

Useful NMR solvent mixture for polyesters: Trifluoroacetic acid-d/chloroform-d

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Summary.

NMR spectra of high molecular weight polyesters such as polyglycolide (PG) and poly(ethylene terephthalate) (PET) have not been available because of low solubility in suitable NMR solvents. Although PG is not soluble enough at ambient temperatures for NMR spectra in either chloroform-d or trifluoroacetic acid-d alone, it dissolves readily to over 0.9% in a mixture of the two. At this concentration, ^1H and ^{13}C spectra can be obtained on samples where end group signals are visible from which molecular weights can readily be determined. The solutions are stable up to at least four days when moisture is excluded. NMR spectra of PET can likewise be obtained at ambient temperatures in the solvent mixture which dissolves up to at least 0.6% of PET.

Introduction.

Many high-molecular weight polyesters such as polyglycolide (PG) and poly(ethylene terephthalate) (PET) are insoluble at ambient temperatures in solvents commonly used for NMR. Recently (1) NMR spectra of low molecular weight PET were determined at a probe temperature at 140°C in DMSO- d_6 with hexamethyl disiloxane as internal reference. Since it has been reported (2,3) that DMSO decomposes into methyl mercaptan, bis(methylthio)methane, and other products at elevated temperatures caution should be exhibited in using this solvent at high temperatures. High molecular weight polyesters are slightly soluble at ambient temperatures in hexafluoroisopropanol (HFIP) which has relatively recently become commercially available. Thus for example, HFIP has recently been used for molecular weight determination of highly insoluble poly-4-hydroxymethylbenzoates (4) by ^1H NMR end group analysis. One problem with this solvent is that the absorptions at 4.4 and 4.9 δ in ^1H NMR interfere with sample signals in these regions useful for end group analysis for molecular weight determinations.

Experimental Chemicals.

Chemicals were commercial products used in purity grades listed: trifluoroacetic anhydride (99+%), deuterium oxide (99.9%), deuteriochloroform (99.8% D) with 0.03% tetramethylsilane internal reference, and HFIP (99+%). Polyglycolide was prepared according to a previous procedure (5) from chloroacetic acid. Trifluoroacetic acid-d was prepared by adding 2.00 g (0.100 mol) of deuterium oxide dropwise with stirring to ice-cooled trifluoroacetic anhydride (21.03 g, 0.100 mol) under a blanket of argon.

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Procedures.

Polyglycolide spectra.

NMR spectra were run on a Bruker AMX-360 FT spectrometer. ^1H spectra were at 360 and ^{13}C spectra at 90 MHz. All equipment and solvents must be thoroughly dry to avoid hydrolysis. PG (0.0112 g, 1.93×10^{-4} mol) was placed in a dry NMR tube which was capped with a teflon stopper and weighed. Chloroform-d (0.875 g; 75% of total solvent weight) and trifluoroacetic acid-d (TFAD) (0.295 g, 2.57×10^{-3} mol; 25% of solvent weight) were added; the tube was sealed with teflon tape. The mixture was shaken to effect solution. The solubility of PG in the solvent mixture was 0.957% by weight. The ^1H spectrum (Fig. 1) shows the polymeric CH_2 group at 4.95 δ and CH_2/CH_3 signals of the triethylammonium end group at 3.6 and 1.4 δ respectively ($J(t,q)=7.5$ Hz). The ^{13}C NMR spectrum (Fig. 2) shows the polymeric CH_2 and $\text{C}=\text{O}$ signals at 61.4 and 168.4 δ respectively. The terminal COO^- carbon is at 173 δ . The corresponding values for PG dissolved in HFIP (Fig. 3) were the following. ^1H NMR: The ethyl peaks of the triethylammonium end group appeared at the same positions of in TFAD/ CDCl_3 . The poly CH_2 signal at 4.89 δ (lit.⁶ 4.91) was interfered with by absorption from the OH of HFIP solvent. When a few drops of concentrated HCl was added the OH peak was shifted to 6.1 δ but the resolution of the ethyl groups of the triethylammonium end groups was poor and appeared as broad peaks instead of a triplet/quartet probably because of N-H exchange. ^{13}C NMR (Fig. 4): The polymeric CH_2 and $\text{C}=\text{O}$ signals appeared at 61.38 and 168.67 δ respectively (lit.⁶ 63.0 and 170.6 respectively) and the CH_2 , CH_3 , and COO^- of the end groups at 40.16, 6.74, and 173.37 δ respectively.

Poly(ethylene terephthalate) (PET) spectra.

