

Trifluoroethanol/Chloroalkane Mixtures: Excellent Novel Solvents for Aliphatic Polyamides

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Synopsis

Certain mixtures of TFE/ CHCl_3 were found to be excellent solvents for aliphatic polyamides such as nylon-6, nylon-66, nylon-11, nylon-12, nylon-69, nylon-610, and nylon-612. Intrinsic viscosities were measured and Mark-Houwink coefficients determined for nylon-6/TFE/ CHCl_3 , indicating TFE-rich mixtures to be better solvents than TFE alone. Similar results were obtained for TFE/ CH_2Cl_2 . Four ternary phase diagrams were constructed for nylon-6/TFE/chloroalkanes, of which the ones with CHCl_3 and CH_2Cl_2 are the most interesting. In the nylon-6/TFE/ CHCl_3 diagram higher nylon-6 solubility in TFE-rich mixtures and a biphasic region in the CHCl_3 -rich compositions are evident. In the TFE/ CH_2Cl_2 system, the higher dissolution of nylon-6 is observed, but no biphasic regions are detected. In certain solvent compositions and/or polymer concentrations the polymer is incompletely soluble, making the phase diagrams rather complicated. Observed thermodynamic excess properties appear to relate to the quality of TFE/chloroalkanes as solvents for nylon-6. Studies on swelling of nylon-6 networks immersed in TFE/ CHCl_3 show a behaviour previously described by Krigbaum and Carpenter for a general case where the formation of contacts between molecules of the two solvents is discouraged and their preferential solvation of the polymer is, therefore, encouraged. The phenomena observed in this work can be qualitatively explained as arising from antagonistic interaction of TFE molecules with chloroalkane ones. The presence of the polyamides in solution reduces such contacts, enhancing the dissolution of the polymer in the (TFE-rich) solvent mixtures.

INTRODUCTION

For analytical purposes it is desirable to have low viscosity solutions of polymers, from which the nonreactive solvent can be completely evaporated at rather low temperatures. However, most solvents for aliphatic polyamides have high boiling temperatures,^{1,2} such as *m*-cresol, or are highly acidic, such as formic and sulfuric acids.² The acidic solvents tend to degrade aliphatic polyamides, especially in the presence of moisture.³ Furthermore, these solvents are highly viscous. This combination of undesirable properties results in high viscosity solutions of polyamides which cannot easily be filtered, and from which the solvent cannot be evaporated off at reasonable temperatures. To overcome these drawbacks, 2,2,2-trifluoroethanol (TFE) is commonly used as a low boiling, moderate viscosity solvent during analytical manipulation of polyamides such as poly(ϵ -caprolactam) (nylon-6) and poly(hexamethylene adipamide) (nylon-66). When polyamides containing longer $-\text{CH}_2-$ sequences between the amide groups, such as polyundecanoamide (nylon-11) and polylauro lactam (nylon-12), are being studied, hexafluoroisopropanol (HFIP) is often used for dissolution purposes. Both fluorinated solvents pose certain health hazards and are very costly, especially HFIP.

There are several methods to determine whether a given liquid or a mixture of liquids is a solvent, and how good a solvent it is for a particular polymer. A qualitative method, that goes no further than its great and immediate usefulness, is the estimation of the rate of polymer dissolution. Here, equal amounts of polymer of a given grain size are metered into equal volumes of the tested liquids and treated identically. The order in which complete dissolution is effected is considered to reflect the "goodness" or quality of the solvents. A more quantitative method to determine solvent quality is through the determination of the saturation point of a given polymer in a series of solvents being evaluated. The liquid or liquid mixture in which saturation occurs at the highest polymer concentration is considered to be the best solvent, and so on. Comparison of the polymer concentrations at saturation gives us a quantitative estimate (not an exact determination) of the relative quality of the various solvents tested.

A well-known procedure to determine solvent quality is by measuring the volume of swelling a given volume of lightly crosslinked polymer experiences when in equilibrium with an excess amount of solvent. This procedure is quantitative for systems where the solvent contains only one species.^{4,5} However, when the swelling liquid is a mixture of two or more liquids, which can interact with the crosslinked network differently from one another, then the determination of solvent quality from the degree of swelling of the crosslinked polymer may not be as straightforward as in the case of a single species solvent.

Another method to assess the quality of solvents or solvent mixtures is by measuring at a constant temperature the intrinsic viscosity $[\eta]$ of a series of fractions of a given polymer in each evaluated solvent system, and to determine the Mark-Houwink exponent a in each such system:

$$[\eta] = KM^a \quad (1)$$

where M is the molecular weight of the polymer fraction and K is a universal constant for each polymer-solvent-temperature system. For random coil polymers, it is well accepted⁴ that the larger a is, the better the solvent. Thus, for a given polymer, increasing values of a indicate an improvement in the quality of the solvents, at least relative to one another if not in absolute quantitative terms. At our disposal we had fractions only of nylon-6. Their weight average molecular weight M_w was determined from their intrinsic viscosity values in *m*-cresol according to⁶

$$[\eta] = 5.26 \times 10^{-4} M_w^{0.745} \quad (2)$$

GPC scans and vapor pressure osmometry conducted on several of these fractions indicated their ratio of weight average to number average molecular weight, M_w/M_n , to be very close to 2.0.

In a search for less expensive, low boiling, and low viscosity solvents for nylon-6, we have discovered that mixtures of certain low boiling chloroalkanes and TFE over broad ranges of composition act as excellent solvents for several aliphatic polyamides. Our observations will be presented in this report. From all polyamides tested, the results of nylon-6 will be especially emphasized.

