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

36. Synthesis and Characterization of Various Nitrile-Telechelic Polyisobutylenes

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SUMMARY

α, ω-Di(nitrile)polyisobutylenes (nitrile-telechelic polyisobutylenes) have been synthesized by reacting α, ω-di(hydroxy)polyisobutylenes (hydroxyl-telechelic polyisobutylenes) with acrylonitrile, p-cyanobenzoyl chloride, p-cyanobenzoic acid and p-cyanobenzyl chloride by the use of a variety of catalysts, e.g. N-benzyltrimethylammonium hydroxide, 4-N,N'-dimethylaminopyridine, dicyclohexylcarbodiimide, tetrabutylammonium hydrogen sulfate and tricaprylymethylammonium chloride. IR and ^{1}H-NMR analyses of models and polymer products suggest quantitative functionalization, except with p-cyanobenzyl chloride where only ~ 80% functionalization was achieved. Methanesulfonation of the polymer-diol with methanesulfonyl chloride followed by reaction with NaCN in the presence of tricaprylymethylammonium chloride phase transfer catalyst gave quantitatively α, ω-di(nitrile)polyisobutylene.

INTRODUCTION

The synthesis and characterization of linear and three-arm star telechelic polyisobutylenes (PIB's) containing propenyl, -OH, epoxy, aldehyde, -Si-H, Si-Cl, tosyl ester, sulfonyl, etc. end groups have been recently reported from this laboratory (1-7). Intensive studies on quantitative modification of hydroxyl-telechelic PIB's have been continued. In the course of these investigations we became interested in the synthesis of nitrile-telechelic PIB's and have decided to prepare a series of representative aliphatic and aromatic nitrile-telechelic derivatives. A literature search indicated that our objective could be reached by substituting the terminal -OH groups in α, ω-dihydroxy-PIB by the -CN function by various routes. After considerable scouting and model experimentation with 2,4,4-trimethyl-1-pentanol (TMP) several methods have been developed that led to the quantitative terminal derivatization of α, ω-dihydroxy-PIB. Schemes 1 and 2 outline the model reactions and polymer derivatizations investigated, respectively.

EXPERIMENTAL

Materials. 2,4,4-Trimethyl-1-pentanol (TMP, Aldrich) was dried over molecular sieves (4 Å). p-Cyanobenzyl chloride (Pfaltz and Bauer, Inc.), 4-N,N-dimethylaminopyridine (DMAP, Aldrich), p-cyanobenzoic acid (Aldrich), p-cyanobenzoyl chloride (Aldrich), methanesulfonyl chloride (Aldrich), triethylamine (TEA, Aldrich, dried over KOH), tetrabutylammonium hydrogen sulfate (TBAB, Aldrich), tricaprylylmethylammonium chloride (Aliquat 336,

