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### A Comparative Study on Some Fluoroalcohols as Potential Solvents for Aliphatic Polyamides

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## A Comparative Study on Some Fluoroalcohols as Potential Solvents for Aliphatic Polyamides\*

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### ABSTRACT

Several fluoroalcohols have been prepared by the free-radical addition of methanol, ethanol and isopropanol to such fluoroolefins as  $C_3F_6$ ,  $CFH=CF-CF_3$ ,  $(CF_3)_2CFCF=CFCF_3$ , and  $H(CF_2)_4CF=CF_2$ . Proper experimental conditions for their synthesis are described. Owing to their strong tendency to form hydrogen bonds, fluoroalcohols are excellent solvents for polymeric materials which possess receptive sites for hydrogen bonding formation. The solvent power of the fluoroalcohols on some polar polymers, mostly aliphatic polyamides, has been tested. 2,2,3,4,4-Hexafluorobutanol (HFB) shows the best solvent ability among compounds of this class. Its properties and solvent power have been evaluated and compared to those of trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP).

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Some toxicological data related to HFB, TFE, and HFIP are also reported. Our data suggest that HFB may be useful as a solvent for some aliphatic polyamides such as PA 6 and PA 66.

## INTRODUCTION

In the past few years the search of solvents able to dissolve aliphatic polyamides (nylons) and other polar polymers at room temperature has experienced a considerable growth of interest, mostly because of the potential advantages in the field of molecular characterization. Their use may eventually be implemented to include other technologically relevant utilizations.

As an example, the capability to perform GPC analyses on these polymers in mild conditions not only allows evaluation of the original molecular mass distribution without the spurious contributions induced by high temperature dissolution, but also provides a useful information on both the kinetics of the reactions governing the synthesis and the correlations between structure and properties of the resultant polymers.

Indeed, the relatively high degree of crystallinity together with the polar character of the most important aliphatic polyamides (PA) is responsible for the peculiar differences in solution properties as compared to other classes of polymers. Moreover, the behavior of nylon solutions in solvents usually employed for their molecular characterization is often complicated by various factors such as aggregation, hydrolysis, and degradation phenomena.

In general, the solubilization tendency of a polyamide is negatively affected by the presence of polar amide groups which give rise to the formation of strong interamide hydrogen bonds in the polymer. Solvents capable of dissolving nylons must contain polar groups able to interact with the polymer amide groups so strongly that almost all interchain hydrogen bonds are destroyed.

As is well known [1], the most common one-component solvents able to dissolve polar nylons at moderately low temperatures are usually classified in the following four groups:

- Inorganic and organic acids (such as sulfuric acid, formic acid)
- Phenolic derivatives (e.g., *m*-cresol)
- Hexamethylphosphorotriamide (HMPT)
- Aliphatic fluorinated alcohols [e.g., trifluoroethanol (TFE), hexafluoroisopropanol (HFIP)]

Both the first and second solvent groups may cause polymer aggregation, hydrolytic breakage of the amide groups, and degradation of the polyamide as widely reported in literature [2, 3]. HMPT,

after initial promising results [4], has been abandoned because of its suspected carcinogenicity [5, 6].

The best results are therefore those obtained by the last class of the aforementioned compounds, notably HFIP. This fluorinated alcohol is able to dissolve at room temperature not only PA 6, PA 66, PA 4, and PA 3, but also several other polar polymers such as polyethylene terephthalate (PET), polyacrylonitrile (PAN), polymethyl methacrylate (PMMA). Moreover, its complete UV transparency, low refractive index value, and low viscosity are excellent prerequisites for its use as a GPC solvent with good results [7].

Indeed, more recent findings [1] underline some problems in the compatibility of HFIP with  $\mu$ -Bondagel, and presumably also  $\mu$ -Styragel, which are the usual stationary phases of the columns used in HPGPC.

