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

25. Synthesis and Characterization of α, ω-Di(Allyl) Polyisobutylene

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SUMMARY

α,ω-Di(hydroxy)polyisobutylene was converted to the corresponding α,ω-di(allylether)- and α,ω-di(allylphthalyl)polyisobutylene by reacting the diol with allyl bromide in the presence of alkali and tetrabutylammonium bisulfate phase transfer catalyst, and monoallyl phthalic acid chloride in the presence of 4-N,N-dimethylaminopyridine, respectively. The reaction conditions were defined by suitable model experiments. IR and ^{1}H-NMR analysis of the reaction products indicates quantitative conversions.

INTRODUCTION

Earlier reports from this laboratory have shown that alcohol-telechelic polyisobutylenes (PIB's) can be quantitatively converted to a variety of telechelic products, i.e., carboxylic acid (1), tosylate (2), which in turn could be converted to new block copolymers (2) and/or networks (3). This communication demonstrates further synthesis possibilities offered by alcohol-telechelic PIB's and describes the synthesis and spectroscopic characterization of α,ω-di(allylether)- and α,ω-di(allylphthalyl)polyisobutylenes.

SYNTHESIS ROUTE

Scheme 1 serves to visualize the chemical transformations employed for the synthesis of a key intermediate IV and of the target allyl-telechelic polymers VI and VIII.

EXPERIMENTAL

A. Materials. Two α,ω-di(hydroxy)polyisobutylene samples ($\bar{M}_n$ = 2000, $\bar{M}_w/\bar{M}_n$ = 1.70, $\bar{F}_n$ = 2.0 and $\bar{M}_n$= 4780, $\bar{M}_w/\bar{M}_n$ = 1.72, $\bar{F}_n$ = 2.0) were synthesized and characterized (4-6). Allyl alcohol, allyl bromide, phthalic anhydride, thionyl chloride, tetrabutylammonium bisulfate (TBAB), 4-N,N-dimethylaminopyridine (DMAP), and triethylamine (TEA) (all from Aldrich) were used as received. Methylene chloride was dried over $LiAlH_4$, while the other solvents (hexanes, dimethylformamide (DMF)) were used as received.

B. Techniques. ^{1}H-NMR analysis was carried out using a Varian T-60 NMR spectrometer at room temperature, CCl_4 solutions and TMS as internal standard. IR spectra were obtained by using a Perkin-Elmer 521 infrared spectrophotometer and polymer films over KBr pellets. Molecular weights were determined by GPC using a Water Associates 6000 A (high pressure) pump, UV and RI detectors and a series of 10^6, 10^5, 10^4, 10^3, 500 Å micro-Styragel columns. Elution counts were calibrated by polyisobutylene standards. The terminal functionality of α,ω-di(hydroxy)polyisobutylene was determined by quantitative esterification of HO- end groups with p-cyano-

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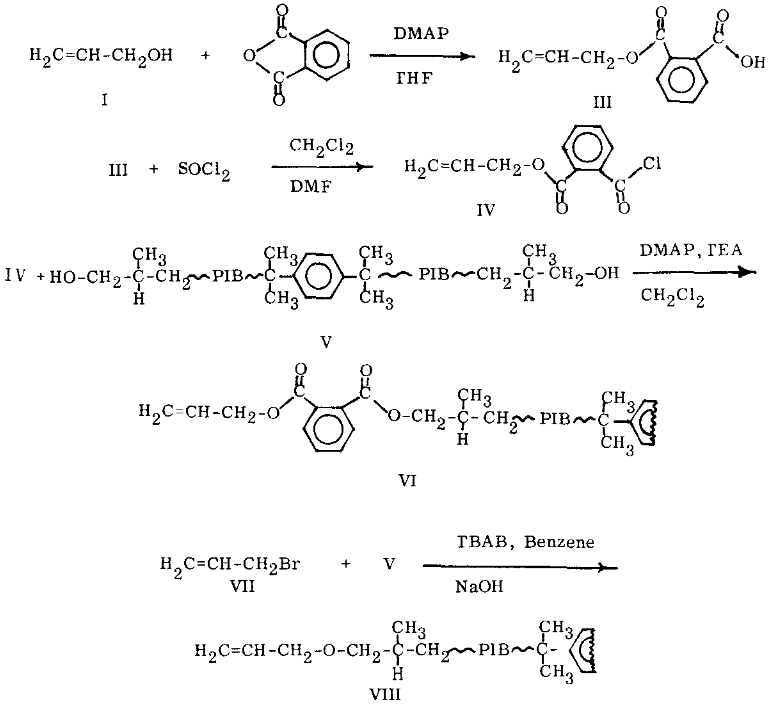
Scheme-1

Synthesis Routes for Allyl-Telechelic Polyisobutylenes



benzoyl chloride in the presence of DMAP catalyst and determining the ratio A/B where A = protons in the terminal benzoyl group (δ = 7.65 ppm, 4 protons; δ = 8.05 ppm, 4 protons) B = protons in the central disubstituted aromatic ring of the inifer residue (δ = 7.18 ppm, 4 protons) (7).

