Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Living Carbocationic Polymerization. LIX. The Synthesis of Novel Asymmetric Telechelic Polyisobutylenes

Jiaoshi Si[a]; Joseph P. Kennedy[a]
[a] Institute of Polymer Science The University of Akron, Akron, Ohio

To cite this Article Si, Jiaoshi and Kennedy, Joseph P.(1993) 'Living Carbocationic Polymerization. LIX. The Synthesis of Novel Asymmetric Telechelic Polyisobutylenes', Journal of Macromolecular Science, Part A, 30: 12, 863 — 876
To link to this Article: DOI: 10.1080/10601329308009432
URL: http://dx.doi.org/10.1080/10601329308009432

J.M.S.—PURE APPL. CHEM., A30(12), pp. 863–876 (1993)

LIVING CARBOCATIONIC POLYMERIZATION. LIX. THE SYNTHESIS OF NOVEL ASYMMETRIC TELECHELIC POLYISOBUTYLENES†

JIAOSHI SI and JOSEPH P. KENNEDY*

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325-3909

ABSTRACT

The synthesis of novel asymmetric telechelic polyisobutylenes (PIB) carrying a CH_3OCO- headgroup and a $-CH_2C(CH_3)_2Cl$ tailgroup by the use of novel initiators mediating the living carbocationic polymerization (LC^+Pzn) of isobutylene (IB) is described. Subsequently, the parent headgroup has been quantitatively converted into a $HOCO-$ group, and the parent tailgroup into a $-p\text{-}C_6H_4OH$ group. Scheme 1 summarizes the synthesis routes to the initiators, as well as the polymerizations and functionalizations leading to various asymmetric telechelic PIBs. The CH_3OCO- headgroup of the initiator most likely functions as an internal electron donor during the LC^+Pzn of IB.

INTRODUCTION

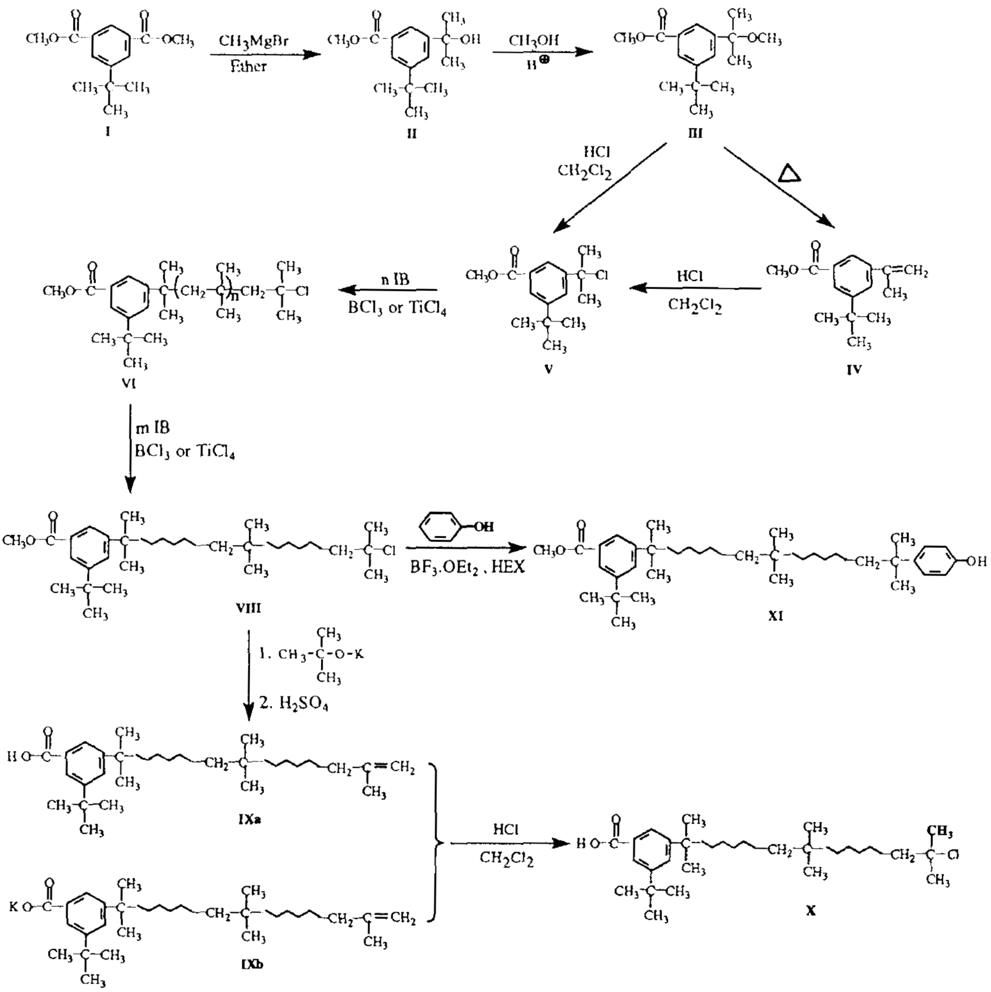
The synthesis of asymmetric telechelic prepolymers is a rather difficult undertaking because the two dissimilar terminal functions may react with each other in the course of the synthesis. One route to these structures is by "protecting" at least one of the termini during the polymerization and removing the protecting group at the end of the procedure. Recently, we found [1, 2] that *tert*-lactones in conjunction

