
its second derivative of IIIb. Comparison of absorp-

16
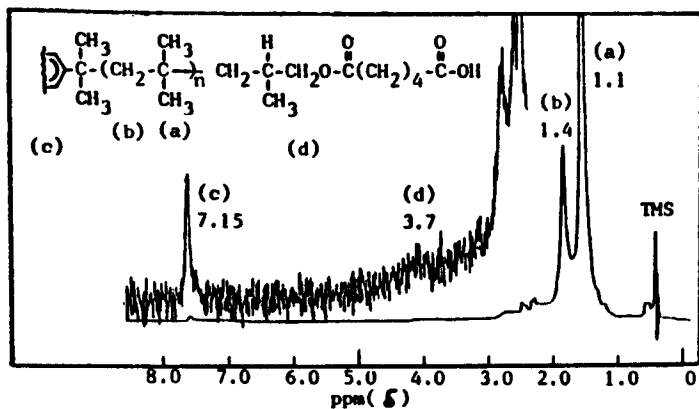
Fig. 5: The NMR spectrum of IIIa (CCl₄)
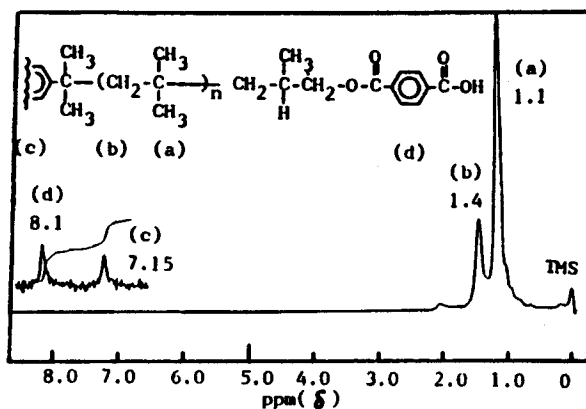
Fig. 6: The NMR spectrum of IIIb (CCl₄)
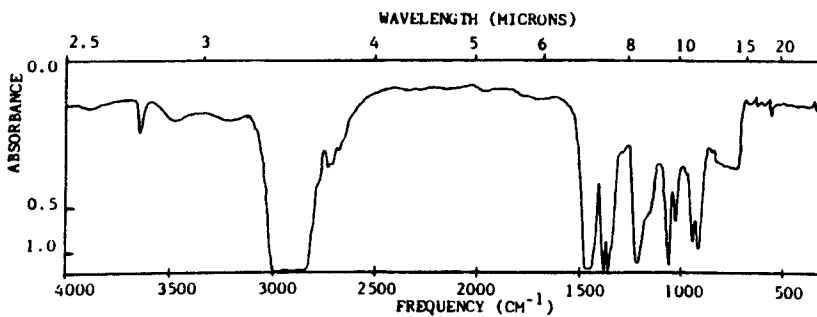
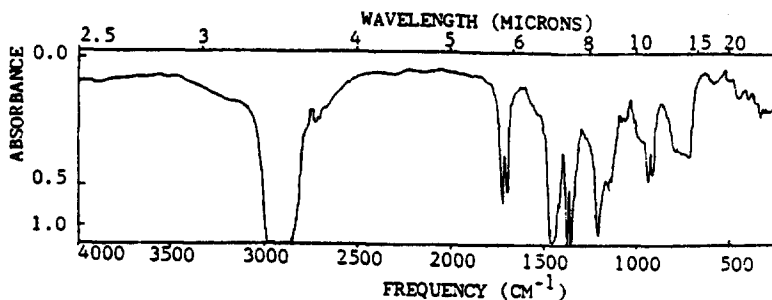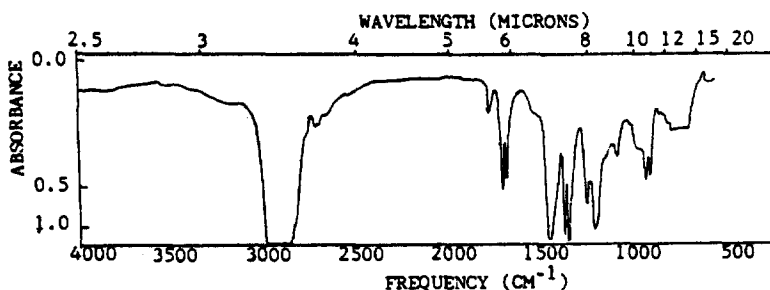Fig. 7: IR spectrum of $HOCH_2-PIB-CH_2OH$ (in CCl₄)

Fig. 8:   IR spectrum of IIIa (in CCl₄).

