Polymer Bulletin 9, 570–576 (1983)

Polymer Bulletin

New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers)

35. Synthesis and Characterization of α, ω-Di(Ethynyl)Polyisobutylenes

V. Percec*, S. C. Guhaniyogi and J. P. Kennedy

Institute of Polymer Science, The University of Akron, Akron, OH 44325, USA

SUMMARY

The synthesis and characterization of linear telechelic polyisobutylenes having propargyl ether, propargyl ester and propiolic ester end groups are described. The syntheses were accomplished by reacting α, ω-di(hydroxy)-polyisobutylene with propargyl bromide or phthalic anhydride followed by propargylic alcohol or monopropargylic ester of phthalic acid chloride, or propiolic acid in the presence of different catalysts at room temperature (see Scheme 2). According to IR and ^{1}H-NMR analyses quantitative conversions were obtained.

INTRODUCTION

Interest in functional polymers containing pendant or terminal triple bonds is increasing and advances have recently been reviewed (1). The synthesis and characterization of α, ω-di(nitrile)polyisobutylenes are reported separately (2). This paper describes the synthesis and characterization of telechelic polyisobutylenes carrying propargyl ether, propargyl ester and propiolic ester as end groups. Model experiments carried out with 2,4,4-trimethyl-1-pentanol have been studied to define reaction conditions. Schemes 1 and 2 outline the model reactions and polymer derivatizations investigated, respectively.

EXPERIMENTAL

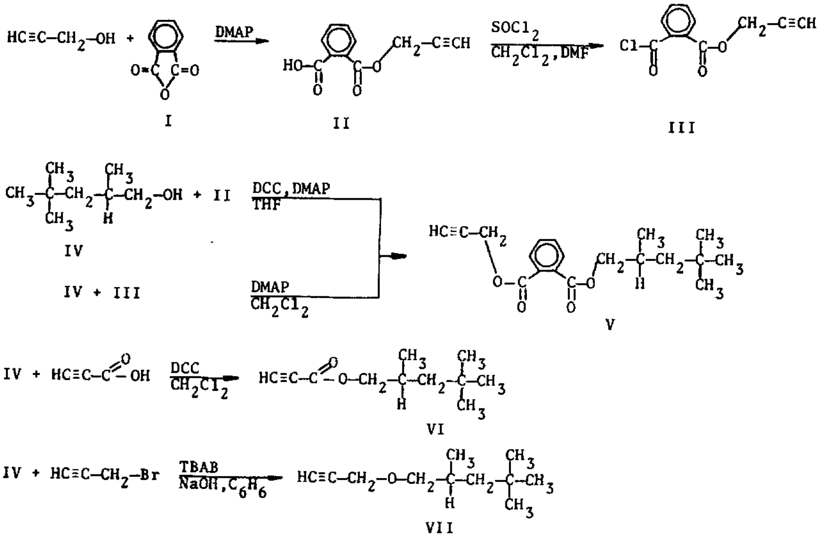
α, ω-Di(hydroxy)polyisobutylene ($\overline{F}_n$ = 2.0, $\overline{M}_n$ = 3400) was synthesized and characterized as reported (4). Propargyl bromide (Aldrich), propargyl alcohol (Aldrich), and propiolic acid (Aldrich) were distilled before use. 4-N,N-dimethylaminopyridine (DMAP) (Aldrich), dicyclohexylcarbodiimide (DCC) (Aldrich), tetrabutylammonium bisulphate (TBAB) (Aldrich), phthalic anhydride (Aldrich) and $SOCl_2$ (Aldrich) were used as received. Solvents were dried by conventional methods and distilled before use. Dimethylformamide (DMF) was dried on molecular sieves (4 Å) and distilled. Experimental and instrumental techniques have been described (4).