---

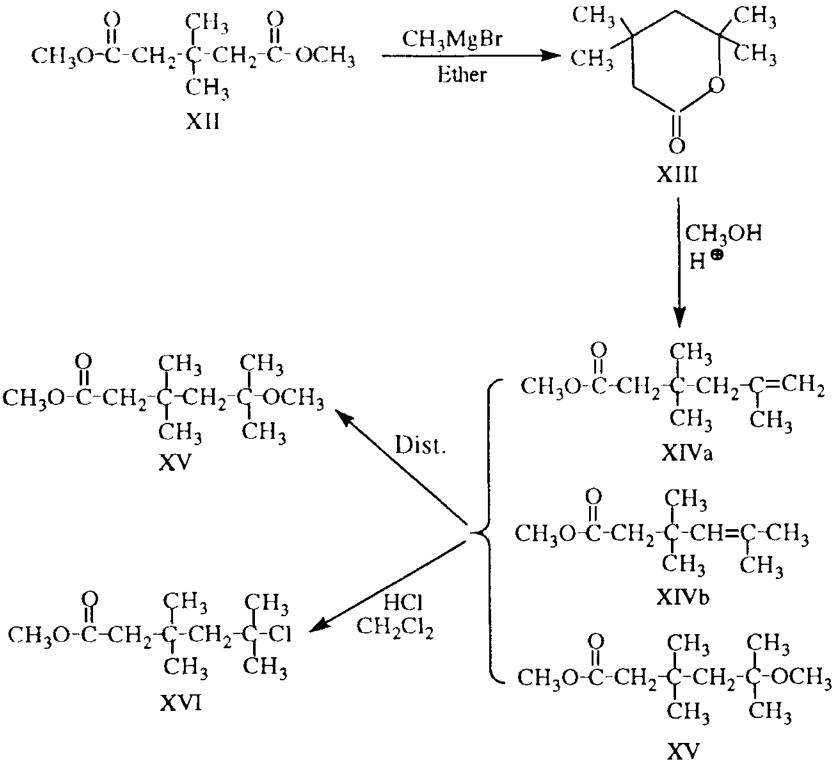
†Part LVIII, Y. Tsunegae and J. P. Kennedy, *J. Polym. Sci., Part A, Polym. Chem.*, In Press.

with BCl_3 initiate the living carbocationic polymerization (LC^+Pzn) of isobutylene (IB) and yield asymmetric telechelics with the ester headgroup and *tert*-chlorine tailgroup. In this instance, the ester is protected ("hidden") during the synthesis in the form of a cyclic structure.

The present research concerns the synthesis of asymmetric telechelic PIBs by LC^+Pzn using novel aromatic and aliphatic initiators in the presence of $TiCl_4$ or BCl_3 coinitiators, and the quantitative conversion of the head- and tailgroups to various other functions, i.e., the headgroup into HOCO— and the tailgroup into $-CH_2C(CH_3)=CH_2$ and $-C_6H_4OH$ groups. Scheme 1 outlines the synthesis of the aromatic initiators (III and V) and the subsequent polymerization route to the target parent asymmetric telechelic PIB (VIII). Scheme 2 shows the route to the aliphatic initiators.



SCHEME 1. Synthesis of novel aromatic asymmetric initiators, polymerization of IB to asymmetric telechelic PIB, and derivations of the latter.



SCHEME 2. Synthesis of aliphatic initiators.

Most of the research was carried out with the aromatic initiators because 1) the rate of polymerization initiation was higher with these than with the corresponding aliphatic compounds (i.e., initiation efficiencies were higher with the aromatics than with the aliphatics) so that the molecular weight distribution of the products obtained with the former compounds was narrower than those produced with the latter compounds, and 2) the spectroscopic characterization of the polymers obtained by the aromatic initiators is much facilitated by the presence of the aromatic moieties in the polyisobutylenes.

EXPERIMENTAL

The source and purity of IB, CH_3Cl, $TiCl_4$, hexanes, CH_2Cl_2, and BCl_3 have been described [3, 4]. Dimethyl 5-*t*-butylisophthalate (I), *N*,*N*-dimethylacetamide (DMA), and phenol were used as received.

Synthesis of Initiators

Synthesis of Aromatic Initiators. To a mixture of 70 g of I in 800 mL THF, 186 mL methyl magnesium bromide (3 M solution in ether) was slowly added. The addition rate was controlled to keep the temperature below 5°C. The charge was