EXPERIMENTAL

Materials. Chloroalkanes of the highest available grades were obtained from chemical supply houses. 1,1,2-Trichloro-1,2,2-trifluoroethane (TCTFE) of commercial quality is an Allied Corp. product sold under the trade name Genetron 113. 2,2,2-Trifluoroethanol (TFE) 99+ % of Gold Label grade was obtained from Aldrich Chemical Co. Several nylon-6 grades were used, most of them commercially produced by Allied Corp. The grade most frequently used in this work was Allied's grade 8207, of $M_w = 42,650$ and $M_n \approx 20,000$. Nylon-66 was DuPont's Zytel grade 101L. Nylon-12 was obtained from Emser Industries in two grades, Grilamid L-16 and L-20. Nylon-11 was Rilsan Corp.'s BMNO grade. Poly(hexamethylene nonanediamide) (nylon-69), poly(hexamethylene sebacamide) (nylon-610), and poly(hexamethylene dodecanediamide) (nylon-612), were all purchased from Aldrich Chemical Co. Poly(trimethylhexamethylene terephthalamide) (Trogamid T) was purchased from Dynamit Nobel A.G. All polymers were of molecular weight sufficiently high to be of industrial use. All materials were used as received.

Procedures. Solvents which were found to be miscible in all proportions were mixed in volume/volume ratios in 100 mL volumetric flasks with graduated necks, and the mixtures were allowed to equilibrate prior to use. For the purpose of preparing phase diagrams of nylon-6 and determining the amounts and rates of dissolution, polymer solutions were prepared in glass vessels as follows. The desired amount of polymer, in pellets or coarse grind form, was weighed in. The solvent or solvent mixture carefully metered in with the aid of a graduated cylinder, and the sealed vessel was then maintained at ambient temperature (21–22°C) with occasional wrist shaking. In most cases complete dissolution was achieved within 24 h. In less favorable instances, complete solubility, partial solubility, or insolubility were determined after 4–14 days in the solvent. Insolubility of the polyamide was defined as instances where the solvent was filtered off the polymeric solids after 14 days of immersion and the amount of extractables (monomers and mostly dimers) in it never surpassed 0.1% of the immersed polymer. In the case of fully or partly soluble systems, heating the mixture to $\leq 45^\circ\text{C}$ for several hours greatly accelerated the dissolution process.

In most solvent systems, intrinsic viscosities (all in units of dL/g) were measured at 25°C in Cannon-Ubbelohde internal dilution glass viscometers with efflux time between 100 and 300 seconds. When dichloromethane, CH_2Cl_2 , was used with TFE, its high evaporation rate at 25°C dictated the preparation of each polymer solution separately in a sealed vessel and the immediate measurement of its viscosity. Solution viscosities over broad concentration ranges were measured at about 21°C with a Nametre Direct Readout Viscometer. Temperature changes upon mixing of solvents were crudely measured by keeping a thermometer in the graduated flasks during the mixing and equilibration periods. Wide angle X-ray diffraction (WAXD) patterns were obtained with a Philips diffractometer operating in parafocus geometry and using monochromatized copper K_α radiation. The determination of percent crystallinity was performed following the procedure of Hermans and Weidinger. Estimates of crystallite size were obtained from line width at half height. Both procedures are described in the book by Alexander.⁷

To determine the quantity and composition of solvents absorbed by nylon-6 networks from solvent mixtures, the polymer was crosslinked at its chain ends as shown below. After purification and immersion in TFE/chloroalkane mixtures, the solvent imbibed by the crosslinked network was analyzed in a Hewlett-Packard Model 5840 gas chromatograph (GC) as follows: about 2 g of purified dry crosslinked nylon-6 were placed in sealed vessels containing not less than 30 mL of the desired TFE/chloroalkane mixture. Depending on the solvent composition, the crosslinked polymer swelled to different degrees, in some instances reaching a slimy gel consistency. After equilibrating for over 2 weeks with the solvent in the sealed vessel, the solvent was completely decanted and the swollen crosslinked polymer air dried on a filter paper for 2–3 min. At that point the swollen polymer was carefully weighed to allow the determination of the total solvent absorption by the polymer. Conversion to volume/volume ratios was performed using a density of 1.13 g/cm³ for nylon-6, 1.373 g/cm³ for TFE, 1.483 g/cm³ for chloroform, and 1.316 g/cm³ for methylene chloride. After air drying, small samples obtained from the cores of the swollen crosslinked nylon-6 specimens were placed into 1 dram vials equipped with septum screw-caps. The vials were heated to 60°C for 10 min, and then 50 μ L of head space were taken with a heated (60°C) gas-tight syringe at vial pressure, and injected onto a 3 ft \times 0.125 in. SS Porapak PS column operated from 75 to 160°C at 20°C/min with 1 min hold at limit. The injection port temperature was 225°C and the flame ionization detector temperature was 300°C. The data were obtained via electronic integration with calibration using 1:4, 1:1, and 4:1 v/v TFE/chloroalkane mixtures.