This fact, together with the relevant cost of HFIP, its high vapor pressure at room temperature, and its toxicity, unfortunately behaves as a relevant limitation to any practical application, both in GPC and in other kinds of measurements of polyamide solution properties.

Another interesting solvent for aliphatic polyamides is TFE. Several papers suggest its use in GPC, but the results do not exhibit convincing agreement [1]. Similar to HFIP, two factors severely limit utilization of TFE: the high cost and the insolubility of polystyrene standards, thus making it more difficult to obtain a calibration curve.

Another class of solvents employed in the study of solution properties and molecular characterization of aliphatic polyamides is based on multicomponent systems made of either alcoholic solutions of inorganic salts [2] or organic solvent pairs [1].

Even if these systems can overcome some difficulties, such as the polyelectrolyte effect and aggregation, at least for the first group, and enhance the solvent thermodynamic power by changing its composition, they also introduce various complications such as difficulties in keeping the balance between the components of the mixture constant, and therefore they cannot be easily used in GPC analyses.

Furthermore, a unique solvent mixture composition cannot be adopted for all polyamides because the solvent power is a function of the polar character of the specific nylon under study. Sulfuric and formic acid can also be regarded as multicomponent systems because of their variable water content which strongly affects solvent properties.

On the basis of what has been reported in literature, HFIP seems to be the best room temperature solvent for aliphatic polyamides, even (with some precautions) for GPC applications. On these grounds we have undertaken a thorough study on some fluorinated alcohols of similar structure, which can be more easily synthesized than HFIP, in order to evaluate their potential use as solvents of polar polymers and polyamides.

## EXPERIMENTAL

Materials

Hexafluoropropene, 1H-pentafluoropropene, and di-*t*-butyl peroxide were obtained from Montedison S.p.A., Divisione Prodotti Industria. Hexafluoropropene dimers were prepared according to the literature [8]. The terminally unsaturated fluoroolefins were synthesized by thermal decomposition of the dry sodium salts of the corresponding fluorocarboxylic acids [9].

All the alcohols were of analytical reagent grade.

2, 2, 3, 4, 4, 4 - Hexafluorobutanol (HFB). The procedure followed for synthesis was similar to the one described by La Zerte and Koshar [10]. 0.62 g (4.25 mmol) di-*t*-butyl peroxide and 34 mL (0.85 mol) of methanol were placed in a stainless steel autoclave (300 mL of volume) which was cooled in a Dry Ice-acetone bath; 30 g of hexafluoropropene (0.2 mol) was added to the content of the autoclave which was rocked at 145°C for an hour. 11 g of hexafluoropropene was bled from the autoclave at room temperature.

Fractionation of the reaction mixture gave 18 g of  $\text{CF}_3\text{CFHCF}_2\text{CH}_2\text{OH}$ , bp 114°C (750 mmHg). NMR (neat):  $^1\text{H}$  (ppm from TMS):  $\delta$  3.85 (C(1)-H<sub>2</sub>);  $\delta$  5.2 (C(3)F-H).  $^{19}\text{F}$  (ppm from  $\text{CFCl}_3$ ):  $\delta$  -75.3 (C(4)-F<sub>3</sub>);  $\delta$  -120.8,  $\delta$  -122.2 (C(2)-F<sub>2</sub>);  $\delta$  -215.8 (C(3)H-F).

Better conversion values were obtained by increasing the reaction time to 2-3 h and by working at 135-140°C.

Similar results for this reaction and the following ones were also obtained by using a 5-L stirred stainless steel autoclave and operating on a scale of 30:1.