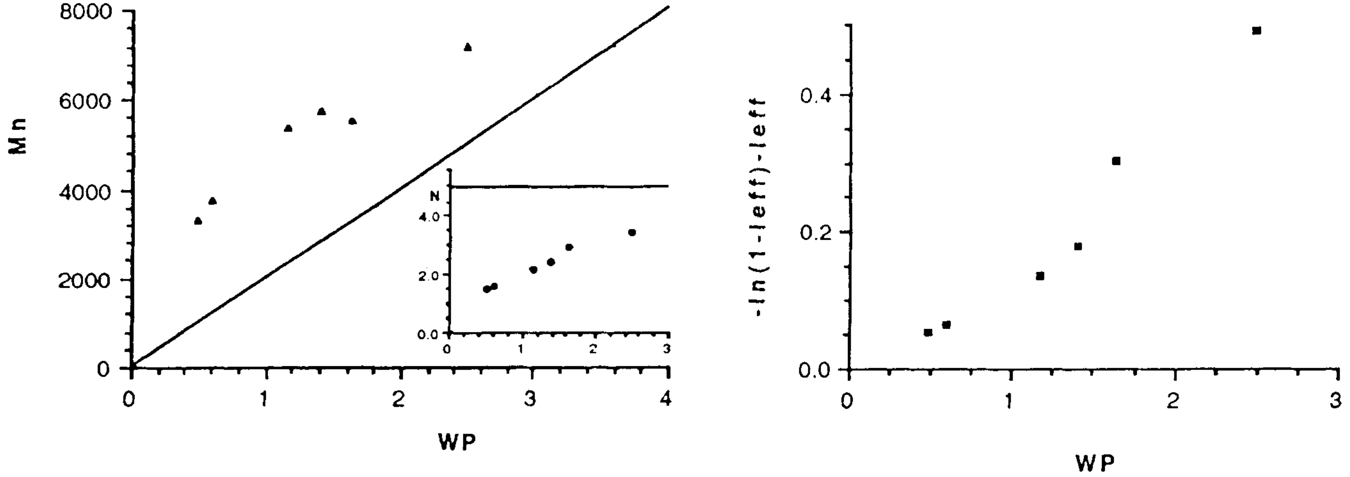


FIG. 1. Living polymerization of IB by V/$TiCl_4$ combination ($[I_0]$ = 4.99 × 10^{-4} M, $[TiCl_4]$ = 0.365 M, [DMA] = 0.03 M, CH_3Cl/*n*-C_6H_{14}, 40/60 v/v, V_0 = 25 mL, −80°C, 60 minutes).

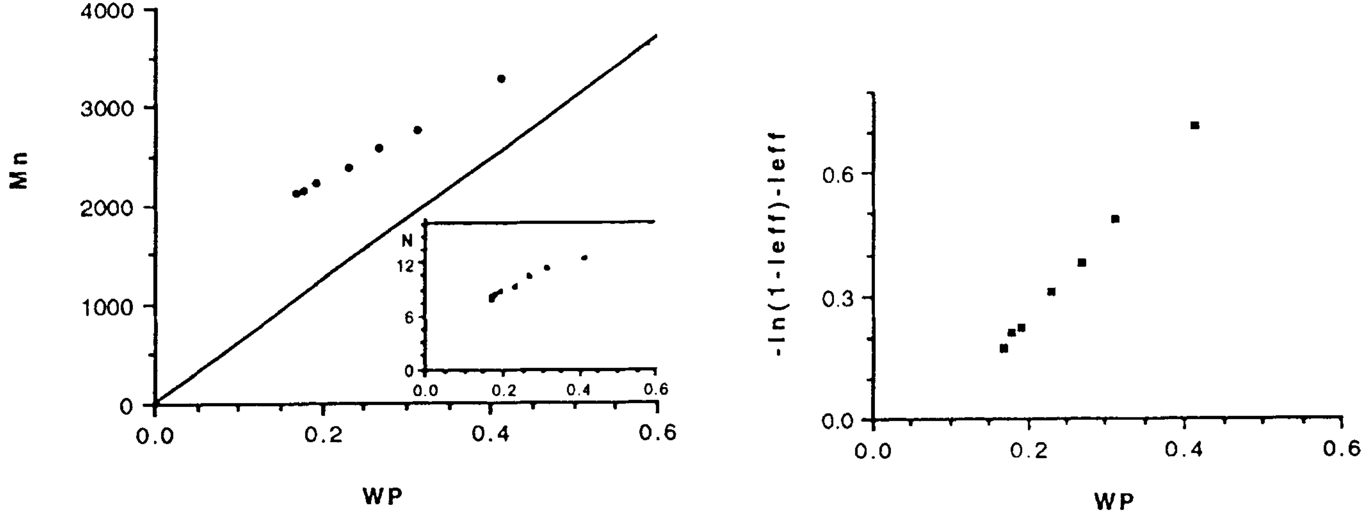


FIG. 2. Living polymerization of IB by V/BCl$_3$ combination ([I$_0$] = 3.27×10^{-2} M, [BCl$_3$] = 0.89 M, [DMA] = 0.03 M, CH$_3$Cl solvent, V_0 = 1.6 L, −45°C, 3 hours).