Nylon-6 Crosslinking, Purification and Characterization Procedures

For the purpose of crosslinking, nylon-6 with $M_w \cong 39,000$ and $M_n \cong 19,000$ was used. Its chain ends were about 80% amine-terminated, the rest being carboxyl-terminated. The well-ground and thoroughly dry polymer was tumble-mixed in a sealed container with 1,3,5-benzenetricarboxylic acid in such amounts that the number of polymeric amine groups corresponded to the number of carboxyl groups in the benzenetricarboxylic acid. To this mixture, 1.50% by weight of triphenylphosphite (TPP) were added with thorough mixing. The mixture was fed into a 1 in. Wayne extruder equipped with a $L/d = 24$ single-stage mixing screw. The nominal temperature in the extruder was set at 285°C, and the residence time at this temperature was 25 min. The extrudate was collected, ground at liquid nitrogen temperature in a Wiley Mill, and the solubles were exhaustively extracted over several days in large excesses of TFE and 2:1 TFE/CHCl₃. The insoluble highly swollen gel was separated from the soluble fraction by filtration through a copper wire window screen. The extraction and filtering sequence was repeated two additional times. Finally, the solvents were completely evaporated. Gravimetry indicated that during the high temperature crosslinking in the extruder, 76% of the polymer became crosslinked while 24% remained soluble. At this point the insoluble nylon-6 network was deemed to be sufficiently pure for the swelling experiments. It should be noted that

the high temperature reactions between free primary amine and carboxylic acid in the presence of certain organic phosphites take place with no measurable chain cleavage.^{8,9} Thus, the effected crosslinks are supposed to involve chain ends only.

Amine end group analysis of the purified crosslinked nylon-6 and the uncrosslinked parent polymer indicated that from every eight amine groups in the starting polymer only one survived unreacted in the crosslinked network. Recalling that $\sim 80\%$ of all chain ends of the parent polymer were amine-terminated, one finds that in the purified network each chain contributes 1.4 crosslinks to the network. The large majority of these links is to the trifunctional 1,3,5-benzenetricarboxylic acid nuclei, and only a very small number to carboxyl endgroups of other nylon-6 chains. This indicates that only 70% of $M_n \cong 19,000$ may be considered as contributing to the network by being crosslinked at both ends. That is, the average molecular weight between adjacent crosslinks is $M_c \cong 13,300$. The 24% soluble material retrieved during the purification of the crosslinked polymer contained, most likely, a hefty fraction of the chains terminated by only one amine group and almost all chains terminated by carboxyl groups at both ends.

Films of the purified crosslinked nylon-6 were prepared by casting the highly swollen network from 2:1 TFE/ CHCl_3 and drying at room temperature. Similar films were prepared from solutions of the parent polymer in the same solvent mixture. Part of the films was studied by X-ray techniques once all the solvent was removed at ambient temperature, and the rest were annealed for 4 h at 100, 120, and 160°C before the X-ray studies. In all instances the nylon-6 crystallized in the α -form. The results indicate no correlation of the percent crystallinity and crystallite size with the drying or annealing temperature. Thus, the percent crystallinity of the uncrosslinked nylon-6 was $49 \pm 3\%$ and of the crosslinked nylon-6 $45 \pm 3\%$, irrespective of the annealing temperature. The crystallite sizes also showed no dependence on the drying/annealing temperature, with the largest crystallite size, in the 200 direction, being 115 Å for the uncrosslinked polymer and 96 Å for the crosslinked polymer. Here, too, the crystallite sizes were about the same, immaterial of whether the specimens were dried at ambient or elevated temperature. The similarity of the purified crosslinked to the uncrosslinked nylon-6 indicated to us that conclusions about crosslinked polymer-solvent interactions are expected to be valid also for the uncrosslinked soluble analogs.

RESULTS

The large majority of our results were obtained from solutions of nylon-6 in TFE/ CHCl_3 mixtures. Several other aliphatic polyamides and TFE/chloroalkanes were studied, but to much lesser extent. The following will, hence, reflect the preponderance of data about nylon-6 in TFE/ CHCl_3 .

Chloroalkanes which are liquid at room temperature and TFE were mixed and evaluated with respect to their mutual miscibility. In all cases, the range of composition tested was broader than from 1:9 TFE/chloroalkane to 4:1 TFE/chloroalkane. Chloroform, methylene chloride, CH_2Cl_2 , and 1,2-dichloroethane, $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, were found to be miscible with TFE in all

proportions. Trichlorotrifluoroethane (TCTFE), $\text{CCl}_2\text{F}-\text{CClF}_2$, with a boiling point of $T_b = 47.6^\circ\text{C}$, was also found to be miscible with TFE in all proportions. Chlorinated solvents immiscible with TFE over a broad range of composition were: carbontetrachloride, CCl_4 , perchloroethane, $\text{CCl}_3-\text{CCl}_3$, tetrachloroethane, $\text{CHCl}_2-\text{CHCl}_2$, tetrachloroethylene, $\text{CCl}_2=\text{CCl}_2$, 1,1,2-trichloroethane, $\text{CHCl}_2-\text{CH}_2\text{Cl}$, and 1,1,2-trichloroethylene, $\text{CCl}_2=\text{CHCl}$. Unlike chloroform, bromoform is immiscible with TFE.