2, 3, 4, 4, 4 - Pentafluoro-1-butanol (PFB). The addition of methanol to 1-H-pentafluoropropene, not previously reported, was carried out in a manner similar to that described above; bp of the fluorinated alcohol: 120°C (750 mmHg). NMR (neat):  $^1\text{H}$  (ppm from TMS):  $\delta$  3.9 (C(1)-H<sub>2</sub>);  $\delta$  4.9 (C(2)F-H, C(3)F-H).  $^{19}\text{F}$  (ppm from  $\text{CFCl}_3$ ):  $\delta$  -77,  $\delta$  -78 (C(4)-F<sub>3</sub>);  $\delta$  -204.2,  $\delta$  -210.2 (C(2)H-F);  $\delta$  -212.3,  $\delta$  -218.8 (C(3)H-F).

The other fluoroalcohols used in this work, except octafluoropentanol, were synthesized in a similar way.

2, 2, 3, 3, 4, 4, 5, 5 - Octafluoropentanol.  $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OH}$  was prepared as reported in the literature [11] by operating at 140°C and 10 atm from methanol, tetrafluoroethylene, and di-*t*-butyl peroxide (molar ratio 8:1:0.04) and isolated from the other telomers by rectification, bp 140-142°C.

The polymers used for the solubility tests are PA 3, PA 6 (both anionic and hydrolytic), PA 66, PET, PAN, PMMA, and a fluorinated aliphatic polyamide (F-PA) with the repeat unit structure  $-\text{CO}-\text{CF}_2\text{O}(\text{CF}_2\text{O})_n(\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_2-\text{CO}-\text{NH}(\text{CH}_2)_6-\text{NH}-$ .

PA3, PA 6 (anionic), and F-PA are laboratory preparations, synthesized as described in Refs. 12, 13, and 14, respectively. Before testing, careful washing to remove catalyst residues, oligomers, and low mass by-products was performed. All other polymers were commercial products and were used without any further purification.

The solubility tests have been performed at 25 and 50°C by adding 10 mL of the solvent to 0.1 g of finely ground polymer, followed by vigorous stirring for 24 h.

Intrinsic viscosity determinations in HFB were carried out on unfractionated PA 6 samples (hydrolytic) with a Ubbelohde viscometer, thermostatted at 25°C. Sodium trifluoroacetate (0.1%) was added to the solvent in order to eliminate the polyelectrolyte effect.

IR and NMR spectra were performed on a Perkin-Elmer 399B and a Varian EM-360-L apparatus, respectively.

## RESULTS AND DISCUSSION

### Synthesis of Fluoroalcohols

The fluoroalcohols studied in the present work were prepared by the addition reaction of aliphatic alcohols to perfluoroolefins or monohydroperfluoroolefins containing three or more carbon atoms in the presence of a free radical initiator, as described in the Experimental section.

The reaction conditions enable us to obtain only one product from a single reaction in most cases, apart from stereoisomers.

Figure 1 shows the reaction scheme of the alcohol addition to the hexafluoropropene double bond in the presence of a free radical initiator. The behavior of the other fluoroolefins used in this work is similar.

The addition of the carbinol carbon atom on position 1 of the terminally unsaturated fluoroolefins is highly favored. Only 4% of the product carrying the carbinol group on position 2 has been found. In the case of an internal double bond, the addition of the carbinol group is governed by steric effects.

Various initiators, such as di-benzoyl peroxide, bis(4-*t*-butyl cyclohexyl)peroxidicarbonate, azobisisobutyronitrile, di-*t*-butyl peroxide, and ammonium persulfate, were tested and their efficiency compared by a proper choice of the reaction temperature. At similar decomposition rates di-*t*-butyl peroxide gives the best yields in fluoroalcohols and has been chosen as the most suitable radical initiator.

Some relevant data, referred to the fluoroalcohols synthesis, are given in Table 1.