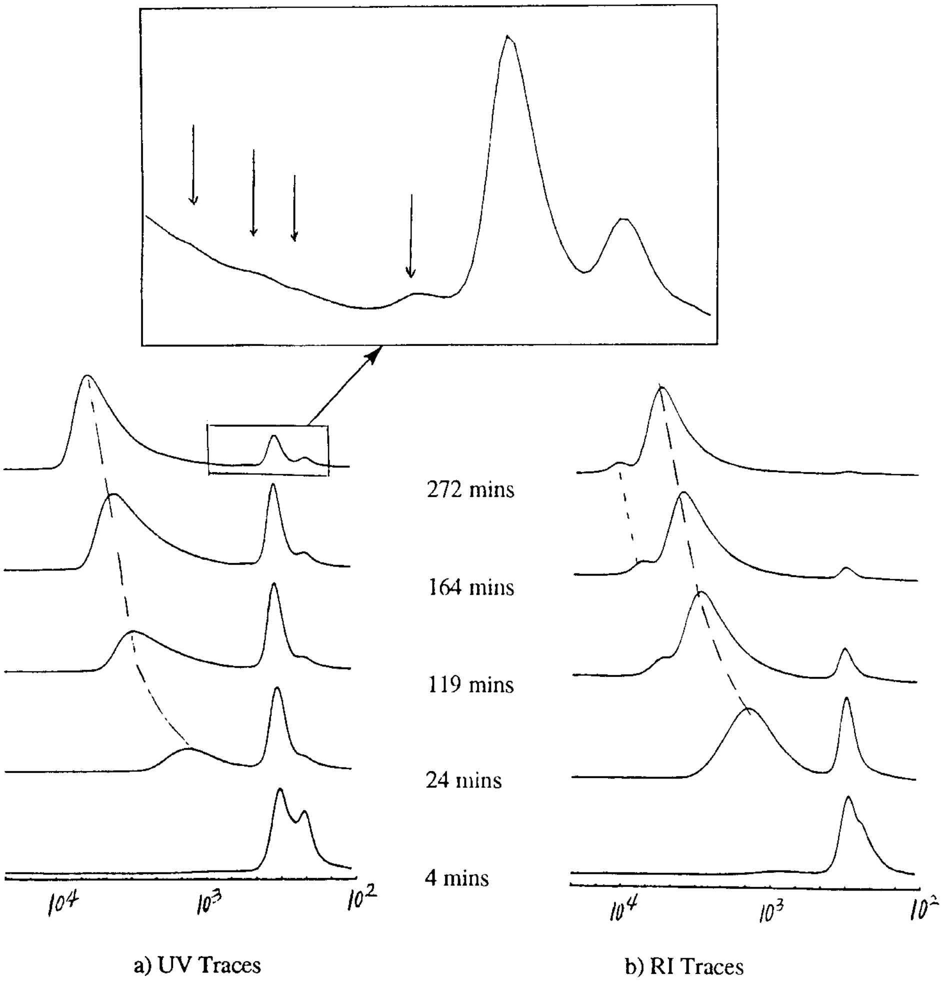


FIG. 3. GPC traces of samples obtained at various times, V/BCl_3 combination ($[I_0] = 3.27 \times 10^{-2}$ M, $[BCl_3] = 0.89$ M, [DMA] = 0.03 M, CH_3Cl solvent, −45°C).

maintained at this temperature overnight. The red mixture was poured onto 500 g ice, and the ether layer was separated and collected. After drying over $MgSO_4$ and evaporating the solvent, the crude product was recrystallized from 200 mL hexanes. Yield: 50.2 g or 72% of methyl 3-*t*-butyl-5-(α-hydroxylpropyl)benzoate (II) was obtained. To a mixture of 20 g II in 150 mL methanol, a few drops of sulfuric acid were added as catalyst. The mixture was refluxed for 12 hours. The methanol solution was concentrated to about 50 mL, then diluted with 100 mL hexanes, and repeatedly washed with water. After drying and evaporating the solvent, 19.0 g (90%) methyl 3-*t*-butyl-5-(α-methoxylpropyl)benzoate (III) was obtained. Subsequently, 11.9 g III was heated at 70°C, then distilled under vacuum, and a fraction with a boiling point of 142–145°C/5 mmHg was collected. Thus, 8.0 g (79%) methyl 3-*t*-butyl-5-isopropenylbenoate (IV) were obtained. To a mixture of 21.0 g

TABLE 1. Polymerization of IB with the XV/$TiCl_4$ and the XVI/$TiCl_4$ Combination (CH_3Cl/n-C_6H_{14}, 40/60 v/v, [$TiCl_4$] = 0.216 M, V_0 = 25 mL, −80°C, 60 minutes)

Initiator	[I_0] × 10^2 M	[DMA] × 10^2 M	[IB] M	Conversion, %	$\overline{M}_n$ g/mole	$\overline{M}_w/\overline{M}_n$	I_{eff}, %
XVI	1.33	0	0.51	89	17,642	1.43	11
	0.99	0	1.03	91	32,072	1.41	16
	1.20	0	1.54	91	35,675	1.43	18
	1.13	3	0.51	93	22,372	1.51	11
	1.30	3	1.03	96	31,088	1.46	14
	1.33	3	1.54	97	37,070	1.48	17
XV	1.06	0	0.51	93	27,790	1.34	9
	0.96	0	1.03	93	40,544	1.36	10
	0.91	0	1.54	99	50,750	1.41	19

IV in 100 mL CH_2Cl_2, hydrogen chloride gas was bubbled for 3 hours at 0°C. Samples were taken to check by NMR spectroscopy until the olefin peaks completely disappeared. The CH_2Cl_2 solution was washed with water. After drying and evaporating the solvent, 19.3 g (91%) methyl 3-t-butyl-5(α-chloropropyl)benzoate (V) was obtained. The crude product was purified by crystallization from hexanes, and its structure was identified by its ^{1}H-NMR spectrum [δ 1.35 ppm (s) 9H; δ 2.00 ppm (s) 6H; δ 3.91 ppm (s) 3H; δ 7.85 ppm (t) 1H; δ 8.00 ppm (multiplet) 2H].

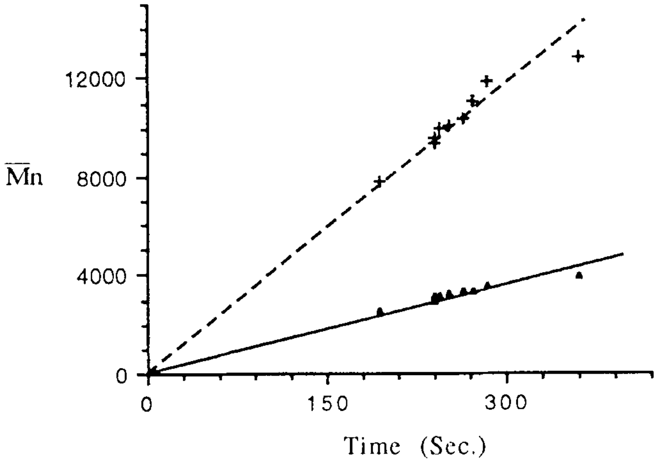


FIG. 4. Polymerization of IB by (V + water)/BCl_3 combination ([I_0] = 3.27 × 10^{-2} M, [BCl_3] = 0.89 M, [DMA] = 0.03 M, CH_3Cl solvent, V_0 = 1.6 L, −45°C). Solid line: Initiation by V. Dotted line: Initiation by "H_2O."