In all cases of miscible pairs, the mixtures increased in volume as compared with the combined volumes of the parent solvent, with a concomitant reduction in their temperature. This reduction was rather dramatic in the cases of TFE/ CHCl_3 , TFE/ CH_2Cl_2 , and TFE/ $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, and much smaller in the case of TFE/TCTFE. Such volume increases and corresponding cooling were not observed in mixtures of CHCl_3 /methanol and CHCl_3 /ethanol. The volume increases upon mixing and equilibration followed the same pattern as the temperature reduction: They were very large in the first three TFE/chloroalkane mixtures, and negligible in the TFE/TCTFE one. The data for TFE/ CHCl_3 in Figure 1 and for TFE/ CH_2Cl_2 in Figure 2 are typical of the first mixtures, where the volume expansion for 1:1 v/v mixtures was always in the 1.0–1.2% range. Unlike these, a 1:1 v/v TFE/TCTFE mixture increased by only 0.3 vol %. In addition to volume expansion and temperature reduction upon mixing, the intrinsic viscosities of nylon-6, grade 8207, in several TFE/ CHCl_3 and TFE/ CH_2Cl_2 compositions are shown in Figures 1 and 2, respectively. The measurements were conducted only in solvent mixtures in which more than 0.5 wt % were soluble in a single phase solution. From the figures it is obvious that the intrinsic viscosity of

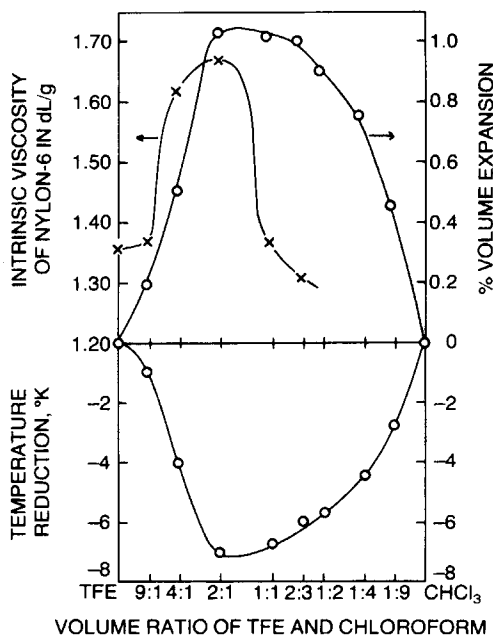


Fig. 1. Percent volume expansion (O) and temperature reduction (O) upon mixing TFE and chloroform, and the intrinsic viscosity (X) of nylon-6 grade 8207 as a function of TFE/ CHCl_3 composition.

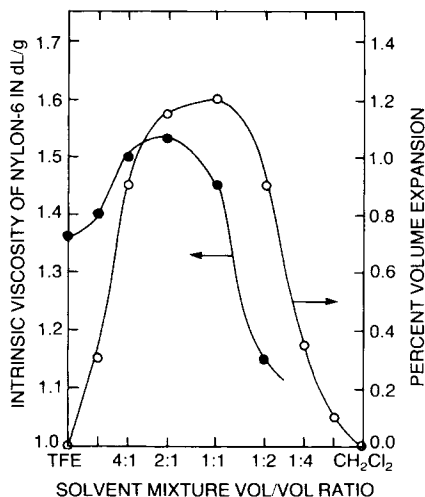


Fig. 2. Percent volume expansion (○) upon mixing TFE and methylene chloride, and the intrinsic viscosity (●) of nylon-6 grade 8207 as a function of TFE/CH₂Cl₂ composition.

this nylon-6 fraction in TFE-rich mixtures of TFE/CHCl₃ and TFE/CH₂Cl₂ is higher than in pure TFE. As will be shown later, this was found to be the case for nylon-6 in general and is not limited to any particular fraction. It is also evident from Figures 1 and 2 that the large volume increases of solvent mixtures do not necessarily go hand-in-hand with commensurate improvements in the ability of the mixtures to dissolve polyamides and, especially, nylon-6.

It is of interest to note that from the two better solvent mixtures tested, namely, TFE/CHCl₃ and TFE/CH₂Cl₂, the first forms an azeotrope while the second does not. The azeotrope, whose composition was determined by GC to be 30:70 v/v TFE/CHCl₃, boils at 55.0°C, while the boiling point of TFE is 74°C and that of chloroform is 61°C.

The quality of a solvent or solvent mixture for a given polymer is manifested by the level of macromolecular chain expansion, which is, in turn, reflected in the intrinsic viscosity of the polymer. The higher the intrinsic viscosity of a randomly coiled polymer, the better is the solvent. To check on the quality of several TFE/chloroalkane solvent mixtures, and to compare with some of the commonly used solvents, seven nylon-6 samples were dissolved and their reduced viscosity, η_{sp}/c , and intrinsic viscosity determined in six solvent systems. One of these solvents was *m*-cresol, allowing us to determine the M_w of the nylon-6 samples according to eq. (2) above. As will be seen below, our results in *m*-cresol were extremely close to those of Tuzar et al.,⁶ producing essentially the same M_w values. The nylon-6 samples are tabulated with their codes, intrinsic viscosities in *m*-cresol and M_w in Table I.

Using the calculated M_w , the data in all solvent systems were plotted on log-log paper, yielding straight lines with rather low scatter (worst scatter was with TFE). From the slopes and intercepts the following Mark-Houwink equations were obtained:

$$\text{nylon-6 in 2:1 TFE/CHCl}_3 \quad [\eta] = 4.74 \times 10^{-4} M_w^{0.751} \quad (3)$$

TABLE I
 Characteristics of Nylon-6 Fractions

Sample code	$[\eta]$	M_w	Sample code	$[\eta]$	M_w
FAV 33	1.08	27950	8205	2.33	78450
LSB	1.39	39200	I.V. = 3.62	2.77	98940
8207	1.48	42650	$\eta_{sp}/c = 3.06$	2.93	106680
BHS	1.56	45780			

$$\text{nylon-6 in 2:3 TFE/CHCl}_3 \quad [\eta] = 7.24 \times 10^{-4} M_w^{0.695} \quad (4)$$

$$\text{nylon-6 in 2:1 TFE/CH}_2\text{Cl}_2 \quad [\eta] = 4.07 \times 10^{-4} M_w^{0.785} \quad (5)$$

$$\text{nylon-6 in TFE} \quad [\eta] = 4.58 \times 10^{-4} M_w^{0.742} \quad (6)$$

$$\text{nylon-6 in } m\text{-cresol} \quad [\eta] = 5.24 \times 10^{-4} M_w^{0.749} \quad (7)$$

$$\text{nylon-6 in 90\% aqueous formic acid} \quad [\eta] = 4.63 \times 10^{-5} M_w^{0.970} \quad (8)$$

