S0032-3861(96)00377-1

Polymer Vol. 37 No. 21, pp. 4873–4875, 1996
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0032-3861/96/$15.00 + 0.00

Hexafluoroisopropoxy-containing polyesters

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(Received 18 May 1995; revised 19 February 1996)

A series of new polyesters containing the hexafluoro-2-propoxy group was synthesized by solution polycondensation. The 4-(2-hydroxyhexafluoro-2-propyl)benzoyl chloride was synthesized by dichromate oxidation of commercial available 4-(2-hydroxyhexafluoro-2-propyl)toluene and subsequent reaction with $SOCl_2$. The homopolyester of this acid chloride as well as several copolyesters of 1,3- and 1,4-bis(2-hydroxyhexafluoro-2-propyl)benzene were synthesized. These highly crystalline polyesters show limited solubility in common organic solvents but are all soluble in dimethylacetamide–LiCl. Inherent viscosities ranged from 0.12 to 0.85 dl g^{-1}. All of the polyesters showed similar thermal stabilities, exhibited weight loss in a single step and decomposed completely with negligible quantity of residue. Copyright © 1996 Elsevier Science Ltd.

(Keywords: aromatic fluorine-containing polyesters; bis(2-hydroxyhexafluoro-2-propyl)benzene; high temperature polymers)

Introduction

Significant recent effort has been made toward the synthesis, characterization and evaluation of fluorine-containing condensation polymers. Polymers containing hexafluoroisopropylidene-linked aryl groups in the-backbone have excellent properties and have, therefore, been extensively studied[1,2]. On the other hand, the synthesis and characterization of polymers containing the hexafluoro-2-propoxy group has focused primarily on epoxy polymers[3–6], polyurethanes[5–8], polyacrylates[9–11] and a poly(ether-ester)[12] in which the relatively unreactive 2-hydroxyhexafluoro-2-propyl group is not involved in the polymerization reaction itself. The direct polymerization of 2-hydroxyhexafluoro-1-propylarenes has not been systematically investigated beyond a brief note by Keller in which it was reported that the direction reaction between 1,3-bis(2-hydroxyhexafluoro-2-propyl)benzene and either adipyl or glutaryl chloride does not go to completion even after heating for 48 h at 130°C[13]. He was, however, able to obtain oliogomeric, alcohol-terminated or acid chloride-terminated prepolymers ($DP \approx 4$–6) by combining the diol and diacid chloride in non-stoichiometric ratios; these prepolymers were then converted to copolyurethanes or copolyesters by reaction with diisocyanates or diols respectively. The new, fluorinated polyesters, which appeared to have a very low surface energy, adhered strongly to polytetrafluoroethylene for which they exhibit good wetting properties[13].

It is the purpose of this paper to report the direct synthesis of several copolyarylates derived from 1,3- and 1,4-bis(2-hydroxyhexafluoro-2-propyl)benzene (1,3- or 1,4-HFAB) as well as the homopolyester of 4-(2-hydroxyhexafluoro-2-propyl)benzoic acid.

Experimental

Materials. The 4-(2-hydroxyhexafluoro-2-propyl)-toluene was obtained from Fairfield and used without purification. The diols, 1,3- and 1,4-HFAB were obtained from Central Glass Co., Ltd., and were distilled and sublimed respectively prior to use. Terephthaloyl chloride and isophthaloyl chloride were obtained from Aldrich and were crystallized from dry hexane. 2,5-Difluoroterephthalic acid (2F diacid) chloride was prepared following a method previously described[14]. Thionyl chloride, sulfuric acid, sodium dichromate and 4-dimethylaminopyridine (DMAP) were obtained from Aldrich and were used as received. Triethylamine and all solvents employed were purified according to standard techniques[15].