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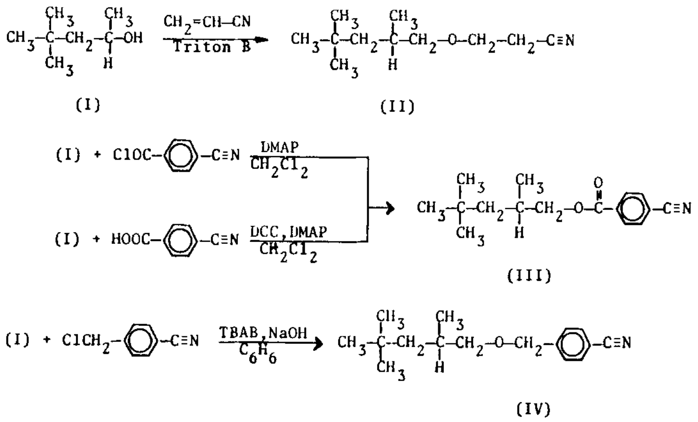
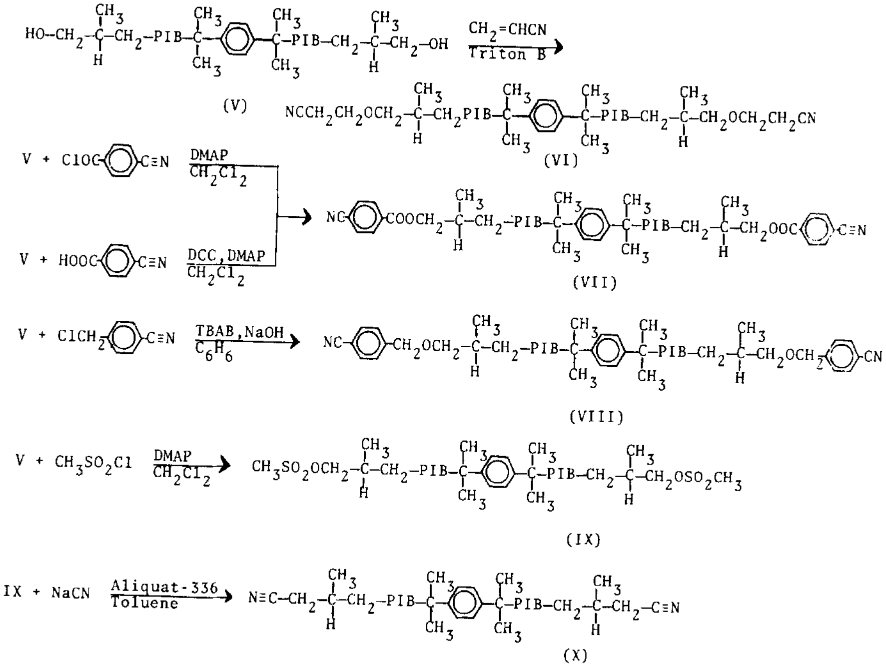


Scheme 1: Model Reactions Examined for the Synthesis of Nitrile-Telechelic PIB's



Scheme 2: Synthetic Routes Used for the Synthesis of Nitrile-Telechelic PIB's

Aldrich) and tetrahydrofuran (THF, Fisher) were used as received. N-Benzyltrimethylammonium hydroxyde (Triton-B, Aldrich, 40% methanol solution) was used as 40% aqueous solution after replacing the methanol by water. Two α,ω-dihydroxy-PIB samples ($\overline{M}_n$ = 3400, $\overline{M}_w/\overline{M}_n$ = 1.70, $\overline{F}_n$ = 2.0, and $\overline{M}_n$ = 4800, $\overline{M}_w/\overline{M}_n$ = 1.72, $\overline{F}_n$ = 2.0) were prepared by the method reported (1,2).

Techniques. ^{1}H-NMR spectra were recorded on a Varian T-60 NMR spectrometer at room temperature using CCl_4 or $CDCl_3$ solutions and TMS internal standard. A Perkin-Elmer 521 infrared spectrophotometer was used to record IR spectra of films on KBr pellets. Molecular weights were determined by using a Water high pressure GPC instrument, equipped by RI and UV detectors and a series of 500, 10^3, 10^4, 10^5, and 10^6 Å Microstyragel columns. The calibration curve was prepared with a series of a well fractionated PIB samples.

SYNTHESIS AND RESULTS

The procedures used for synthesis of model nitriles and α,ω-di(nitrile)-PIB's are outlined in Schemes 1 and 2, respectively. The roman numerals in this section refer to the compounds in Schemes 1 or 2.

Synthesis of II by cyanoethylation of 2,4,4-trimethyl-1-pentanol (I)