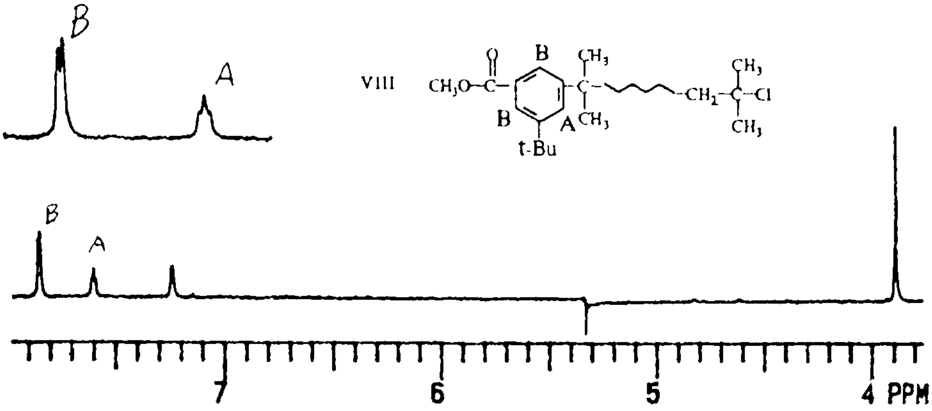


FIG. 5. ^{1}H-NMR spectra of parent polymer VIII (see text for details).

Synthesis of Aliphatic Initiators. To a 5-L 3-neck flask containing 2.4 L methyl magnesium bromide ether solution (3 M) and 1.5 L THF, 265 g dimethyl-3,3-dimethylglutarate (XII) was added dropwise under a blanket of nitrogen over 6 hours. The addition rate was controlled to keep the temperature below the boiling point of ether. The mixture was stirred overnight at 0°C. The mixture was poured over 1 kg ice, then extracted with ether. The ether extract was washed with water and dried. After evaporating the solvent, colorless needles of crystalline 2,6-dihydroxyl-2,4,4,6-tetramethylheptane were formed. The needles were filtered, and the yellow liquid obtained was placed in a refrigerator overnight, then filtered, and the procedure was repeated until the precipitation of crystalline material ceased. This yellow liquid is almost pure 4,4,6,6-tetramethyl-δ-valerolactone (XIII), yield 82 g (38%). The crude lactone was purified by vacuum distillation (bp 99–100°C/5 mmHg) [5].

To a solution of 29.1 g XIII in 380 mL methanol, a few drops of sulfuric acid were added as catalyst. The mixture was refluxed over 24 hours, then poured onto 200 g ice and extracted with pentane. After removing the pentate, a slightly orange liquid was obtained (yield 12.5 g). This is a mixture of methyl 3,3,5-trimethylhexene-5-noate (XIVa), methyl 3,3,5-trimethylhexene-4-noate (XIVb), and methyl 3,3,5-trimethyl-5-methoxylhexanoate (XV). Compound XV (1.5 g or 5%), was separated from the mixture by distillation under reduced pressure (bp 85–92°C/5 mmHg). The residue was used for the preparation of methyl 3,3,5-trimethyl-5-chlorohexanoate (XVI).

In order to prepare XVI, HCl gas was bubbled into the residue obtained above [6]. Thus HCl was bubbled into a solution of 8.2 g of the residue in 75 mL CH_2Cl_2. The originally colorless solution turned yellow, orange, and ultimately green. A series of samples were withdrawn during this period to check by ^{1}H-NMR spectroscopy for the presence of unsaturation. We found that the unsaturation disappeared when the solution turned green. At this point the solution was washed with water and dried over $MgSO_4$. After removing the solvent, 8.0 g (80%) of colorless liquid was obtained. According to the ^{1}H-NMR spectrum, this product is pure XVI [δ