*Instrumentation. FT*i.r. analyses were performed with a Perkin-Elmer 1600 series *FT*i.r. Solid state n.m.r. spectra were obtained by using a Bruker n.m.r. spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ, USA. Inherent viscosities were determined at a concentration of 0.25 g dl^{-1} in dimethylacetamide–LiCl or THF at 25°C using a Cannon-Fenske 100 bore Viscometer. Thermogravimetric analyses (t.g.a.) and differential scanning calorimetry (d.s.c.) of polymers were performed with a Du Pont 9900 thermal analyser at Texas Research Institute, Austin, TX, USA. Experiments were carried out under a N_2 atmosphere at a heating rate of 20°C min^{-1}.

Synthesis of 4-(2-hydroxyhexafluoro-2-propyl)benzoyl chloride. To a 250 ml, round-bottom flask fitted with a condenser was added 4-(2-hydroxyhexafluoro-2-propyl)-toluene (15 g, 58 mmol), sodium dichromate (3.3 g, 110 mmol) and 48 ml of water. To this was slowly added conc. H_2SO_4 (47 ml), and the reaction mixture was heated

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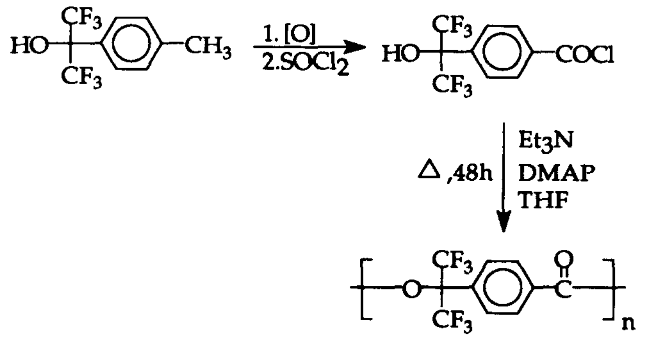


Figure 1

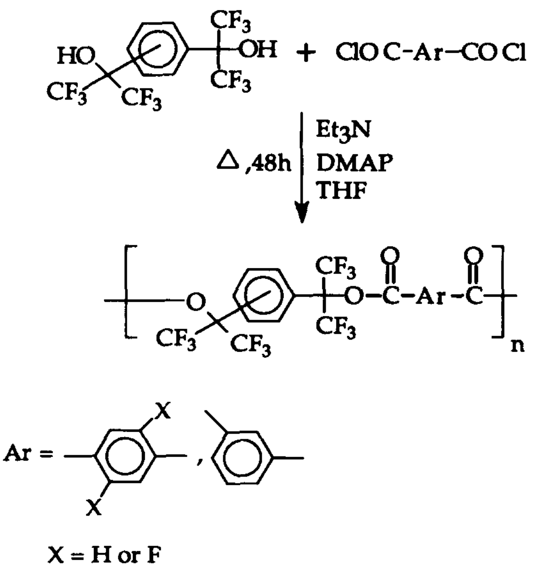


Figure 2

at reflux for 48 h. After cooling, the mixture was poured into water (100 ml) to give a white precipitate which was filtered and washed with water. The 4-(2-hydroxyhexafluoro-2-propyl)benzoic acid was recrystallized from hexane and dried in vacuum to yield 12 g (73%), m.p. 121°C (lit.[16] 121–123°C).

The acyl chloride of the above acid was prepared by refluxing in thionyl chloride with a drop of DMF. Excess thionyl chloride was removed by distillation, and the acid chloride was purified by sublimation, mp 61–63°C.

Homopolyester of 4-(2-hydroxyhexafluoro-2-propyl)-benzoyl chloride. The 4-(2-hydroxyhexafluoro-2-propyl)-benzoyl chloride (2.00 g, 0.0069 mol) was dissolved in THF (10 ml) and to this was added a solution of DMAP (0.20 g) and triethylamine (0.8 ml). The reaction mixture was heated at reflux for 48 h. The solid reaction product was added to water (100 ml), stirred for 1 h, filtered, and washed with aqueous sodium bicarbonate and water. After drying *in vacuo* at 60°C, the white polyester weighed 1.9 g (95%). Viscosity 0.49 dl g^{-1} in DMAc–LiCl (7%). Anal. Calcd for $C_{10}H_4F_6O_2$: C, 44.44; H, 1.48. Found C, 44.61; H, 1.63. *FT*i.r. (KBr, cm^{-1}): 1772, 1617, 1269, 1097 cm^{-1}. ^{13}C n.m.r. (solid): δ 160, 130 and 83.