To a stirred mixture of 13.0 g (0.1 mole) I, 50 ml THF and 8 ml (0.12 mole) acrylonitrile cooled by ice water were added 1.2 ml Triton-B (40% aqueous solution) (8). An exothermic reaction took place. After 1 hour of stirring at room temperature the reaction mixture was neutralized with acetic acid. THF and excess acrylonitrile were evaporated on a rotary evaporator at room temperature and the reaction mixture was dissolved in hexanes, washed several times with water and dried over anhydrous $MgSO_4$. After removing the hexanes, the liquid product was subjected to IR and ^{1}H-NMR analyses. IR: 2250 cm^{-1} (ν -C≡N); ^{1}H-NMR (CCl_4, TMS); δ = 0.9 - 1.3 ppm (15 protons, m), δ = 2.45 ppm ($-C\underline{H}_2CN$, t), δ = 3.15 ppm ($-CHCH_3C\underline{H}_2O-$, δ = 3.57 ppm ($-OC\underline{H}_2CH_2CN$, t) (Figure 1a). The resonance for -OH in TMP was absent. The ratio of the signals at δ = 2.45 ppm to δ = 3.15 ppm to δ = 3.57 ppm is equal to 1:1:1. According to this ^{1}H-NMR analysis, the reaction was quantitative. Similar results were obtained when the reaction was carried out in bulk.

Synethesis of VI by cyanoethylation of α,ω-di(hydroxy)-PIB (V)

To a mixture of 5.6 g V ($\overline{M}_n$ = 3400, 1.65 mmole, 3.3 mmole -OH), 50 ml THF and 2.16 ml (33 mmole) acrylonitrile was added 0.16 ml Triton - B while stirring at room temperature. The reaction mixture was stirred for 8 hours at 50°C, cooled and neutralized with acetic acid. THF and excess acrylonitrile were removed and the remaining product was extracted with hexanes. The hexanes-insoluble yellow-brown material was found to be polyacrylonitrile by IR spectroscopy (IR, 2250 cm^{-1}ν -C≡N). The latter was formed by thermal polymerization of acrylonitrile. The hexanes solution was washed several times with water, dried over anhydrous $MgSO_4$ and molecular sieves (4 Å), the solvent was evaporated, and the polymer was vacuum dried.
IR: 2250 cm^{-1} (ν -C≡N). ^{1}H-NMR (CCl_4, TMS): δ = 0.7-2.25 ppm ($C\underline{H}_3$, $-C\underline{H}_2$ of PIB), δ = 2.45 ppm ($-C\underline{H}_2CN$, t) δ = 3.18 ppm (PIB $-C\underline{H}_2O-$, d) δ = 3.57 ppm ($-OC\underline{H}_2CH_2CN$, t), δ = 7.13 ppm (4 aromatic protons from the inifer residue, s) (Figure 1b). The ratio between the areas characteristic of the aromatic protons (δ = 7.13 ppm, 4 protons) and cyanoethylenic protons (δ = 2.45 ppm, 4 protons) was 1.0 and that between those of PIB methylenic protons (δ = 3.18, 4 protons i.e. $-CH(CH_3)-C\underline{H}_2O-$, and cyanoethyl pro-

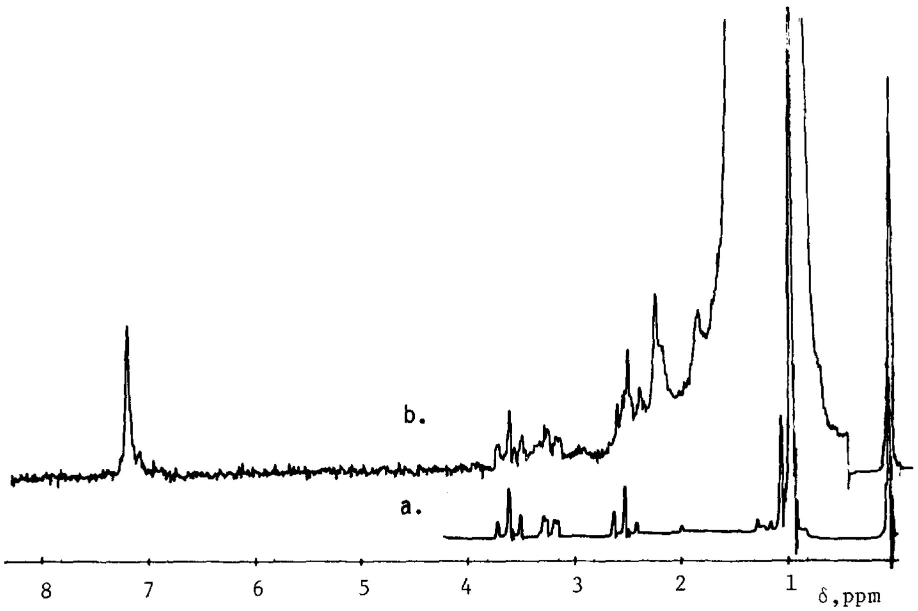


Figure 1. 60-MHz ^{1}H-NMR spectra of (a) model nitrile II and (b) α,ω -di(nitrile)polyisobutylene VI