Fig. 9:   IR spectrum of IIIb (in CCl₄).

TABLE I

Infrared Absorption of Telechelic Diacid-Ester Poly-
isobutylenes

cm^{-1}	Assignment
950(m), 920(m)	$-CH_2-C(CH_3)_2-$, skeletal
1250(s)	$-C(CH_3)_2-$, skeletal
1360(s), 1380(s)	$\delta(CH_3)$ (gem-dimethyl)
1470(s)	ωCH_2
1710(s), 1735(s)	$-COOH$, $-CO-O-$ (aliph.)
1695(s), 1725(s)	$-COOH$, $-CO-O-$ (arom.)
1795(m)	$-CO-O-CO-$ (arom.)
3030(s)	(arom.)
2960(s), 2879(m)	νCH
2925(s), 2850(m)	νCH_3, νCH_2

m = medium,   s = strong

tion peaks of IIIb with those of terephthalic acid
mono-2,4,4-trimethyl-1-pentyl ester, TAMTPE and 1,4-
bis(tert.-butyl)benzene, BTBB (LENG 1962) (see TABLE
II) indicates that the UV spectrum of IIIb may be
viewed as a combination of these model compounds. The
concentration of terephthalic groups in IIIb was cal-

culated by the use of the secondary absorption at 294 nm which in conjunction with $\bar{M}_n$ yielded $\bar{F}_n = 1.81 \pm 0.01$. Evidently the $\bar{F}_n$'s determined by the above spectroscopic methods are in satisfactory agreement.

TABLE II

UV Absorption Peaks (in nm) of IIIb and Model Compounds

	nm							
IIIb	294,	283,	274,	260,	258,	249,	239,	226
TAMTPE	294,	283,	——,	——,	——,	249,	239,	——
BTBB	——,	——,	272,	260,	258,	249,	——,	220

Conclusions
It has been demonstrated that $HOCH_2$-PIB-CH_2OH rapidly reacts with representative aliphatic and aromatic diacid chlorides, adipoyl and terephthaloyl chloride, and that the products are readily hydrolyzed to the corresponding diacid-esters (see Scheme I). Conversions were quantitative with the adipoyl derivative ($\bar{F}_n$ of starting material = 1.95, product 1.95) whereas somewhat less than quantitative with the terephthalate ($\bar{F}_n = 1.80$). These telechelic acid-esters represent valuable intermediates for the preparation of adhesives, coatings, foams and investigations along these lines are in progress.

References
BALDWIN, F. P., FUSCO, J. V. and GASTWIRT, L. E., Adhesives Age, 10, 22 (Feb. 1967).
BALDWIN, F. P., Rubber Chem. Techn., 52, G77 (1979).
IVAN, B., KENNEDY, J. P. and CHANG, V. S. C., J. Polym. Sci., Polym. Chem. Ed., 18, 3177 (1980).
KENNEDY, J. P., CHANG, V. S. C., SMITH, R. A. and IVAN, B., Polymer Bulletin, 1, 575 (1979).
KENNEDY, J. P. and SMITH, R. A., J. Polym. Sci., Polym. Chem. Ed., 18, 1523 (1980).
LENG, L., "Absorption Spectra in the Ultraviolet and Visible Region", Academic Press Inc., Pub., New York, 51(IX), 63(VIII) (1962).
SMITH, D. M. and BRYANT, W. M. D., J. Am. Chem. Soc., 57, 841 (1935).
SONNTAG, N. O. V., Chem. Rev., 52, 295 (1953).