SYNTHESES AND RESULTS

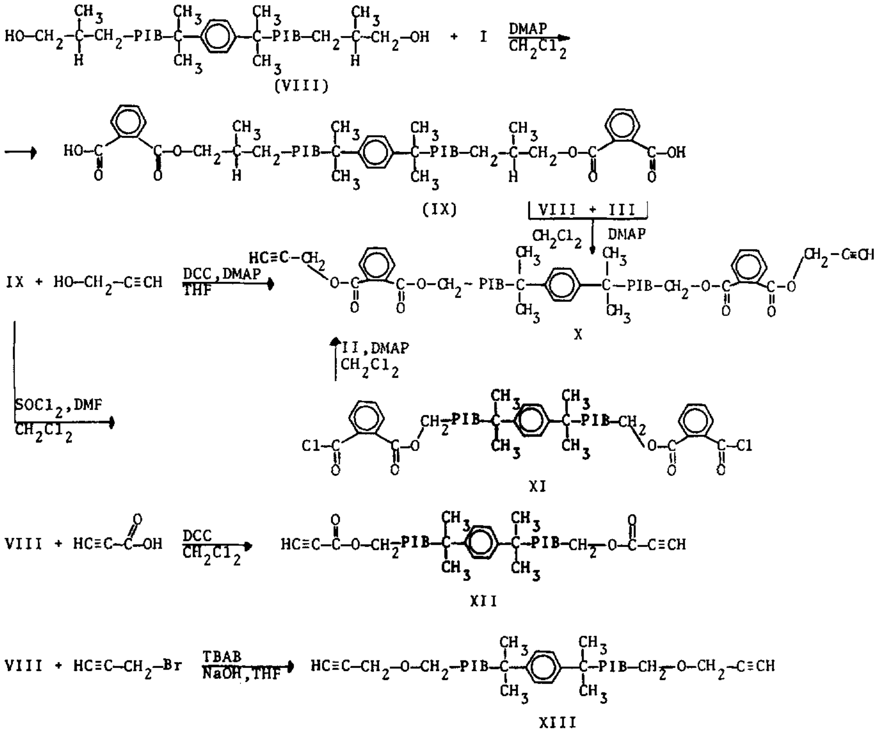
The procedures used for the preparation of model compounds and telechelic acetylenes are outlined Schemes 1 and 2, respectively. The roman numerals in this section refer to the compounds in the Schemes 1 and 2.

---

* Present address: Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA



Scheme 1: Model Reactions Examined for the Synthesis of α, ω-Di-(ethynyl)polyisobutylenes.



Scheme 2: Synthetic Routes Used for the Synthesis of α, ω-Di-(ethynyl)polyisobutylenes.

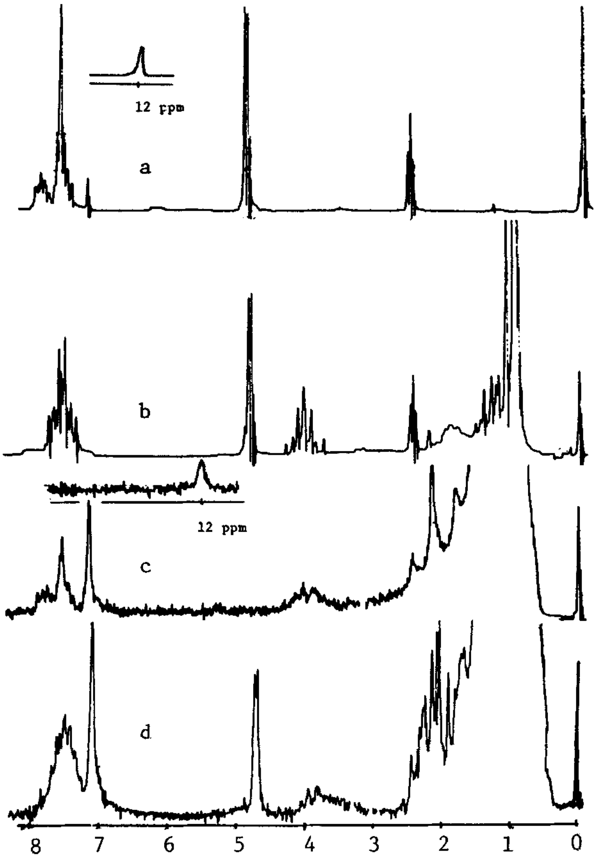


Figure 1: ^{1}H-NMR spectra of compounds: II (a); V (b); IX (c); X (d).