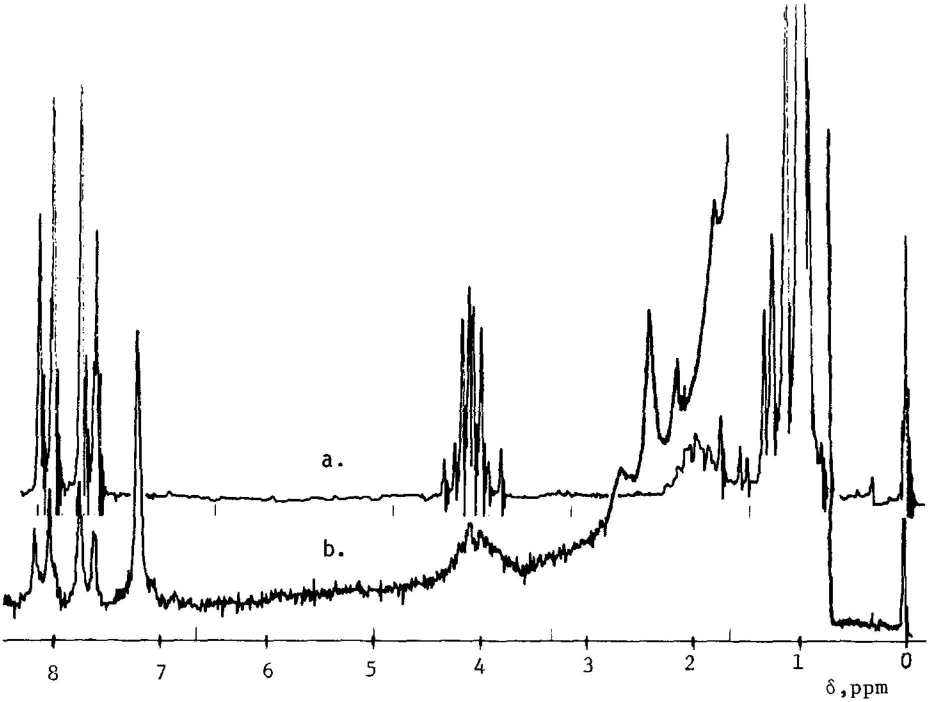
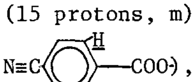
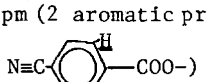
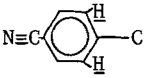
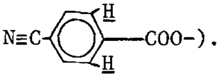


Figure 2. 60-MHz ^{1}H-NMR spectra of (a) model nitrile III and (b) α,ω -di(nitrile)polyisobutylene VII

tons (δ = 2.45 ppm, δ = 3.57 ppm, 8 protons) was 0.5, indicating quantitative cyanoethylation.

Synthesis of III by esterification of I with p-cyanobenzoyl chloride. To a cooled (ice-water) solution of 3.26 g (25 mmole) I and 5.38 g (32.5 mole) p-cyanobenzoyl chloride in 25 ml dry CH_2Cl_2 was added dropwise a solution of 4 g (32.5 mole) of DMAP (9) in 15 ml CH_2Cl_2. An exothermic reaction took place. The reaction was continued at room temperature for 10 hours. The solution was then washed successively with water, aqueous HCl, aqueous $NaHCO_3$ and water, and finally dried over anhydrous $MgSO_4$. After the solvent was evaporated, the product was analyzed by IR and ^{1}H-NMR. IR: 2225 cm^{-1} (ν-C=C), 1600 cm^{-1}(ν C=C of phenyl ring). ^{1}H-NMR (CCl_4, TMS): δ = 0.8-2.2ppm (15 protons, m); δ = 4.1 ppm ($-C\underline{H}_2OCO-$ d); δ = 7.65 ppm (2 aromatic protons, d,  ,δ= 8.04 ppm (2 aromatic protons, d,  (Figure 2a). The ratio of the signals at δ = 4.1 ppm, δ = 7.65 ppm and δ = 8.04 ppm was 1:1:1 indicating quantitative esterification.