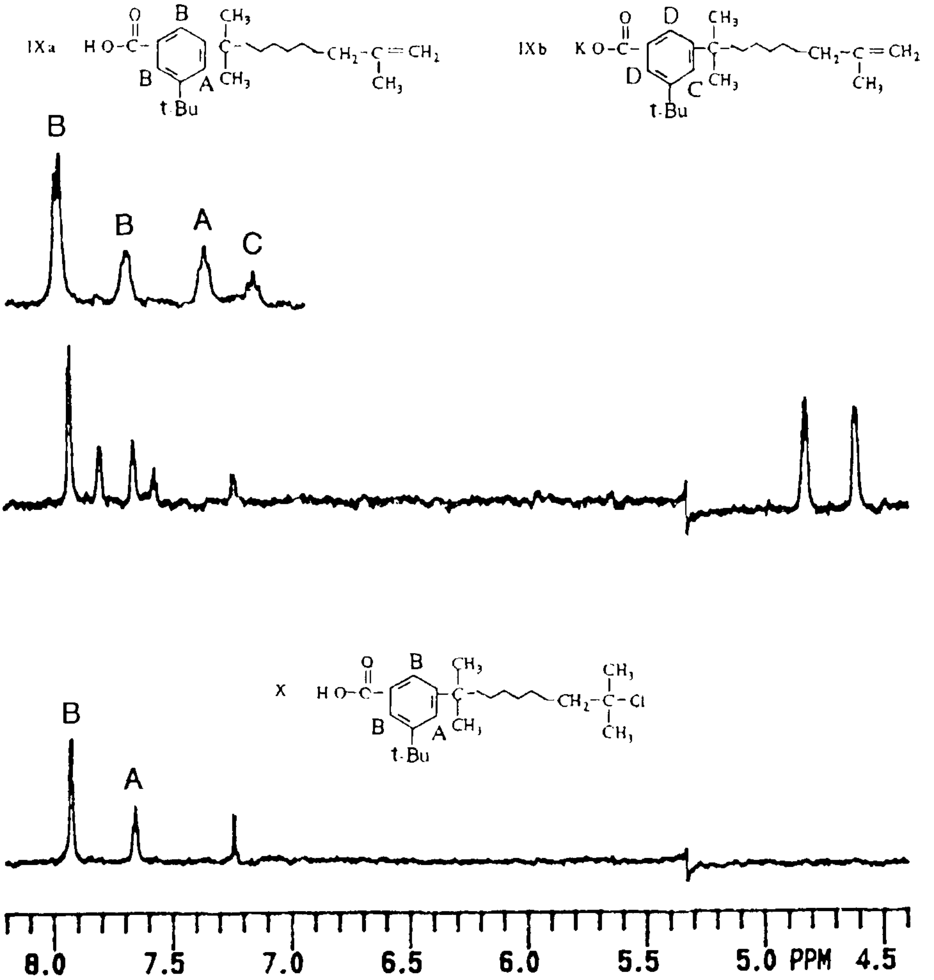


FIG. 6. Proton NMR spectra of functionalized polymer. Top: Mixture of IXa and IXb. Bottom: X (see text for details).

1.15 ppm (s) 6H; δ 1.64 ppm (s) 6H; δ 1.96 ppm (s) 2H; δ 2.38 ppm (s) 2H; δ 3.62 ppm (s) 3H].

Polymerization and Functionalization

Polymerization. Polymerizations were carried out in a dry box under a blanket of nitrogen. The experiment described in Fig. 1 was carried out in large test tubes. The experiment described in Fig. 2 was carried out in a 2-L round bottom flask. The procedures have been described [7, 8]. PIB molecular weight and $\overline{M}_w/\overline{M}_n$ were determined by a Waters high pressure GPC, using RI/UV dual detectors. Proton NMR spectra were obtained by the use of a Varian Gemini-200 MHz instrument.

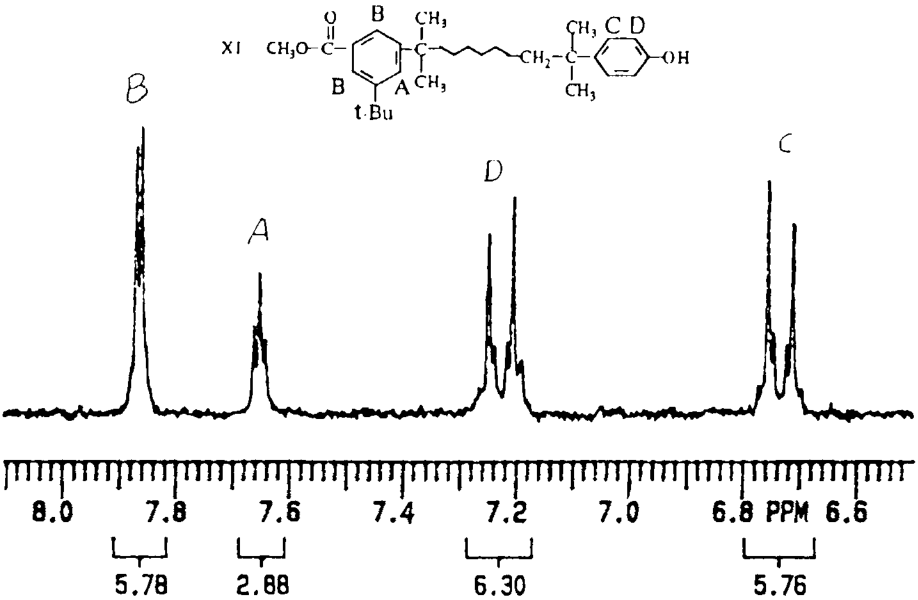


FIG. 7. Proton NMR spectrum of phenol-terminated polymer XI.

Phenolation. Phenolation was carried out in hexanes solution [9]. Thus, a solution of 50 g VII ($\overline{M}_n$ = 4100, $\overline{M}_w/\overline{M}_n$ = 1.29) in 140 mL hexanes was added dropwise to a solution of 50 g phenol in 160 mL hexanes at 40–45°C over 3 hours in the presence of $BF_3 \cdot OEt_2$ (2.6 mL) catalyst. The mixture was maintained at this temperature for 48 hours. Then 300 mL water was added and the charge was stirred overnight at room temperature. The mixture was separated to remove the water, and the hexanes solution was washed and dried. After removing the solvent, the ω-phenol-ended asymmetric PIB (XI) was obtained.