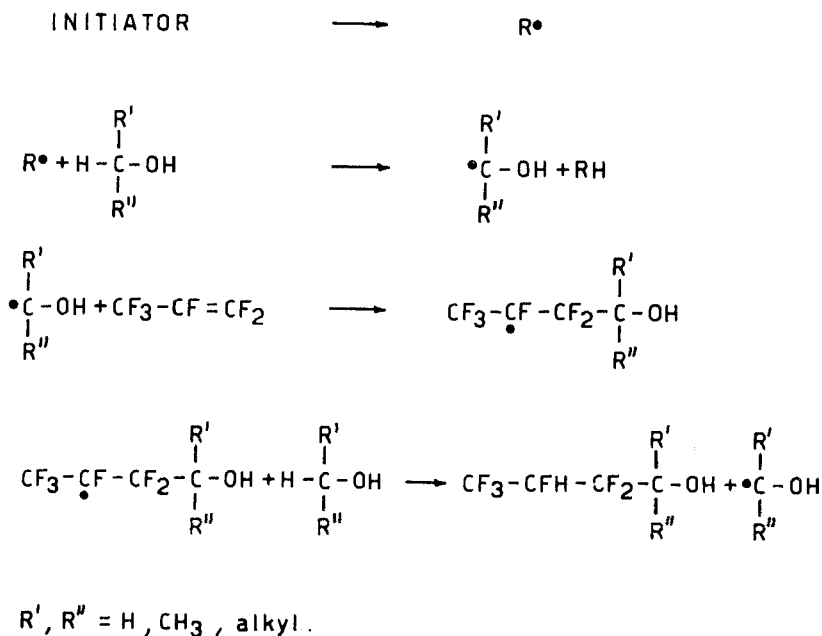


FIGURE 1.

### Solvent Properties

In order to overcome the difficulties connected with the utilization of HFIP (toxicity, high vapor tension, high cost), the fluorinated alcohols, synthesized as described in the previous section, have been comparatively studied as potential solvents of aliphatic polyamides and other polar polymers. The alcohols tested have a molecular mass higher than TFE and HFIP, with lower vapor pressures at room temperature.

As shown in Table 2, only two of them are able to solubilize polyamide 6 and 66 whereas PA 3 is unaffected: 2,2,3,4,4,4-hexafluorobutanol and 2,3,4,4,4-pentafluorobutanol.

The lower yields obtained in the synthesis of the latter, however, suggested that we focus our attention mostly on HFB. Some of the most relevant physical properties of HFB are given in Table 3 and compared to those of TFE and HFIP. This new solvent for aliphatic polyamides exhibits, besides a higher boiling point and a lower vapor pressure, much lower toxicity values (Table 4). On this basis, its use can be recommended. However, its behavior as an eluent in GPC is still to be tested in terms of interactions with stationary phase materials. This type of characterization is presently under study.

TABLE 1. The Addition of Alcohols to Olefins

Alcohol	Olefin	Reaction time (h)	Conversion <sup>a</sup>	Addition product	Bp (°C)
CH <sub>3</sub> OH	CF <sub>3</sub> -CF=CF <sub>2</sub>	1	60	CF <sub>3</sub> -CFH-CF <sub>2</sub> -CH <sub>2</sub> OH	114
CH <sub>3</sub> OH	H(CF <sub>2</sub> ) <sub>4</sub> -CF=CF <sub>2</sub>	4	40	H(CF <sub>2</sub> ) <sub>4</sub> -CFH-CF <sub>2</sub> -CH <sub>2</sub> OH	149
CH <sub>3</sub> OH	(CF <sub>3</sub> ) <sub>2</sub> -CF-CF=CF-CF <sub>3</sub>	4	40	(CF <sub>3</sub> ) <sub>2</sub> -CF-CFH-CF-(CF <sub>3</sub> )-CH <sub>2</sub> OH	141
CH <sub>3</sub> OH	(CF <sub>3</sub> ) <sub>2</sub> -C=CF-CF <sub>2</sub> -CF <sub>3</sub>	4	35	(CF <sub>3</sub> ) <sub>2</sub> -CH-CF-(CF <sub>2</sub> CF <sub>3</sub> )-CH <sub>2</sub> OH	137
CH <sub>3</sub> OH	CF <sub>3</sub> -CF=CFH	8	10	CF <sub>3</sub> -CFH-CFH-CH <sub>2</sub> OH	120
CH <sub>3</sub> CH <sub>2</sub> OH	CF <sub>3</sub> -CF=CF <sub>2</sub>	1	74	CF <sub>3</sub> -CFH-CF <sub>2</sub> -CH-(CH <sub>3</sub> )-OH	118
(CF <sub>3</sub> ) <sub>2</sub> CHOH	CF <sub>3</sub> -CF=CF <sub>2</sub>	1	95	CF <sub>3</sub> -CFH-CF <sub>2</sub> -C-(CH <sub>3</sub> ) <sub>2</sub> -OH	123