Synthesis of VII by esterification of V with p-cyanobenzoyl chloride. The reaction was carried out under identical experimental conditions as for the model compound. After 12 hours of stirring at room temperature, the conversion was found to be quantitative. IR: 2230 cm^{-1} (ν -C≡N), 1720 cm^{-1} (ν -C=O), 1602 cm^{-1} (ν C=C of phenyl ring). ^{1}H-NMR (CCl_4, NMR): δ = 1-3 ppm ($-C\underline{H}_3$, $-C\underline{H}_2-$ of PIB), δ =4.05 ppm ($-C\underline{H}_2OCO$), δ = 7.18 ppm (4 aromatic protons, inifer rest), δ = 7.65 ppm (4 aromatic protons, , δ = 8.05 ppm (4 aromatic protons, .

The signal for the $-C\underline{H}_2O-$ of the parent PIB diol which usually appears at δ = 3.2 ppm has shifted to δ = 4.05 ppm (Figure 2b). The ratio of the integrals of the signals at δ = 4.05 ppm, δ = 7.18 ppm, δ = 7.65 ppm and δ = 8.05 ppm (1:1:1:1) indicates that this reaction is quantitative. The difference between the chemical shifts of aromatic proton resonances associated with the cyanobenzoyl group and inifer rest permitted the calculation of the ratio between internal and terminal aromatic protons. Evidently this reaction is quantitative and can be used for the determination of PIB diol and triol functionalities.

Synthesis of III by esterification of I with p-cyanobenzoic acid. To an ice-water cooled solution of 2.6 g (20 mmole) I, 6.03 g (30 mmole) p-cyanobenxoic acid, 0.24 g (2.0 mmole) DMAP in 20 ml CH_2Cl_2 and 25 ml THF, was added a solution of 6.19 g (30 mmole) DCC in 20 ml CH_2Cl_2. An exothermic reaction took place and N,N'-dicyclohexylurea precipitated as a white powder (10). After 10 hours of stirring at room temperature the precipitated urea was filtered off, the solvent was evaporated in vacuum, the product was redissolved in CH_2Cl_2 and filtered again. Then the solution was washed several times with dilute HCl, saturated $NaHCO_3$, water and dried over anhydrous $MgSO_4$. After removing the solvent, the product was analyzed by IR and ^{1}H-NMR spectroscopies and found to have the same structure as that obtained by esterification with p-cyanobenzoyl chloride.

Synthesis of VII by esterification of V with p-cyanobenzoic acid. The esterification of V by p-cyanobenzoic acid was carried out under conditions similar to those used for the model experiment (see previous section). Esterification was quantitative, and the IR and ^{1}H-NMR spectra were identical to those obtained for VII synthesized by esterification of V with p-cyanobenzoyl chloride.

Synthesis of IV by etherification of I with p-cyanobenzyl chloride
A mixture of 2.6 g (20.0 mmole) I, 3.03 g (20.0 mmole) p-cyanobenzyl chloride, 50 ml benzene, 10 ml NaOH (50% solution) and 0.34 g TBAB (5% of I) was stirred at 25°C for 10 hours (12). The solution was washed with water, dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated. IR: 2222 cm^{-1} (ν -C≡N), 1600 cm^{-1} (ν C=C phenyl ring), 1080 cm^{-1}(ν C-O-C), 810 cm^{-1} (ν -CH of p-disubstituted phenyl ring). ^{1}H-NMR (CCl_4, TMS): δ = 0.9 - 1.9 ppm (15 aliphatic protons), δ = 3.25 ppm (PIB—$C\underline{H}_2O$), δ = 4.5 ppm (Ph-$C\underline{H}_2O$-), δ = 7.55 ppm (4 aromatic protons). According to the ^{1}H-NMR spectrum (ratio between signals at δ = 3.25 ppm and δ = 4.5 ppm or between δ = 4.5 ppm and δ = 7.55 ppm) the yield was only 85%.