Dehydrochlorination. Dehydrochlorination was done by a routine procedure [10]. Thus, a mixture of 52 g VIII ($\overline{M}_n$ = 2948, $\overline{M}_w/\overline{M}_n$ = 1.23) and 8 g potassium *t*-butoxide in 500 mL THF was refluxed for 24 hours. The mixture was cooled to room temperature and 1-L hexanes was added. Then 100 mL of 50% sulfuric acid was added to the resulting emulsion. The acid layer was removed, and the hexanes solution was washed with 5% sulfuric acid and then with water. After removing the solvent, α-isopropylidene-ω-(3-*t*-butyl)-5-benzoic acid PIB (IXa) was obtained.

Homogeneous Phase Acidification. HCl gas was bubbled for 3 hours into a solution of 9.1 g olefin-ended PIB (synthesis described above) in 50 mL CH_2Cl_2 cooled in an ice-bath. The resulting mixture was washed with water and dried over $MgSO_4$. After removing the solvent by Rotavap, α-*t*-chloro-ω-(3-*t*-butyl)-5-benzoic acid PIB (X) was obtained.

RESULTS AND DISCUSSION

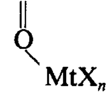
Schemes 1 and 2 outline the routes selected for the synthesis of initiators III, V, and XV, XVI to induce the LC$^+$Pzn of IB, and hence the route to the target asymmetric telechelic PIB. These four initiators seem to be novel (absent by computer search of *Beilstein* 1880–1959 and *Chemical Abstracts* 1950–1992). Also, the method used for the synthesis of XIII is much more convenient than that described in the literature [3]. Compounds similar to III, V, XV, and XVI, i.e., cumyl chloride [11], cumyl methyl ether [4, 7], and cumyl alcohol [8, 12], are efficient initiators for the LC$^+$Pzn of IB.

The results of orienting experiments summarized in Figs. 1 and 2 confirmed our expectation that III and V indeed initiate the living polymerization of IB and produce the sought prepolymers. In line with the diagnostic plots for slow initiation [13], the rate of initiation is lower than that of propagation. Follow-up experiments with the III/$TiCl_4$ combination showed initiator efficiencies (I_{eff}) in the range of 30 to 50% at 100% conversion (Fig. 1). With the III/BCl_3 system, I_{eff} was ~85% at 60% conversion (Fig. 2).

The relative rate of initiation was determined quantitatively by removing samples as a function of time and analyzing them by dual detector (RI and UV) GPC instrumentation. Figure 3 shows the findings. The strong UV absorptions (see Fig. 3a) at molecular weights of ~240, ~360, and ~460, together with the series of humps indicated by the arrows and made visible in the enlargement, and the final large peak (which, by the way, is also visible in the RI traces), are due to the high extinction coefficient of the $CH_3OCOC_6H_3$— headgroup in V. This series of peaks indicate, respectively, the presence of unconverted V (MW = 266) and polymeric species containing two, three, etc. isobutylene units up to high molecular weight polymer. With increasing polymerization time (see Fig. 3), the initial peaks (associated with V and VI and very low polymers) gradually disappear while that associated with the growing polymer (VIII) increases and moves to higher molecular weights. These observations also show that the rate of initiation is slow relative to propagation.

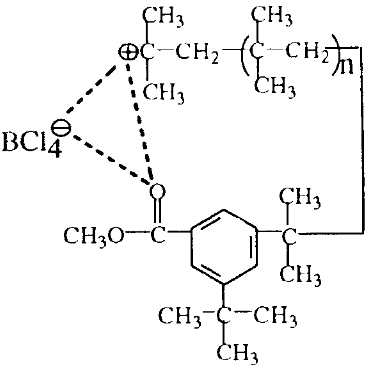
Similar results have also been obtained with the aliphatic initiators XV and XVI. Table 1 summarizes the data obtained. Since the rate of initiation was apparently even lower than those observed with the corresponding aromatic compounds [see initiator efficiency (I_{eff}) data], experimentation with the aliphatic initiators was discontinued.

The rates of initiation and propagation are most likely reduced by the CH_3OCO— group which functions as an internal ED [14]. This ester group may react with the excess Friedel-Crafts acid to form CH_3OC— (MtX_n = BCl_3 or $TiCl_4$) complexes which then interact with the propagating chainend and thus mediates LC$^+$Pzn.



$\mathrm{CH_3O}\underset{\underset{\diagdown\,\mathrm{MtX}_n}{\mathrm{O}}}{\underset{\|}{\mathrm{C}}}\text{—}$

We postulate that cyclic structures similar to VII may also be involved in these polymerizations. (The formation of these structures is possible at $n \geq 1$ according to Dreiding Stereomodels; the dotted lines indicate nonspecific hypothetical interactions.)



VII

Evidence for the existence of propagating cyclic structures was obtained by GPC analysis. We observed that the GPC traces of the products formed upon initiation by V exhibited two growing peaks (i.e., species): One whose growth could be followed by only the RI trace and one whose growth was indicated by both the UV and the RI trace. We postulate that the former species is due to initiation by moisture ("H_2O") impurities (about 4% of total weight of polymer) and the latter to initiation by V. Figure 3 shows a representative series of five RI and UV traces of 20 samples withdrawn from a living charge as a function of time. As shown in Fig. 3(b), the RI traces start to indicate a rapidly growing species at ~74 minutes which becomes quite distinctive as a separate peak at ~164 minutes $\overline{M}_n \approx 7190$) which we attribute to polymer produced by "H_2O." The same RI traces also indicate a slower growing species which is due to controlled initiation by V. The two broken lines in Fig. 3(b) help to follow the growth of molecular weights. The corresponding UV trace shown in Fig. 3(a) can only be due to polymer produced by V (the broken lines show the growth of this species).