Synthesis of monopropargylic ester of phthalic acid (II). To a solution of 3.7 g (0.025 mole) phthalic anhydride and 2.18 ml (0.037 mole) propargyl alcohol in 50 ml dry THF were added 3.05 g (0.025 mole) DMAP solution in 10 ml THF (5). The reaction was exothermic and a white precipitate appeared. The mixture was stirred for 6 hours at room temperature, poured into cold water and filtered. The white crystalline precipitate was washed successively with water, dilute HCl and water. It was dissolved in $CHCl_3$, dried over anhydrous $MgSO_4$ and finally the solvent was evaporated at room temperature. After recrystallization from CCl_4, 4.5 g (88%) of white crystals were obtained: m.p. 99-100°C. IR (KBr): 3220 cm^{-1} (νHC≡), 2120 cm^{-1} (νC≡C), 1720 cm^{-1} (νC= O), 1650 cm^{-1} (νC=O). ^{1}H-NMR ($CDCl_3$, TMS): δ = 2.5 ppm (≡C$\underline{H}$, t), δ = 4.9 ppm (-C$\underline{H}_2$-C≡, d), δ = 7.45 - 8.0 ppm (four aromatic protons, m) (Figure 1a). $A_{7.45\ -\ 8.0\ ppm}/A_{4.9\ ppm} = 2$ corroborated quantitative nature of the reaction.

Synthesis of III by chlorination of II. To a mixture of 2g II and 10 ml dry CH_2Cl_2, excess $SOCl_2$ was added followed by a few drops of DMF catalyst. After 30 minutes of stirring at room temperature the heterogeneous mixture turned into a clear solution. After refluxing for 2 hours, the $SOCl_2$ and CH_2Cl_2 were removed by distillation. The viscous product crystallized on standing overnight at room temperature. The absence of -OH signals in the IR and ^{1}H-NMR spectra indicated virtually quantitative chlorination.

Synthesis of 2,4,4-trimethyl-1-pentanol ester of monopropargylic ester of phthalic acid (V). This mixed ester was synthesized by direct esterfication of IV with II in the presence of DCC dehydrating agent and DMAP catalyst (6) and by a Schotten-Baumann reaction between IV and III in the presence of DMAP catalyst (5). In both cases the reaction was quantitative as discussed in the following paragraphs.

To a solution of 2.04 g (0.01 mole) II, 1.95 g (0.015 mole) IV in 30 ml dry THF were added 2.064 g (0.01 mole) DDC followed by 0.122 g (0.001 mole) DMAP. An exothermic reaction took place and a white precipitate suddenly appeared. After 4 hours stirring at room temperature the precipitate was filtered and the filtrate was evaporated. The remaining product was dissolved in CH_2Cl_2, filtered, washed successively with dilute HCl, water, aqueous $NaHCO_3$, water, dried over anhydrous $MgSO_4$, and finally the solvent was evaporated. The liquid was characterized by IR and ^{1}H-NMR spectroscopies and found to be V. Conversion appeared to be essentially quantitative. IR (KBr): 3265 cm^{-1} ($\nu\equiv$CH), 2115 cm^{-1} (νC≡C). ^{1}H-NMR CCl_4, TMS): δ 0.9 - 2.0 ppm (15 protons, m), δ = 2.5 ppm (≡CH, t) δ = 4.1 ppm (OCH_2-HC(CH_3)-, m) δ = 4.95 ppm (≡C-CH_2-O, d), δ = 7.35 - 7.85 ppm (4 aromatic protons, m) (Figure 1b). $A_{7.35-7.85\ ppm}/A_{4.95\ ppm} = 2$ indicated quantitative yield of V.

The reaction between IV and III was carried out at room temperature for 5 hours in CH_2Cl_2 with (III)/(IV) = 1.5 and a stoichiometric amount of DMAP. The product was purified in the same manner as described in the previous paragraph. According to IR and ^{1}H-NMR analyses the expected structure for V has been obtained.