Synthesis of VIII by etherification of V with p-cyanobenzyl chloride. Etherification of V under the same reaction conditions, except that the reaction time was increased to 20 hours and the ratio between p-cyanobenzyl chloride and -OH groups was 2.5/1, led to only ~ 80% conversion. No other attempts were made to increase the yield.

Synthesis of IX by etherification of I with methanesulfonyl chloride. To a stirred ice-water cooled solution of 5.2 g PIB diol ($\bar{M}_n$ = 7400, 1.1 mmole, 2.2 mmole -OH), 0.27 g (2.2 mmole) DMAP, 0.92 ml (6.6 mmole) TEA and 100 ml CH_2Cl_2 was added during 10 minutes 0.7 ml (8.8 mmole) methanesulfonyl chloride. The reaction mixture was stirred at room temperature for 15 hours. Then the solution was washed with water, dilute HCl , aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and the solvent was evaporated. The product obtained was dissolved in hexane and purified once more the same way. IR: 1170 cm^{-1} (sulphonate ester group). ^{1}H-NMR (CCl_4, TMS): δ = 7.17 ppm (4 aromatic protons of the inifer residue), δ = 3.86 ppm (PIB-$C\underline{H}_2O$), δ = 2.43 ppm ($-SO_2-C\underline{H}_3$) (Figure 3a). The resonance at δ = 3.25 ppm characteristic of $-C\underline{H}_2OH$ protons in the starting material is absent in the spectrum of the methanesulfonated product. However, the latter exhibits this resonance of the methylene protons at δ = 3.86 ppm which clearly shows that the reaction is quantitative.

Synthesis of X by displacement of $-SO_3CH_3$ end groups of IX with -CN groups. A mixture of 2g (0.43 mmole, 0.86 mmole methanesulfonic ester) IX, 50 ml toluene, NaCN solution in 10 ml water, and 0.17 g (0.43 mmole) Aliquat 336 (12) was stirred at 105°C for 24 hours. Then the solution was washed with water, the solvent was evaporated, the product was dissolved in hexanes, and precipitated twice from acetone. IR: 2240 cm^{-1} (ν -C≡N). ^{1}H-NMR (CCl_4, TMS): δ = 7.15 ppm (4 aromatic protons of the inifer residue), δ = 3.0 ppm ($-C\underline{H}_2CN$) (Figure 3b). Because the methylene and methyl proton signals for $-C\underline{H}_2OSO_2C\underline{H}_3$ of the starting product (Figure 3a) are absent in the ^{1}H-NMR spectrum of compound X (Figure 3b), the reaction may be viewed to be essentially quantitative.

CONCLUSIONS

A number of routes have been developed for the preparation of cyanotelechelic PIB's. In all cases, except for the conversion with p-cyanobenzyl chloride, quantitative conversions have been achieved as judged by ^{1}H-NMR spectroscopy. Intensive investigations by Pinazzi et al. (13) showed that cyanomethylation coupled with hydroboration of olefins leads to a