The large value of the coefficient a obtained for nylon-6 in 90% aqueous formic acid is in a very good agreement with the values obtained by Quadrat and Bohdanecky¹⁰ for nylon-6 in similar aqueous formic acid solutions. Our values for nylon-6 in TFE are rather close to $K = 5.36 \times 10^{-4}$ and $a = 0.75$ reported by Mattiussi et al.³ The inverse relation generally observed between the exponent a and the constant K is in agreement with such a relationship previously shown by Aharoni.¹¹ Comparison of eqs. (3)–(7) clearly indicates that 2:1 v/v mixtures of TFE with chloroform or with methylene chloride are solvents for nylon-6 superior to TFE or *m*-cresol alone. It should be emphasized that neither of the chloroalkanes is a solvent for nylon-6.

Flory's relationship,⁴

$$[\eta] = (6R_G^2)^{3/2} \Phi / M \quad (9)$$

where R_G is the root mean square radius of gyration and Φ is "Flory's constant," was used to calculate the radius of gyration of nylon-6 with $M_w = 39,200$ and $M_w = 106,680$ in the various solvents in Table II. The results listed in the table were calculated using a value of $\Phi = 2.87 \times 10^{21}$ taken from Yamakawa.¹²

 TABLE II
 Intrinsic Viscosity and Radius of Gyration of Nylon-6 in Various Solvent Systems

Nylon-6 code, Solvent system	LSB, $M_w = 39,200$		$\eta_{sp}/c = 3.06$, $M_w = 106,680$	
	$[\eta]$	R_G (Å)	$[\eta]$	R_G (Å)
2:1 TFE/CHCl ₃	1.27	106	2.86	194
2:3 TFE/CHCl ₃	1.12	101	2.14	176
2:1 TFE/CH ₂ Cl ₂	1.37	109	2.88	194
TFE	1.17	103	2.51	185
<i>m</i> -Cresol	1.39	109	2.93	195
90% Aqueous formic acid	1.37	109	3.52	208

TFE-rich mixtures with chloroform and methylene chloride covering the composition range of 9:1 to 1:1 v/v TFE/chloroalkane, were found to be excellent solvents for various aliphatic polyamides beside nylon-6. Of the two systems, TFE/ CHCl_3 has a slight edge over TFE/ CH_2Cl_2 , and the best solvent quality in either system is exhibited over the composition range of 4:1 to 3:2 TFE/chloroalkane. Thus, at ambient temperature, mixtures of TFE and chloroform in 2:1 and 3:2 v/v ratios were found to rapidly dissolve not less, and often much more, than 5 wt % of the following polyamides: nylon-6, nylon-66, nylon-11, nylon-12, nylon-69, nylon-610, and Trogamid T. Under identical conditions nylon-612 was soluble up to only 3% concentration. Comparable mixtures of TFE and CH_2Cl_2 dissolved nylon-11, nylon-12, and nylon-610, to much lesser extent. One must emphasize here that the excellent solvent power the TFE/ CHCl_3 mixtures showed toward nylon-12 and nylon-11 is observed despite the fact that neither TFE nor chloroform alone is a solvent for these polyamides. The rate of nylon-6 dissolution in the mixed solvents was up to seven times faster than in pure TFE. Such a large increase in the dissolution rate was found to be typical of all fully soluble systems tested.

Four ternary phase diagrams were prepared, all at 21°C. Each contained nylon-6, grade 8207, TFE, and a chloroalkane. Figure 3 describes the phase relationships in the system nylon-6/TFE/ CHCl_3 . Figure 4 describes the relationships in the system nylon-6/TFE/ CH_2Cl_2 . Figures 5 and 6 describe, respectively, the phase behavior in the nylon-6/TFE/ $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ and nylon-6/TFE/TCTFE systems. From Figures 5 and 6 one gathers that the addition of 1,2-dichloroethane or trichlorotrifluoroethane to TFE reduces its solvent power towards nylon-6. An added complication is to be found in part of the TCTFE-rich solutions of nylon-6 in TFE/TCTFE. Here, not all

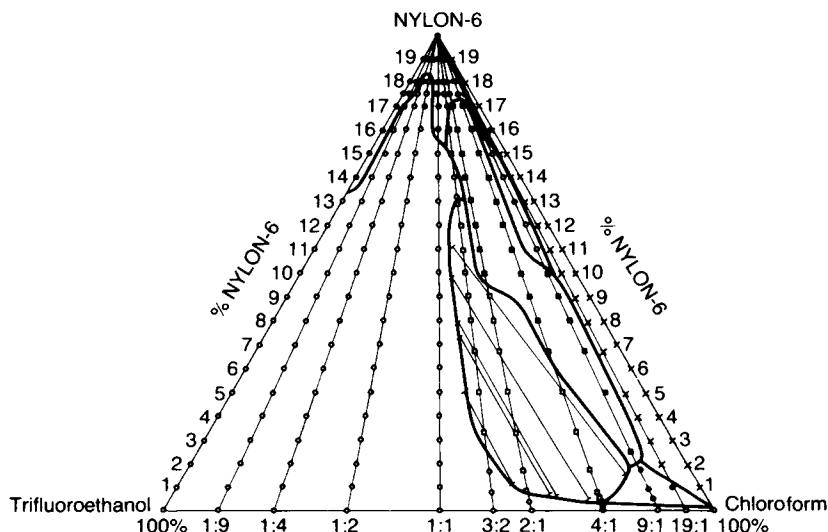


Fig. 3. Ternary phase diagram of nylon-6/TFE/ CHCl_3 : (○) completely soluble in one phase; (●) partly soluble in one phase; (□) completely soluble in two phases; (■) partly soluble in two phases; (X) insoluble.