<sup>a</sup> Based on olefin reacted.



TABLE 2. Solubility<sup>a</sup> of Nylons in Fluoroalcohols<sup>b</sup>

Formula	Solvent viscosity (cS)	PA3		PA 6		PA 66	
		T = 25° C	T = 50° C	T = 25° C	T = 50° C	T = 25° C	T = 50° C
CF <sub>3</sub> -CFH-CF <sub>2</sub> -CH <sub>2</sub> OH	4.4	i	i	s	s	s	s
HCF <sub>2</sub> -CF <sub>2</sub> -CF <sub>2</sub> -CF <sub>2</sub> -CH <sub>2</sub> OH	10.0	i	i	sw	sw	sw	s
H(CF <sub>2</sub> ) <sub>4</sub> -CFH-CF <sub>2</sub> -CH <sub>2</sub> OH	20.5	i	i	sw	sw	i	i
CF <sub>3</sub> -CF-CFH-CF-CH <sub>2</sub> OH   CF <sub>3</sub>	11.3	i	i	i	i	i	i
CF <sub>3</sub> -CH-CF-CH <sub>2</sub> -OH   CF <sub>3</sub>	11.1	i	i	i	i	i	i
CF <sub>3</sub> -CFH-CF <sub>2</sub> -CHOH   CH <sub>3</sub>	4.0	i	i	i	i	i	i
CF <sub>3</sub> -CFH-CF <sub>2</sub> -C-OH   CH <sub>3</sub>	3.9	i	i	i	i	i	i
CF <sub>3</sub> -CFH-CFH-CH <sub>2</sub> -OH	6.4	i	i	s	s	s	s

<sup>a</sup>0.1 g of fine powdered polymer in 10 mL of solvent.<sup>b</sup>s = soluble, i = insoluble, sw = swollen.

TABLE 3. Physical Properties of TFE, HFIP, and HFB

	TFE	HFIP [ 16]	HFB
Formula	$\text{CF}_3-\text{CH}_2\text{OH}$	$(\text{CF}_3)_2-\text{CHOH}$	$\text{CF}_3-\text{CFH}-\text{CF}_2-\text{CH}_2\text{OH}$
Specific gravity at 25° C (g/mL)	1.38 [ 15]	1.59	1.54
Boiling point (° C)	74 [ 15]	58	114
Room temperature vapor pressure (mmHg)	45	115	10
Refractive index ( $n_D^{25}$ )	1.2907 [ 15]	1.2752	1.3141
Viscosity at 20° C (cS)	1.5	1.02	4.4

TABLE 4. Toxicity Data

Alcohol	LD <sub>50</sub> (mg/kg) [ 17]	Primary eye irritation test [ 18]
TFE	330	Moderately irritating
HFIP	300	Extremely irritating
HFB	950	Minimally irritating

TABLE 5. Solubility<sup>a</sup> of the Polymers at Room Temperature

Polymer	TFE	HFIP	HFB
PET	i	s	i
PMMA	s	s	s
PAN	i	s	i
Aliphatic F-PA <sup>b</sup>	i	s	s

<sup>a</sup>0.1 g of polymer in 10 mL of solvent.