The same procedure as for polyglycolide was used for PET solutions. PET (0.0062 g) was dissolved in a mixture of 0.593 g (59% by weight of total solvent) of CDCl_3 and 0.428 g (42%) of TFAD or 0.61% of PET in the solvent mixture. The following chemical shifts were observed (lit.¹ values in parentheses at 140°C in DMSO-d_6): ^1H NMR: CH_2CH_2 signal at 4.78 δ (4.63); C_6H_4 at 8.14 δ (7.95). ^{13}C NMR: CH_2CH_2 at 63.79 δ (66.66); $\text{C}=\text{O}$ at 167.39 δ (163.36); ArC at 130.06 δ (132.09); CH at 133.48 δ (127.38).

Results and Discussion.

The discovery of the solvent combination of trifluoroacetic acid-d/ chloroform-d was made serendipitously. When PG was found to be too insoluble in chloroform-d to obtain an NMR spectrum, trifluoroacetic acid-d (TFAD) was added dropwise whereupon solution occurred. A convenient ratio of solvents was found to be 3:1 by weight of CDCl_3 : $\text{CF}_3\text{CO}_2\text{D}$. It was later found that although PG is soluble in the mixture, it is not soluble in TFAD alone. Since we were concerned about possible acid-catalyzed degradation, we carried out some experiments to check out this possibility. A sample of PG dissolved in a 3:1 mixture of TFAD: CDCl_3 showed $M_n=4,700$ ($\text{DP}=81$) when freshly prepared based on the integrated area of the CH_2 signal of the polymer compared with that of the quartet CH_2 or triplet CH_3 signals of the triethylammonium group. The same value for the same sample was found after four hours and after four days indicating no degradation of the polymer at least up to three days. The end group ^1H NMR signals for triethylammonium which appear at

3.6 and 1.4 δ for CH₂ and CH₃ respectively are not interfered with by small chloroform (impurity) and TFA (from slight amount of hydrolysis) signals at 7.3 and 10-11.5 δ (range) respectively.