C. Synthetic Procedures

Monoallyl Ester of Phthalic Acid (III). To a stirred solution of phthalic anhydride (7.406 g, 0.05 mole) and allyl alcohol (4.09 ml, 0.06 mole) in dry THF (75 ml) were added DMAP (6.11 g, 0.05 mole) and TEA (5 ml). An exothermic reaction occurred and a white precipitate formed. The mixture was stirred for 10 hours at room temperature after which the solvent and excess allyl alcohol were evaporated. The remaining product was taken up in hexanes, washed with water, dilute HCl, water, dried over anhydrous $MgSO_4$ and finally the solvent was evaporated. The colorless viscous liquid, III, (9.2 g, 89.2%) was subjected to IR and ^{1}H-NMR spectroscopy. IR(KBr): 3100 cm^{-1} (ν_{OH}), 1720 cm^{-1} ($\nu_{C=O}$), 1640 cm^{-1} ($\nu_{C=C}$ allyl), 1590 cm^{-1} ($\nu_{C=C}$ aromatic). ^{1}H-NMR ($CDCl_3$, TMS): δ = 4.83 ppm ($-C\underline{H}_2-$, d), δ = 5.1 - 5.6 ppm ($C\underline{H}_2=$, m), δ = 5.67-6.43 ppm ($-C\underline{H}=$, m), δ = 7.33-8.03 ppm (4 aromatic protons, m) (Figure 1).

Monoallyl Ester of Phthalic Acid Chloride (IV). To a mixture of III (8.0 g, 0.039 mole) in 50 ml dry CH_2Cl_2 were added $SOCl_2$ (14.22 ml, 0.195 mole) and a few drops of DMF. The reaction mixture was stirred at room temperature for 2 hours. The charge became homogeneous and it was refluxed for 1 hour. Then the solvent and excess $SOCl_2$ were removed and the viscous

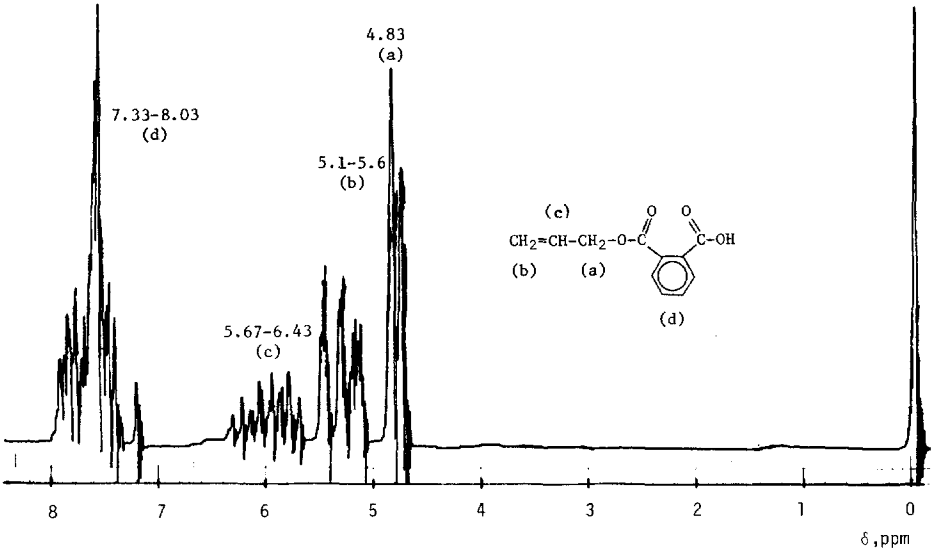


Figure 1. ^{1}H-NMR spectrum of monoallyl ester of phthalic acid

liquid product was stored for a few days at room temperature. During storage the product started to crystallize. The ^{1}H-NMR spectrum ($CDCl_3$, TMS) exhibited the same resonances as III.