Figure 4 shows the $\overline{M}_n$ versus t plots for the growing polymers initiated by "H_2O" and V. The individual data points have been read off directly of GPC traces. According to these results, both in the "H_2O" and the V initiated polymerizations, the $\overline{M}_n$s increase linearly with time in the conversion range studied. The former polymerization is evidently much faster than the latter, presumably because cyclic intermediates cannot form in "H_2O"/BCl_3-initiated systems.

The structures of the product obtained with the III/$TiCl_4$ and V/BCl_3 systems were analyzed by ^{1}H-NMR spectroscopy [15, 16] and end-group transformation reactions. Figure 5 shows a representative spectrum of the parent polymer VIII together with the expanded region for aromatic protons. The ester methoxy group appears at 3.89 ppm while the three aromatic protons as a triplet and a doublet appear at 7.60 and 7.85 ppm, respectively.

The mineral acid hydrolysis of this ester to the acid is difficult because of the different solubility characteristics of the starting material and the product, and the different reactivities of the end functions. However, we were able to develop suitable conditions for the quantitative synthesis of the HOCO— derivative (X). This transformation included treatment of VIII with t-BuOK which yielded a mixture of IXa and IXb (by dehydrochlorination/hydrolysis/salt formation), followed by HCl addition to yield X (see the Experimental Section).

Figure 6(a) (top) shows the proton NMR spectrum of the mixture of IXa and IXb together with the expanded region for aromatic protons. The resonances for the aromatic protons in IXb (the triplet labeled C and the doublet labeled D) shift up 0.13 and 0.09 ppm, respectively, relative to that for IXa (the triplet labeled A and the doublet labeled B). These shifts occur because the aromatic protons in the salt IXb are more shielded than those in the acid. Figure 6(b) (bottom) shows the proton NMR spectrum of the acid derivative. The peaks at 4.6–4.8 ppm and the peaks characteristic of the salt IXb disappeared, indicating that acidification with HCl yields a α-*t*-chlorine-ω-acid asymmetric telechelic polymer.

Figure 7 shows the phenolated product (XI) obtained from VIII plus phenol in the presence of $BF_3 \cdot OEt_2$ [9]. The structure of XI has been derived by quantitative analysis of the ^{1}H-NMR spectrum facilitated by the two built-in aromatic markers in the molecule.

CONCLUSIONS

By the use of novel initiators (III, V), novel asymmetric-telechelic PIBs capped by a CH_3OCO- headgroup and a $-CH_2C(CH_3)_2Cl$ tailgroup have been synthesized by LC^+Pzn. The needed electron donor to achieve LC^+Pzns were most likely provided by the CH_3OCO- headgroup. Evidence was presented that the polymerizations may involve cyclic intermediates. The reactive CH_3OCO- and $-CH_2C(CH_3)_2Cl$ endgroups have been quantitatively converted to $HOCO-$ and p-C_6H_4OH groups, and thus further novel asymmetric telechelic PIBs were obtained.

ACKNOWLEDGMENT

This material is based upon work supported by the National Science Foundation under Grant 89-20826.

REFERENCES

[1] A. F. Fehervari, R. Faust, and J. P. Kennedy, *Polym. Bull.*, *23*, 525 (1990).

[2] A. F. Fehervari, R. Faust, and J. P. Kennedy, *J. Macromol. Sci.—Chem.*, *A28*, 65 (1991).

[3] G. Kaszas, J. E. Puskas, and J. P. Kennedy, *Ibid.*, *A26*, 1099 (1989).

[4] R. Faust and J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed.*, *25*, 1847 (1987).

[5] J. W. Lynn, *J. Org. Chem.*, *26*, 1284 (1961).

[6] H. C. Brown and M.-H. Rei, *Ibid.*, *31*, 1091 (1966).

[7] G. Kaszas, J. E. Puskas, and J. P. Kennedy, *Makromol. Chem., Macromol. Symp.*, *13/14*, 473 (1988).

[8] C. C. Chen, J. Si, and J. P. Kennedy, *J. Macromol. Sci., Pure Appl. Chem.*, *A29*, 669 (1992).

[9] J. P. Kennedy, S. C. Guhaniyogi, and V. Percec, *Polym. Bull.*, *8*, 563 (1982).

[10] J. P. Kennedy, V. S. C. Chang, R. A. Smith, and B. Ivan, *Ibid.*, *1*, 575 (1979).

[11] J. P. Kennedy and R. P. Smith, *J. Polym. Sci., Polym. Chem. Ed.*, *18*, 1532 (1980).

[12] C. C. Chen, G. Kaszas, J. E. Puskas, and J. P. Kennedy, *Polym. Bull.*, *22*, 463 (1989).

[13] M. Zsuga and J. P. Kennedy, *J. Macromol. Sci.—Chem.*, *A26*, 1305 (1989).

[14] J. P. Kennedy and B. Ivan, *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*, Hanser Publisher, 1992, pp. 47–78.

[15] S. Nemes, J. Si, and J. P. Kennedy, *Polym. Bull.*, *23*, 597 (1990).

[16] S. L. Manatt, J. D. Ingham, and J. A. Miller Jr., *Org. Magn. Reson.*, *10*, 198 (1977).

Received January 5, 1993
Revision received March 5, 1993