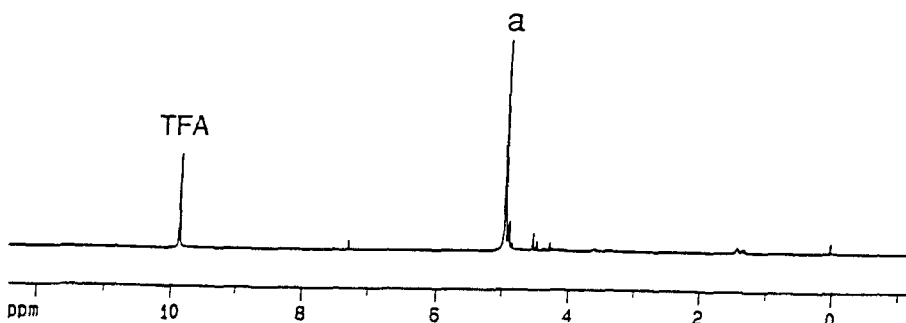


FIG. 1. ¹H NMR SPECTRUM OF POLYGLYCOLIDE IN TFAD/CDCl₃

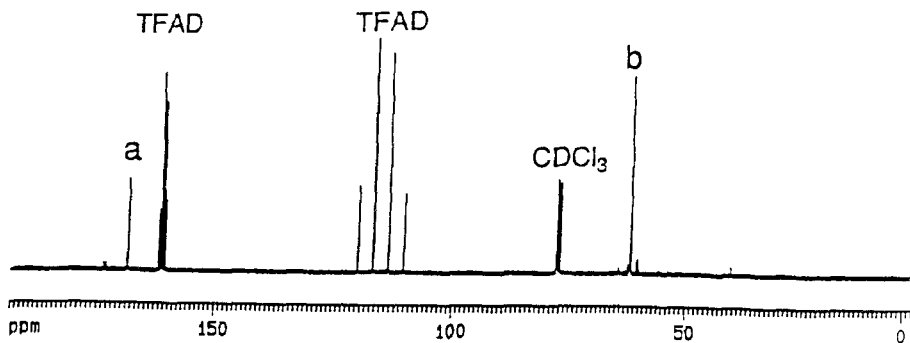


FIG. 2. ¹³C NMR SPECTRUM OF POLYGLYCOLIDE IN TFAD/CDCl₃

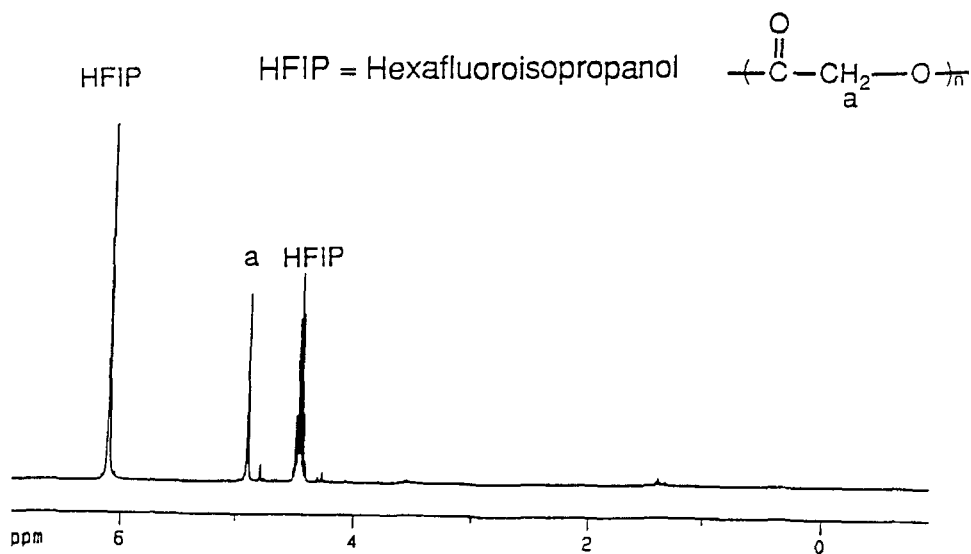


FIG. 3. ^1H NMR SPECTRUM OF POLYGLYCOLIDE IN HFIP/ CDCl_3

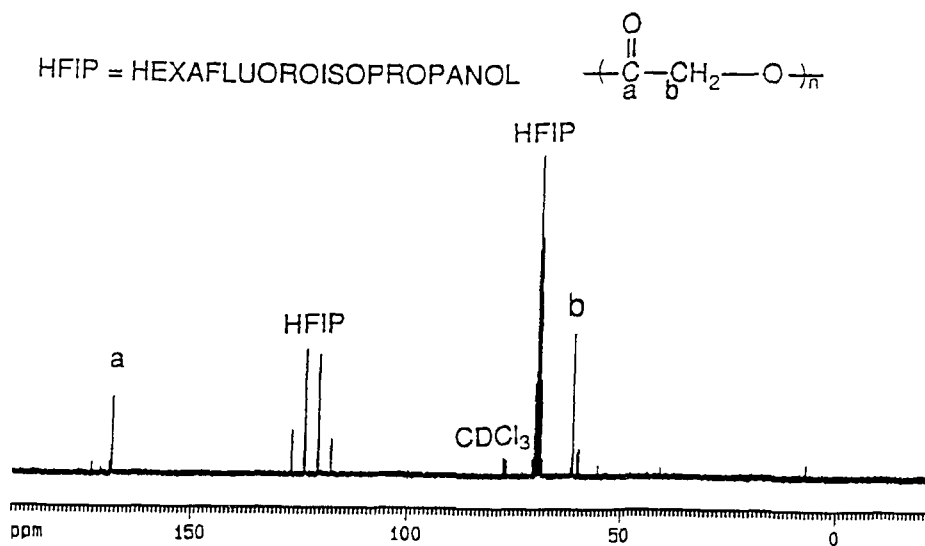


FIG. 4. ^{13}C NMR SPECTRUM OF POLYGLYCOLIDE IN HFIP/ CDCl_3

Advantages of TFAD/ CDCl_3 for NMR: Aside from the solubility aspect which enables solution ^1H and ^{13}C NMR spectra of high molecular polyesters to be obtained, the presence of chloroform-d in the solvent mixture furnishes a needed FT-NMR deuterium lock signal. Absorption from the carboxyl group of TFA (from hydrolysis present in trace amount) is at about 9-11 d which does not interfere with peaks generally used in end group analysis. Solutions in the absence of moisture are stable up to at least four days. At the solubilities used C-H-COSY spectra can also be easily obtained.

Theory. A reasonable explanation of the solubility observations is that trifluoroacetic acid molecules hydrogen-bond to carbonyl oxygens of the polyglycolide chain. This covers the PG chain with a sheath of TFA molecules with the hydrophobic CF_3 ends on the outside (Fig. 5). In effect this converts the more

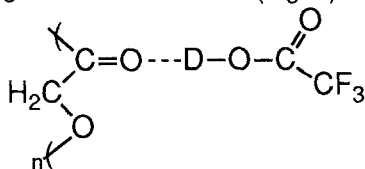


FIG. 5. Trifluoroacetic acid-d complex of polyglycolide

hydrophilic PG chain into one with a more hydrophobic character which makes it more soluble in a more hydrophobic solvent such as chloroform-d. Since the ratio of TFAD molecules to carbonyl groups is about 13:1 ($2.57 \times 10^{-3}/1.93 \times 10^{-4}$), there are more than enough TFAD molecules to hydrogen bond with all of the carbonyl groups of the PG chain. With TFA alone, TFA molecules would still hydrogen-bond to the carbonyl oxygens of the PG chain but the hydrophobic-covered chain would then be insoluble in the highly polar solvent, TFA. The same explanation would also apply to PET and other high molecular weight polyesters.

Acknowledgements.

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