Synthesis of propiolic ester of 2,4,4-trimethyl-1-pentanol (VI). To an ice-cooled solution of 9.12 g (0.07 mole) IV and 6.35 ml (0.105 mole) propiolic acid in 50 ml dry CH_2Cl_2 was added 17.33 g (0.084 mole) DCC dissolved in 25 ml CH_2Cl_2. After 10 hours of stirring at room temperature the white precipitate which appeared was filtered off and the filtrate was washed successively with water, aqueous $NaHCO_3$ and water, dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated. According to IR and ^{1}H-NMR spectroscopies the liquid product was VI. IR (KBr): 3300 cm^{-1} ($\nu\equiv$C-H), 2100 cm^{-1} (νC≡C), 1700 cm^{-1} (νC=O). ^{1}H-NMR (CCl_4, TMS): δ = 3.9 ppm (-CH_2O,d), δ = 2.59 ppm (≡CH, s) δ = 0.9 - 2.0 (15 protons, m).

Synthesis of propargylic ether of 2,4,4-trimethyl-1-pentanol (VII). To a mixture of 3g (0.023 mole) IV, 5 ml propargyl bromide (large excess) and 10 ml benzene were added 7 ml 50% aqueous NaOH solution and 0.39 g (0.00115 mole) TBAB (7). The solution was stirred for 2 hours at room temperature. Then 5 ml propargyl bromide and 0.1 g TBAB were added and stirring was continued for 2 more hours. The solution was washed with water, dried over anhydrous $MgSO_4$ and the solvent and excess reactants were evaporated. IR (KBr): 3310 cm^{-1} ($\nu\equiv$CH), 2110 cm^{-1} (νC≡C). ^{1}H-NMR (CCl_4, TMS): δ = 4.13 ppm (≡C-CH_2-O, d), δ = 3.40 ppm (OCH_2-(CH_3)CH-, d), δ = 2.5 ppm (≡CH, t), δ = 0.7 - 1.7 ppm (15 protons) (Figure 2, a). The value 7.45 for the ratio of the area under the signals at δ = 0.7 - 1.7 ppm and 4.13 ppm suggested quantitative reaction.

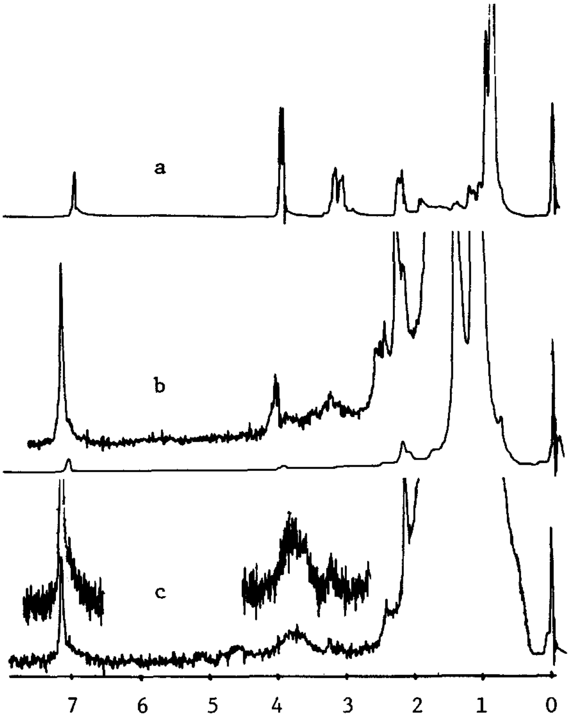


Figure 2: ^{1}H-NMR spectra of compounds: VIII (a); XIII (b); XII (c).

Esterification of VIII with phthalic anhydride (IX). The synthesis of telechelic acid ester polyisobutylenes has already been reported (8). The previous authors esterified α, ω-di(hydroxy)polyisobutylene (VIII) with excess dicarboxylic acid chlorides, however, even in the presence of a large excess of dicarboxylic acid chlorides, chain extension could not be completely avoided. In the present investigation the esterification of VIII with phthalic anhydride was quantitative and chain extension was absent.