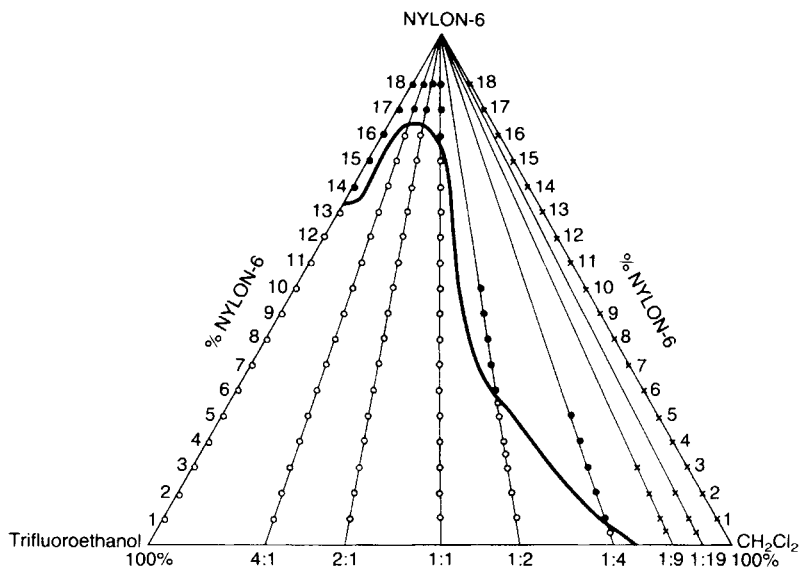


Fig. 4. Ternary phase diagram of nylon-6/TFE/ CH_2Cl_2 : (○) fully soluble in one liquid phase; (●) partly soluble in one liquid phase; (X) insoluble.

the polymer is soluble; yet the soluble fraction induces the solution to separate into two coexisting liquid phases. Because of the diminished solvent power manifested by the systems in Figures 5 and 6, they will not be further discussed in this report.

The systems nylon-6/TFE/ CHCl_3 and nylon-6/TFE/ CH_2Cl_2 both show, in Figures 3 and 4, respectively, that nylon-6 is more soluble in TFE-rich solvent mixtures than in TFE alone. The ternary phase diagram of nylon-6/TFE/ CHCl_3 is highly complicated and not fully understood by us at pres-

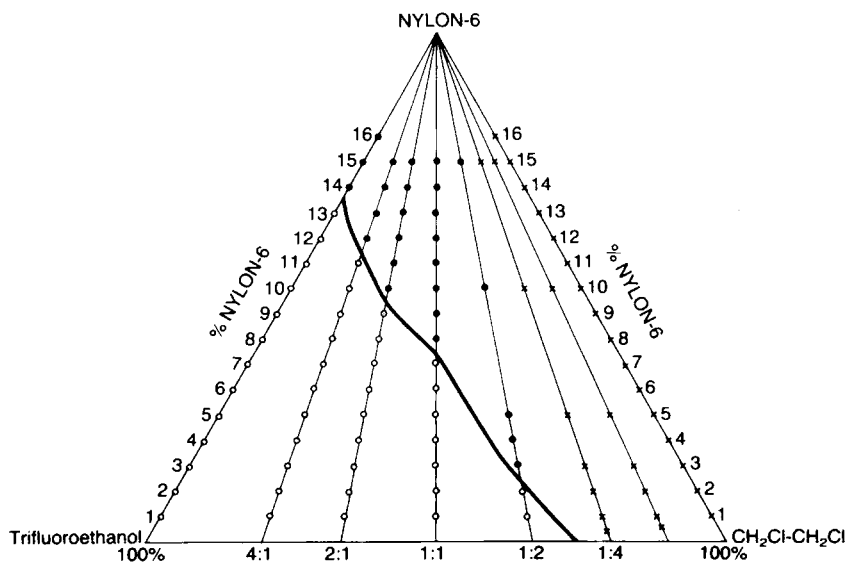


Fig. 5. Ternary phase diagram of nylon-6/TFE/ $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$: (○) fully soluble in one liquid phase; (●) partly soluble in one liquid phase; (X) insoluble.