Synthesis of α,ω-di(allylphthalyl)polyisobutylene (VI). To a stirred solution of α,ω-di(hydroxy)isobutylene (3.5 g, 0.00175 mole, $\bar{M}_n$= 2000, 0.0035 mole OH) in 50 ml CH_2Cl_2 were added successively 1.6 g (0.007 mole) IV, 0.43 g (0.0035 mole) DMAP and 2 ml (large excess) of TEA. The reaction mixture was stirred at room temperature for 12 hours. The solution was washed with water, dilute HCl, concentrated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$ and the solvent was evaporated. IR(KBr): 1700 cm^{-1} ($\nu_{C=O}$), 1640 cm^{-1} ($\nu_{C=C}$ allyl), 1580 cm^{-1} ($\nu_{C=C}$ aromatic). ^{1}H-NMR (CCl_4, TMS): δ = 4.0 ppm $(PIB-C\underline{H}_2O\overset{O}{\overset{\|}{C}}-)$, δ = 4.83 ppm ($-OC\underline{H}_2-$, d), δ = 5.1-5.6 ppm ($C\underline{H}_2=$, m), δ = 5.67 - 6.43 ppm ($-C\underline{H}=$, m), δ = 7.15 ppm (inifer residue, 4 aromatic protons), δ = 7.33-8.0 (8 aromatic protons, 4 per phthalate chain end) (Figure 2). The signal associated with the protons in $-C\underline{H}_2-OH$ of the PIB-diol (δ = 3.2 ppm) disappeared, however, a new resonance indicating the presence of the $PIB-C\underline{H}_2-OCO-$ group arose (δ = 4.0 ppm). Integration of the areas associated with this resonance relative to that characteristic of the protons in the $-OCH_2-CH=CH_2$ group (δ = 4.83 ppm) can be used to estimate quantitatively the number of end groups $\bar{F}_n$. According to this method $\bar{F}_n$= 2.0 for this product.

Synthesis of α,ω-di(allylether)polyisobutylene (VIII). To a mixture of 3.42 g (0.000715 mole, $\bar{M}_n$= 4780, 0.00143 mole OH) V in 50 ml benzene and 1.25 ml (0.0143 mole) freshly distilled allyl bromide were added 1.2 ml 50% aqueous NaOH (0.0143 mole) and 0.024 g (0.072 mmole) TBAB. After 6 hours of stirring at room temperature another 1.25 ml allyl bromide, 1.2 ml 50% aqueous NaOH and 0.024 g TBAB were added and the stirring was continued for 6 more hours. The reaction mixture was washed with water, dried over anhydrous $MgSO_4$, and the solvent was removed. The product was purified by dissolving it in hexanes and precipitating into acetone, redissolving in hexanes, removing the acetone by washing with water, drying over anhydrous $MgSO_4$, and removing the solvent. IR(KBr): 1090 cm^{-1} (ν_{C-O-C}). ^{1}H-NMR (CCl_4, TMS): δ = 3.10 ppm ($PIB-C\underline{H}_2O-$, d), δ = 3.87 ppm ($-C\underline{H}_2-O-$, d),