To a solution of 10.2 g (0.003 mole, 0.006 mole -OH, $\overline{M}_n$ = 3400) VIII and 1.78 g (0.012 mole) I in 50 ml THF was added 0.88 g (0.0072 mole) DMAP (or 0.088 g, 0.00072 mole DMAP and 0.00063 mole TEA) and the reaction mixture was stirred at room temperature for 10 hours. The solvent was evaporated and replaced with 300 ml hexanes. The solution was washed with dilute HCl, water and aqueous $NaHCO_3$ which produced three layers in the separating funnel. The top two layers contained the sodium salt of telechelic acid ester of polyisobutylene and hexanes, respectively. The bottom layer, an aqueous solution of the sodium salt of phthalic acid, was rejected. The remaining two layers were washed with aqueous $NaHCO_3$ 6-7 times. The polymer became soluble in the hexanes when dilute HCl was added. The hexanes layer was washed to neutrality, dried over anhydrous $MgSO_4$, molecular sieves (4Å), the solvent was evaporated, and the polymer was vacuum dried. IR (KBr): 1720 cm^{-1} (νC=O), 1590 cm^{-1} (νC=C aromatic). ^{1}H-NMR (CCl_4, TMS): δ = 7.25 - 8.0 ppm (8 aromatic protons, 4 from each phthalic residue), δ = 7.16

(4 aromatic protons, inifer residue, s), δ = 4.0 ppm (PIB, $C\underline{H}_2O$,d), δ = 12 ppm (OH, carboxylic) (Figure 1, c). The ratio between aromatic protons of phthalic (δ = 7.25 - 8.0 ppm) and inifer (δ = 7.16 ppm) residue was found to be 2. This confirmed the funcitonality of the obtained polymer IX to be $\bar{F}_n$ = 2.

Synthesis of X from VIII and III. To a solution of 3 g (0.0088 moles, 0.00176 moles -OH, $\bar{M}_n$ = 3400) VIII and 0.6 g (0.0027 moles) III in 50 ml CH_2Cl_2 were added 0.26 g (0.0021 mole) DMAP and 2 ml TEA. The solution was stirred at room temperature for 10 hours followed by washing with water 10% HCl, aqueous $NaHCO_3$, water and then dried over anhydrous $MgSO_4$. After evaporating the solvent compound X was obtained in quantitative yield. IR (KBr): 3320 cm^{-1} ($\nu \equiv$ CH), 2120 cm^{-1} (νC≡C), 1720 cm^{-1} (νC=O), 1590 cm^{-1} (νC=C) aromatic). ^{1}H-NMR (CCl_4, TMS): δ = 7.0 - 8.0 ppm (12 aromatic protons, inifer residue and phthalic protons), δ = 4.8 ppm (≡C-$C\underline{H}_2O$, d), δ = 4.0 = ppm ($OC\underline{H}_2$-PIB), d) (Figure 1, d). The ethynylic proton resonance was covered by the PIB proton resonances. The ratio of signals at δ = 7.0 - 8.0 ppm, δ = 4.8 ppm and δ = 4.0 ppm (12:4:4) proves the quantative nature of this reaction.

Synthesis of X from IX and propargyl alcohol. The synthesis was carried out in the same manner as compound V from IV and II. The reaction time was 10 hours and the solvent used was THF. The compound obtained had a functionality $\bar{F}_n$ = 1.90, as estimated from ^{1}H-NMR analysis.

Synthesis of XI by chlorination of IX. IX was chlorinated with a large excess of $SOCl_2$ in the presence of a few drops of DMF in CH_2Cl_2 under reflux conditions for 4 hours. The solvent and $SOCl_2$ were evaported, and to remove traces of $SOCl_2$ the product was redissolved in dry CH_2Cl_2 which was again removed. This process was repeated and the reaction was found to be quantitative. The ratio between two different kinds of aromatic protons 7.25 - 8.0 ppm and 7.16 ppm by ^{1}H-NMR spectra was found to be 2.0 . This, along with absence of -COO$\underline{H}$ proton resonance indicates quantitative chlorination of IX.