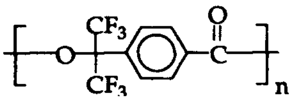
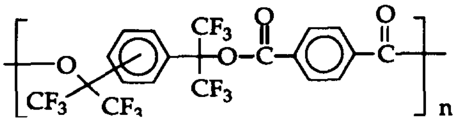
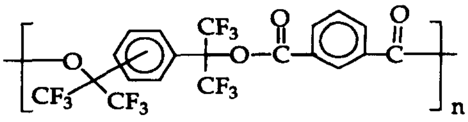
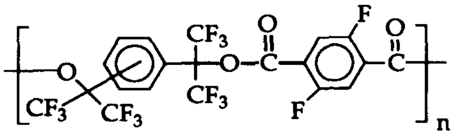
Copolyesters of HFAB. Copolyesters were obtained by the polycondensation of the 1,3- or 1,4-HFAB with equimolar amounts of diacid chloride using DMAP as a catalyst.

The HFAB (1,3- or 1,4-), DMAP and triethylamine were dissolved in THF and to this was added a solution of acid chloride (terephthaloyl chloride, isophthaloyl chloride or 2,5-difluoroterephthalic acid chloride) in THF. The reaction mixture was stirred at reflux for 48 h. The precipitated polymer was separated, washed and dried in the same way as described for the homopolyester.

Results and discussion

The homopolyester was synthesized starting from 4-(2-hydroxyhexafluoro-2-propyl)benzoic acid (prepared from the tolyl precursor), which was converted to the acid chloride, and then polymerized as shown in *Figure 1*. The oxidation of the 4-(2-hydroxyhexafluoro-2-propyl)toluene

Table 1 Properties of polyesters

Polyester	%Y	Elemental analyses Cal:Obs	[η] (dl g^{-1})	T.g.a. N$_2$^{d} (°C)	D.s.c. T_g (°C)
	95	44.44:44.61%C 1.48:1.63%H	0.49^a	374	ND
	52	44.44:44.42%C 1.48:1.72%H	0.85^b	376	115
	40	44.44:44.99%H 1.48:1.62%H	0.59^b	363	ND
	27	44.44:43.79%C 1.48:1.50%H	0.36^c	317	183
	22	44.44:44.05%C 1.48:2.10%H	0.23^c	361	ND
	67	41.69:41.37%C 1.05:0.92%H	0.61^a	358	171
	45	41.69:42.03%H 1.05:0.94%H	0.12^a	—	—

^{a} In DMAc–LiCl$_4$ (7%), ^{b} in DMAc–LiCl$_4$ (4%), ^{c} in THF, ^{d} 10% weight loss, ND: not detected with HNO_3 has been reported[16], but the sodium dichromate oxidation has not been previously applied to this system. The homopolyester, which was synthesized by solution (THF) polycondensation in the presence of DMAP as catalyst and triethylamine as HCl acceptor, is not soluble in common organic solvents but is soluble in DMAc–LiCl (7%).

The copolyesters were prepared from equimolar mixtures of 1,3- or 1,4-HFAB and a diacid chloride in THF solvent in the presence of DMAP and triethylamine, as shown in *Figure 2*.

The polymers precipitated out of the reaction mixture as the polymerization proceeded. The homopolyester and copolyesters of terephthaloyl chloride and 2F diacid chloride are not soluble in common organic solvents but are soluble in dimethylacetamide–LiCl. Isopthalate copolymers are soluble in common organic solvents, a common dependence of solubility on aryl catenation.