<sup>b</sup>Repeating unit:  $-\text{CO}-\text{CF}_2\text{O}(\text{CF}_2\text{O})_n(\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_2-\text{CO}-\text{NH}-$   
 $(\text{CH}_2)_6-\text{NH}-$ .

The solvent properties of HFB, as compared to TFE and HFIP, have been tested for such other polar polymers as PET, F-PA, PAN, and PMMA. The results are quoted in Table 5.

The solubility of polyamides in fluorinated alcohols can be directly related to the formation of hydrogen bonds between polyamide carbonyls and alcoholic hydroxyls, where the acidity is emphasized by the presence of such strong electron-pulling substituents as CF<sub>3</sub>.

There are many papers in the literature concerning the evaluation of the acidity of alcohols, both qualitatively and quantitatively. The results show that, in a manner analogous to other classes of organic compounds, in alcohols containing highly electron-pulling substituents, such as CCl<sub>3</sub> or CF<sub>3</sub>, the acidity is strongly enhanced as compared to the corresponding nonhalogenated alcohols [ 15].

To a good approximation, one can say that fluorinated alcohols containing terminal groups, such as  $-\text{CF}_2\text{CH}_2\text{OH}$  (a),  $-\text{CH}(\text{CF}_3)\text{OH}$  (b), and  $-\text{C}(\text{CF}_3)_2\text{OH}$  (c), show pK<sub>a</sub> values in the following order: 12.5, 9.5, 5.5 [ 15]. They are therefore much more acidic than the corresponding nonfluorinated alcohols. That is, the acidities of (b)- and (c)-type alcohols are comparable to those of phenols and organic acids.

We may therefore conclude that one of the most relevant characteristics of fluoroalcohols is their ability to act as extremely strong hydrogen donors in hydrogen bonding [ 19].

TABLE 6. Red Shift of the Amide Carbonyl Band Induced by Fluoroalcohols

Substrate	C=O frequencies (cm <sup>-1</sup> )					C=O shifts (cm <sup>-1</sup> )	
	Solid state	Solution in					
		Nonassociating solvents (1)	HFB (2)	HFIP (3)			
Caprolactam	1655	1670 <sup>b</sup>	1650	1630	20	40	
Caprolactam cyclic dimer	1640	1662 <sup>b</sup>	1622	1610	40	52	
PA 6	1640	-	1622	1610	-	-	
Aliphatic F-PA <sup>a</sup>	1710	1730 <sup>c</sup>	1715	1715	15	15	

<sup>a</sup>Repeating unit:  $-\text{CO}-\text{CF}_2\text{O}(\text{CF}_2\text{O})_n(\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_2-\text{CO}-\text{NH}-(\text{CH}_2)_6-\text{NH}-$ .

<sup>b</sup>In sym-tetrachloroethane.

<sup>c</sup>In  $\text{CF}_2\text{ClCFCl}_2$ /diglyme 50% vol/vol mixture.

It should also be taken in account that fluoroalcohols show weak intra- and intermolecular bonds as evidenced by IR studies on HFIP [20]. As a consequence, there is a facile tendency to form hydrogen bonds with lone pair donors, and these alcohols behave as good solvents of compounds containing atoms with such properties. The weak intermolecular forces, typical of fluorinated alcohols, are also responsible for their lower viscosities as compared to other hydroxyl solvents such as m-cresol.

Hydrogen bond formation is confirmed by a comparison between the IR band of amide carbonyl in nonpolar aprotic solvents and in fluoroalcohol solution.

It was not possible to carry out this investigation directly on nylons, owing to their insolubility in nonpolar solvents. We therefore used caprolactam, its cyclic dimer (which shows a solid-state IR spectrum similar to PA 6), and a fluorinated elastomeric polyamide as suitable substrates. Table 6 reports some IR data of these compounds. Our data show that the carbonyl frequency is red shifted when oxygen is hydrogen-bonded. The extent of the shift is generally larger in HFIP owing to its stronger bonding power.