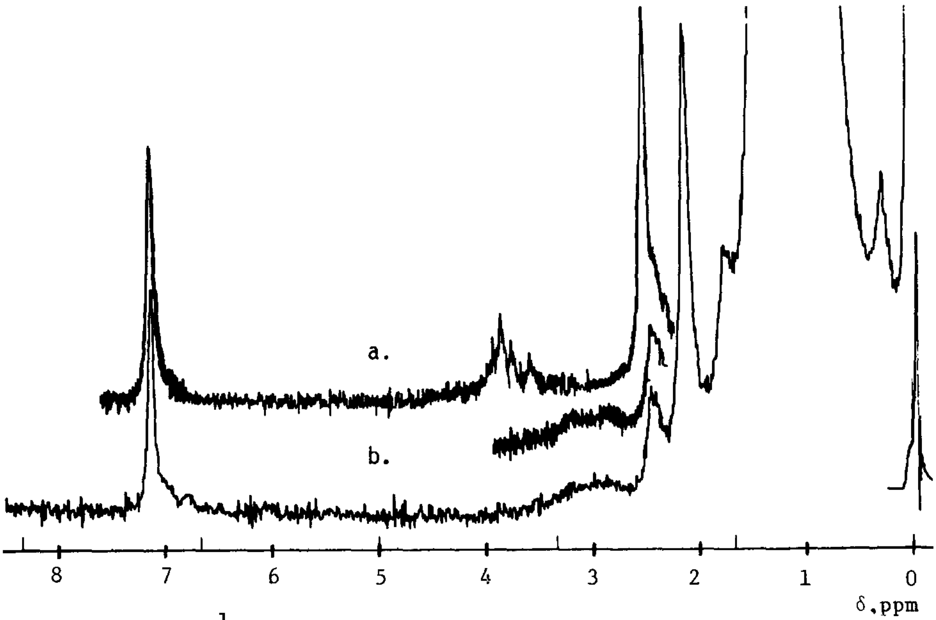


Figure 3. 60 MHz ^{1}H-NMR spectra of (a) methanesulfonic ester of polyisobutylene IX and (b) α,ω-di(nitrile)polyisobutylene X

maximum yield of 81% nitrile groups. However, cyanoethylation of OH-telechelic PIB's in the presence of Triton B (phase transfer catalyst and strong base) was quantitative. 4-N,N-Dimethylaminopyridine, an acylation catalyst whose specific catalytic activity is about 10^4 times greater than that of pyridine (9), was used for the quantitative esterification of OH-telechelic PIB's with p-cyanobenzoyl chloride and methanesulfonyl chloride. p-Cyanobenzoyl esters can be used for the determination of number average diol and triol functionalities in OH-telechelic PIB's by ^{1}H-NMR spectroscopy. Phase transfer catalysts were of paramount importance for nucleophilic substitutions on telechelic PIB's due to their insolubility in polar solvents (synthesis of compounds IV and X). Cyano-telechelic PIB's on account of the versatile -CN group are useful functional prepolymers for the preparation of other derivatives.

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REFERENCES

1. J.P. Kennedy, V.S.C. Chang, A.R. Smith and B. Ivan, Polym. Bull., 1, 575 (1979)
2. B. Ivan, J.P. Kennedy, and V.S.C. Chang, J. Polym. Sci., Polym. Chem. Ed., 18, 3177 (1980)
3. J.P. Kennedy, L.R. Ross, J.E. Lackey, and O. Nuyken, Polym. Bull., 4, 67 (1981)

4. J.P. Kennedy, V.S.C. Chang, and W.P. Francik, J. Polym. Sci. Polym. Chem. Ed., 20, 2809 (1982)
5. J.P. Kennedy, V.S.C. Chang, and A. Guyot, Adv. Polym. Sci., 43, 1 (1982)
6. V.Percec, S.C. Guhaniyogi, J.P. Kennedy, and B. Ivan, Polym. Bull., 8, 25 (1982)
7. J.P. Kennedy and R.F. Storey, 28th IUPAC International Symposium on Macromolecules, July 12-16, 1982, Amherst, Preprints, p. 905
8. H.A. Bruson, Organic Reactions, Vol. V, Ed. Adams, R., p. 1, Wiley, 1949
9. G. Hofle, W. Steglich, and H. Vorbruggen, Angew. Chem. Int. Ed., 17, 569 (1978)
10. B. Neises, and W. Steglich, Angew. Chem. Int. Ed., 17, 522 (1978)
11. H.H. Freedman, and R.A. Dubois, Tetrahedron letters., 38, 3251 (1975)
12. C.M. Starks, J. Am. Chem. Soc., 93, 195 (1971)
13. G. Pinnazi, J. Vassort, and D. Reyx, Europ. Polym. J., 13, 395 (1977)

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