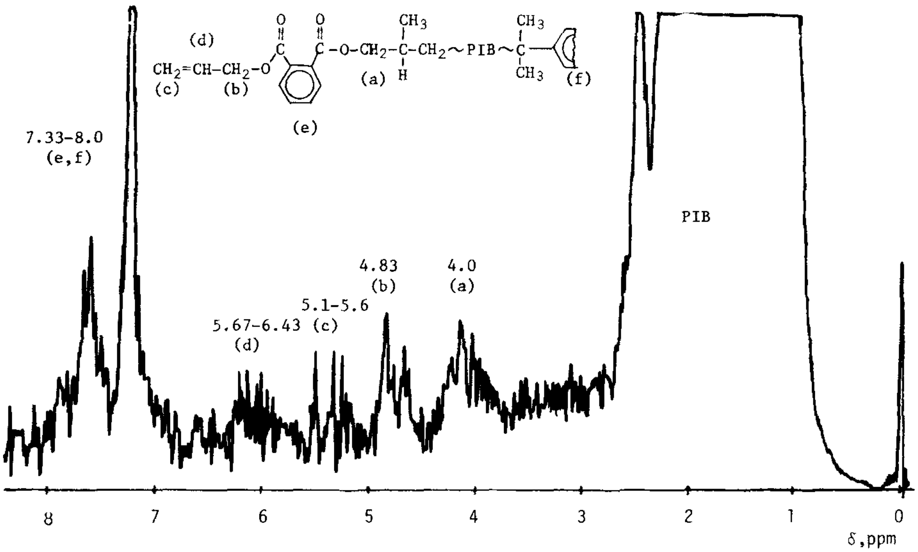


Figure 2. ^{1}H-NMR spectrum of α,ω-di(allylphthalyl)polyisobutylene

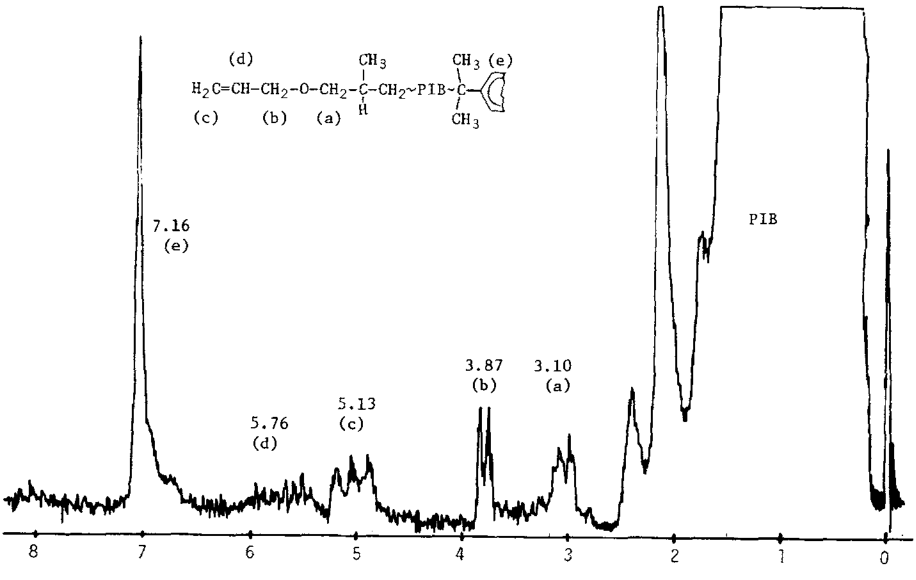


Figure 3. ^{1}H-NMR spectrum of α,ω-di(allylether)polyisobutylene

δ = 5.13 ppm (=$C\underline{H}_2$, t), δ = 5.76 ppm (=$C\underline{H}$-, m), δ = 7.16 ppm (4 aromatic protons of the inifer residue, s) (Figure 3). Terminal functionality, $\bar{F}_n$ = 2.0 was determined by integrating the areas associated with the resonances characteristic of the protons in the central aromatic inifer residue (δ = 7.16 ppm) relative to the protons in the terminal methylene group (δ = 5.13 ppm), and those associated with the protons in the PIB-$C\underline{H}_2$-O- (δ = 3.1 ppm) group relative to the protons in the -O-$C\underline{H}_2$-CH=CH_2 (δ = 3.87 ppm) group.

CONCLUSIONS

The synthesis of two new allyl-telechelic polyisobutylenes, VI and VIII in Scheme 1, has been accomplished. According to ^{1}H-NMR spectroscopic analysis the conversions proceed to completion, $\bar{F}_n$ = 2, in both instances. The use of DMAP catalyst greatly facilitated conversion to VI, and the use of a phase transfer catalyst, i.e., TBAB, was essential for the synthesis of VIII.

These allyl-telechelic PIB prepolymers may represent interesting new starting materials for the preparation of novel thermosetting resins (8).

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REFERENCES

1. LIAO, T.P. and KENNEDY, J.P., Polym. Bull. 5, 11 (1981)
2. PERCEC, V., GUHANIYOGI, S.C., KENNEDY, J.P., and IVAN, B., Polym. Bull. 8, 25 (1982)
3. WONDRACZEK, R.H. and KENNEDY, J.P., Polym. Bull. 4, 445 (1981)
4. KENNEDY, J.P., CHANG, V.S.C., SMITH, R.A. and IVAN, B., Polym. Bull. 1, 575 (1979)
5. KENNEDY, J.P. and SMITH, R.A., J. Polym. Sci. Polym. Chem. Ed. 18, 1523 (1980)
6. IVAN, B., KENNEDY, J.P. and CHANG, V.S.C., J. Polym. Sci. Polym. Chem. Ed. 18, 3177 (1980)
7. PERCEC, V. and KENNEDY, J.P., Polym. Bull., to be published
8. IWATA, K., OGASAWARA, M. and HARA, S., Makromol. Chem. 179, 1361(1978)

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