The NMR data show similar behavior; all the fluoroalcohols reported here show a hydroxyl proton NMR shift of about 1.8 ppm at high dilution in a nonpolar solvent such as tetrachloroethylene. In

TABLE 7. Intrinsic Viscosities of Hydrolytic PA 6

$[\eta]_{\text{m-cresol}}^{25^\circ\text{C}}$	$[\eta]_{\text{HFB}}^{25^\circ\text{C}}$	$\bar{M}_v$
1.05	1.05	27.200
1.39	1.30	38.800
1.56	1.30	45.800
2.47	2.28	84.800
2.97	3.14	109.000

the presence of an equimolecular amount of an amidic substrate, this value shifts downfield. A shift from the unbonded position larger than 3.7 ppm is found for HFB and PFB, which are good solvents. Poor solvents show a smaller shift, while the best solvent, HFIP, shows a larger shift. Thus the solvent ability can be related to the NMR chemical shift of the hydroxyl proton and to the IR carbonyl frequency shift from the unbonded position.

#### Mark-Houwink Parameters for the System HFB-PA 6

Five samples of hydrolytic PA 6 have been used for molecular mass calibration in HFB. From the comparison between their intrinsic viscosities in m-cresol and HFB it is possible to evaluate the parameters  $K$  and  $a$  of the Mark-Houwink equation for the system HFB-PA 6, on the basis of literature data [21] for the corresponding parameters in the system m-cresol-PA 6.

In Table 7 the data used for evaluation of the molecular mass-viscosity relationship in HFB are given.  $K$  and  $a$  are  $4.2 \times 10^{-4}$  dL/g and 0.76, respectively.

The low number of the samples and their polydispersities do not allow us to consider the relationship  $[\eta]$ - $M$  in HFB a very accurate one. For practical purposes, however, it is possible to use our values of  $K$  and  $a$  and determine with good precision the molecular masses of PA 6 by viscosity measurements in HFB instead of in m-cresol. The use of polydisperse PA 6 samples instead of narrow fractions does not seem to affect the calibration curves in m-cresol appreciably [2].

A comparison with the literature values [2, 22] of the corresponding parameters determined for the systems TFE-PA 6 ( $K = 34 \times 10^{-4}$ ,  $a = 0.56$ ) and HFIP-PA 6 ( $K = 48 \times 10^{-4}$ ,  $a = 0.56$ ) reveals that HFB is thermodynamically the best solvent among the three fluorinated alcohols.

## CONCLUSIONS

The present study on the comparative behavior of fluoroalcohols as potential solvents of aliphatic polyamides allows some interesting deductions on their solvent power. First of all, the solvent power is affected by the presence of alkyl substituents in the 2 position, decreasing from primary to secondary to tertiary alcohols. This decrease is presumably due to steric hindrance of the substituents more than to the slight reduction of acidity because of the electron-donating tendency of the alkyl groups. Indeed, the  $pK_a$  values of fluorinated alcohols ending with  $-\text{CH}_2\text{OH}$  or  $-\text{CH}(\text{CH}_3)\text{OH}$  or  $-\text{C}(\text{CH}_3)_2\text{OH}$  are very close [23]. More difficult to explain is the lower solvent power of longer chain fluoroalcohols as compared to HFB and PFB, inasmuch as any appreciable variation of acidity should not be expected. A possible reason may be related to the lower concentration (per unit volume) of the hydroxyl groups, giving rise to a lower polarity of the molecule.

IR and NMR spectra emphasize the relevance of hydrogen bonding to determine the solvent power of fluoroalcohols. However, they are unable to explain fully the mechanism of polyamide dissolution.

Our work shows that HFB can be considered a suitable solvent of the most relevant aliphatic polyamides, PA 6 and 66, and a better choice than HFIP which exhibits several disadvantages such as higher volatility and toxicity.

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