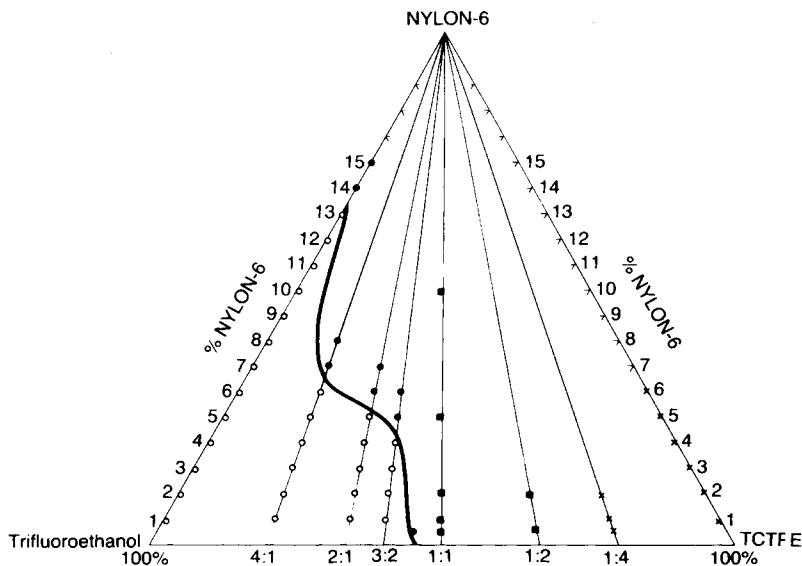


Fig. 6. Ternary phase diagram of nylon-6/TFE/TCTFE: (○) fully soluble in one liquid phase; (●) partly soluble in one liquid phase; (■) partly soluble in two liquid phases; (X) insoluble.

ent. The nylon-6/TFE/ CH_2Cl_2 diagram is far simpler. The main difference is that in no case did we observe two coexisting solutions in the nylon-6/TFE/ CH_2Cl_2 systems, while large composition ranges in the system nylon-6/TFE/ CHCl_3 were characterized by two coexisting solutions, immaterial of whether the polymer was completely or only partly soluble. The data in Figure 3 further indicate that nylon-6 is insoluble in chloroform and in 19:1 chloroform/TFE, yet shows a remarkable solubility at rather high polymer concentrations in 1:9 TFE/ CHCl_3 . This last feature will be dealt with briefly in the following discussion. Despite the differences in many of the details, the data over most of the solvent composition and polymer concentration ranges show gross similarity to the solvent/nonsolvent/polymer ternary phase diagrams of Tompa.¹³

Several of the biphasic liquid solutions in the nylon-6/TFE/ CHCl_3 system were carefully separated, the volume and weight of each liquid phase measured, and then each was evaporated to dryness and the weight of the polymer in it determined. From the measured volume and weights, the amount of polymer and the ratio of the solvents in each phase were determined. The results of this analysis are indicated by the tie-lines in the biphasic region of the ternary phase diagram in Figure 3. Intrinsic viscosity measurements were subsequently conducted on the polymers obtained from all analyzed phases. The determined intrinsic viscosities were all very close to one another, indicating that within experimental error the polymer which separated into the top, TFE-rich layer has the same molecular weight as the polymer which separated into the bottom, chloroform-rich phase. It is of interest to note that, for a fixed TFE/ CHCl_3 ratio, the volumes of the two liquid phases in the biphasic internal change with polymer concentration. Thus, for example, in the 3:2 or 2:1 chloroform/TFE biphasic regions, the TFE-rich top phase comprises a very small fraction of the total volume

at low polymer concentration. With increased concentration, the volume of the top liquid phase gradually increases at the expense of the heavier phase. Finally, the bottom phase vanishes, and a single liquid phase is obtained in which the polymer is fully or partly soluble.

The area of the biphasic region is very sensitive to changes in temperature T . At $T > 25^{\circ}\text{C}$, most of the 3:2 chloroform/TFE two phases collapse into a single solution. At $T > 40^{\circ}\text{C}$, most of the 2:1 chloroform/TFE biphasic interval is replaced by a single solution.

As in all other systems in Figures 3–6, the amount of soluble polymer in the system nylon-6/TFE/ CH_2Cl_2 was determined in each instance by dissolving the premeasured amount of semicrystalline polymer in previously prepared solvent mixtures. However, when the polymer was first fully dissolved in TFE and then the methylene chloride was added, significantly higher amounts of polymer remained in solution. Thus, for example, the 1:4 TFE/ CH_2Cl_2 mixture dissolves less than 1% nylon-6 when the polymer is placed in the mixture, and over 2% nylon-6 when the polymer is first dissolved in TFE and the CH_2Cl_2 then added. In the case of 1:9 TFE/ CH_2Cl_2 , no significant dissolution was observed in the first instance and over 1% solubility when first dissolved in TFE and the CH_2Cl_2 then added. This may indicate that, upon dissolution in TFE followed by dilution with CH_2Cl_2 , nylon-6 gains more free energy than its free energy of crystallization, and when dissolved in TFE/ CH_2Cl_2 mixture the free energy gain of nylon-6 is smaller than its free energy of crystallization.

Explanations of the remarkable solubility of the aliphatic polyamides in TFE/ CHCl_3 , assuming matched solubility parameters, must be invalid. It is well known¹⁴ that the solubility of nylon-66 (and of nylon-6 due to their similar structure and density) is $\delta = 13.6 \text{ cal}^{1/2} \text{ cm}^{-3/2}$. Based on group contributions to molar cohesive energy¹⁴ and the respective solvent density, one calculates solubility parameters of $\delta = 9.4 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ for chloroform and $\delta = 10.24 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ for TFE. Both these values are substantially lower than the solubility parameter of nylon-6 or nylon-66. Such large differences in solubility parameters usually prevent the dissolution of the polymer, unless there exist certain specific interactions between the polymer and the solvent, overriding these large differences.