Synthesis of XII from VIII and propiolic acid. XII was synthesized under the same reaction conditions as VI from IV and propiolic acid (see above). After 10 hours of stirring at room temperature, according to IR and ^{1}H-NMR spectroscopies, the reaction was quantitative. IR (KBr): 3300 cm^{-1} (ν≡CH), 2100 cm^{-1} (νC=C), 1700 cm^{-1} (νC=O). ^{1}H-NMR (CCl_4, TMS): δ = 7.15 ppm (inifer residue, 4 protons), δ = 3.75 ppm (OCH_2-PIB), δ = 3.2 ppm (≡C$\underline{H}$) (Figure 2, c). The chemical shift of the terminal methylene protons of PIB protons changed from δ = 3.5 ppm in α, ω-di(hydroxy)PIB VIII to δ = 3.75 ppm in the esterified product XII. The ratio between the area of signals at δ = 7.15 ppm and δ = 3.75 ppm (4:4) clearly showed quantitative functionalization. In addition, the signal due to the -OH absorption (3645 cm^{-1}) is absent in the IR spectrum of XII.

Synthesis of XIII from VIII. The reaction was carried out under similar conditions as for compound VII except that THF was used as solvent. The reaction time was 12 hours, and the reaction was quantitative based on IR and ^{1}H-NMR analyses. IR (KBr): 3320 cm^{-1} (ν≡CH), 1090 cm^{-1} (νC-O-C). νC≡C absorption could not be detected. ^{1}H-NMR (CCl_4, TMS): δ = 7.15 ppm (inifer residue, 4 protons), δ = 4.0 ppm (≡C-CH_2-O, d), δ = 3.2 ppm (OCH_2 PIB, d), δ = 2.7 ppm (≡C$\underline{H}$, t) (Figure 2, b). The ratio of the areas at δ = 7.15 ppm and δ = 4.0 ppm (4:4) in ^{1}H-NMR spectra and the absence of -OH absorption (3645 cm^{-1}) in IR spectra are evidences for quantitative reaction.

CONCLUSIONS

Several routes have been tested for the synthesis of the propargylic ester of hydroxyl-telechelic PIB (X). The esterification of α, ω-di(hydroxy)polyisobutylene (VIII) with the monopropargylic ester phthaloyl chloride (III) and/or the esterification of α, ω-di(phthaloyl chloride) polyisobutylene (XI) with propargyl alcohol were found to be quantitative by IR and ^{1}H-NMR spectroscopies. The telechelic propargylic ether (XIII) and propiolic ester (XII) of PIB were also obtained. DMAP could not be used as a catalyst in the mild esterification reactions for synthesis of compounds VI and XII because tertiary amines are known to be excellent initiators for the polymerization of propargylic esters (9).

ACKNOWLEDGEMENT

Financial support by the NSF (Grant DMR-81-20964) is gratefully acknowledged.

REFERENCES

1. P.M. Hegenrother, J. Macromol. Sci. Rev. Macromol. Chem., C19(1), 1 (1980).
2. V. Percec, and J.P. Kennedy, Polym. Bull., in press.
3. B. Ivan, J.P. Kennedy, and V.S.C. Chang, J. Polym. Sci. Polym. Chem. Ed., 18, 3177 (1980).
4. V. Percec, S.C. Guhaniyogi, J.P. Kennedy, and B. Ivan, Polym. Bull., 8, 25 (1982).
5. G. Hofle, W. Steglich, and H. Vorbriggen, Angew. Chem. Int. Ed., 17, 569 (1978).
6. B. Neises, and W. Steglich, Angew. Chem. Int. Ed., 17, 522 (1978).
7. H.H. Freedman, and R.A. Dubois, Tetrahedron Letters, 38, 3251 (1975).
8. T.P. Liao, and J.P. Kennedy, Polym. Bull., 5, 11 (1981).
9. C.I. Simionescu, Sv. Dumitrescu, M. Grigoras, and V. Percec, J. Polym. Sci. Polym. Lett. Ed., 17, 287 (1979).

Accepted February 15, 1983

K