In general, as expected for polymerization reactions with low product yields, the molecular weight of the polymers was relatively low, as reflected by their low viscosities. In an effort to obtain high molecular weight polyesters different techniques and reaction conditions were employed but high molecular weight polyesters were not obtained, in agreement with reports in the earlier literature[7,8]. The properties of all of the new polymers are given in *Table 1*. The solution viscosities in DMAc–LiCl or THF ranged from 0.12 to $0.85\,dl\,g^{-1}$. The 1,4-HFAB based copolyesters have lower viscosities than 1,3-HFAB analogues, which could be due to the *para* catenation. However, both of the polyisophthalates exhibited lower inherent viscosities than either of the terephthalate analogues (*Table 1*) and were formed in lower yield. The poly(1,3-HFAB difluoroterephthalate) also had a higher η_{inh} than either of the polyisophthalates; however, the analogues derived from 1,4-HFAB could only be prepared with $\eta_{inh} = 0.12\,dl\,g^{-1}$. Elemental analyses showed good agreement with the calculated values of carbon and hydrogen for all of the polymers.

The Fourier transform infra-red spectra for all the polymers showed the disappearance of both hydroxyl and carboxyl groups which confirmed polymer formation. The spectra of the polyesters revealed a band at about $1770\,cm^{-1}$ from the ester C=O and absorption at about $1270\,cm^{-1}$ characteristic of C–F absorption. Solid state n.m.r. spectra of the terephthaloyl chloride-based polymers were in agreement with the structure, and the spectrum of the homopolyester was nearly identical to the spectra of these copolyesters. The spectra for the polymers showed resonance at about 160 ppm which was assigned to carbonyl carbon of the ester and the aromatic and CF_3 carbon resonances occurred between 129 and 133 ppm.

Thermal behaviour of these polymers was studied by t.g.a. and d.s.c. and is summarized in *Table 1*. The thermal stability (10% weight loss in N_2) of the polyesters ranged from 317 to 376°C. The homopolyester started decomposing at 302°C and reached 10% weight loss at 374°C, whereas the copolyesters started decomposing at about 320°C and reached 10% weight loss at 317–376°C. Thermal analysis of poly(1,4-HFAB difluoroterephthalate) is not reported because of the low value of $\eta_{inh} = 0.12\,dl\,g^{-1}$. All of the polymers exhibited weight loss in a single step and decomposed completely in nitrogen with a negligible quantity of residue. Glass transitions were only observed for the 1,3-HFAB derived polymers and ranged from 115°C for poly(1,3-HFAB terephthalate) to 183°C for the isophthalate analogue.

Conclusions

The homopolyester of 4-(2-hydroxyhexafluoro-2-propyl)benzoyl chloride and the copolyesters of 1,3- and 1,4-bis(2-hydroxyhexafluoro-2-propyl)benzene with three aromatic diacids were prepared and characterized by i.r., n.m.r., t.g.a. and d.s.c. The inherent viscosities of these polymers ranged from 0.12 to $0.85\,dl\,g^{-1}$. Thermal stabilities as measured by 10% weight loss under nitrogen ranged from 317°C to 376°C.

Acknowledgements

This material is based in part upon work supported by the Texas Advanced Research Program under Grant No. 003615-101. The authors would also like to thank the Robert A. Welch Foundation, Houston, TX (Grant AI-0524) and NASA Langley Research Center, Hampton, VA (Grant NAG 1-631/ASR) for their generous and continued financial support of this work. Thanks are due to Mr Rick Thomas of Texas Research Institute, Austin, TX, for the thermal analyses, and C. G. Johnson of University of Southern Mississippi for ^{13}C n.m.r. analyses. We gratefully acknowledge the gift of 1,3- and 1,4-HFAB from Central Glass Company, Ltd., in Tokyo, Japan.

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