The question arises if the polyamide chain in TFE/chloroalkane mixtures preferentially adsorbs molecules of one solvent or the other? To check on this point, two series of experiments were conducted as is described in the Experimental section, using lightly crosslinked nylon-6 and several TFE/ CHCl_3 and TFE/ CH_2Cl_2 mixtures. After normalizing with respect to the initial volume of the purified crosslinked polymer, the volumes of the solvent that were imbibed by the network were plotted as a function of the composition of the solvent mixture used for the polymer immersion. The results for TFE/ CHCl_3 and TFE/ CH_2Cl_2 were very similar, and Figure 7, for TFE/ CHCl_3 , is typical of both cases. It is obvious that the largest amount of solvent absorbed by the crosslinked nylon-6 is from the 2:1 TFE/ CHCl_3 mixture. Interestingly, even in pure chloroform, there was about 15 vol% solvent absorption. This indicates that small amounts of chloroform do penetrate the amorphous part of semicrystalline nylon-6. The insolubility of nylon-6 in chloroform indicates that this penetration is limited to the

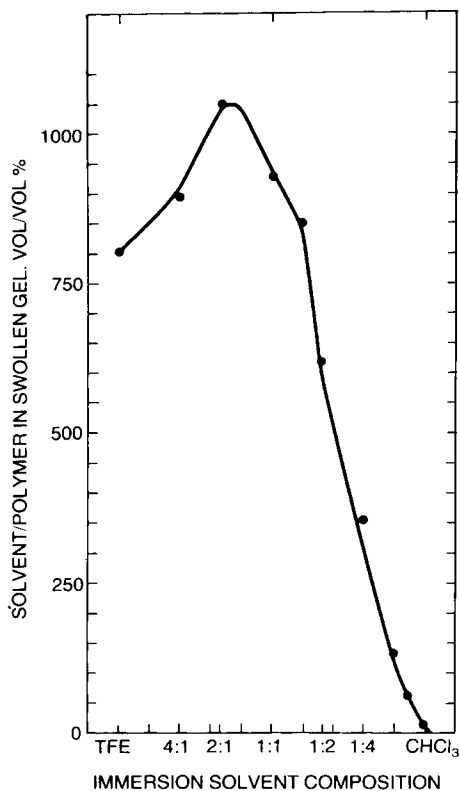


Fig. 7. Volume percent solvent imbibed by crosslinked nylon-6 network in TFE/CHCl₃, as a function of the immersion mixture composition.

amorphous fraction only, and that the nylon-6 crystallites remain intact in the presence of pure chloroform. A comparison of Figure 7 with the intrinsic viscosity curve in Figure 1 and with the boundary of complete nylon-6 solubility in a single liquid phase in Figure 3 shows a gross similarity in the shape of the three curves. This indicates, we believe, that the results obtained from the lightly crosslinked nylon-6 can be considered as representative of results from uncrosslinked polymer.

The composition of the solvent mixture imbibed by the swollen equilibrated crosslinked nylon-6 networks was determined by GC. The results for TFE/CHCl₃ and TFE/CH₂Cl₂ are plotted in Figures 8 and 9, respectively, in terms of the ratio R of each solvent found in the swollen network to its amount in the immersion solvent mixture. In each figure, the two curves, for TFE and chloroalkane, reveal a complicated dependence of the solvent composition in the network on its composition out of the network. The chloroalkane curves indicate that, throughout most of the composition range, less chloroalkane entered the swollen network than was present in the solvent mixture. Only when the amount of chloroalkane in the mixture fell to about 20%, we see an increase in the amount of chloroalkane in the swollen network to concentrations substantially above 20%. Mixtures containing less than 20% chloroform were not studied in this case, resulting in an incomplete CHCl₃ curve and a question mark concerning the exact

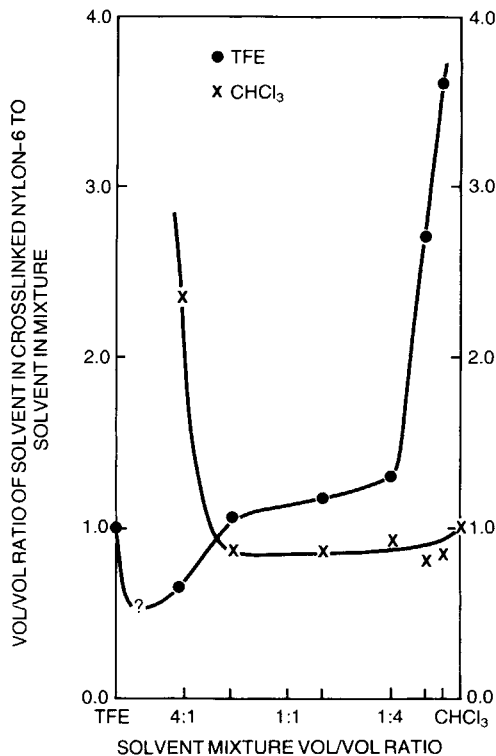


Fig. 8. Ratio of solvent in swollen nylon-6 network to its amount in the solvent mixture, plotted as a function of the immersion mixture composition; (●) TFE; (X) CHCl₃.

shape of the TFE curve in Figure 8. In the case of methylene chloride, mixtures containing down to 10% CH₂Cl₂ were studied, resulting in the more complete curves plotted in Figure 9. The TFE curves in both figures indicate that in all mixtures containing 2/3 or less TFE, the swollen nylon-6 network contained more TFE than the solvent mixture. The disparity between the volume fraction TFE in the swollen network and the volume fraction TFE in the immersion solvent mixture is especially large in mixtures poor in TFE. That is, when present in concentrations of 20% or less in the immersion mixtures, either chloroalkane or TFE will be absorbed by the swelling nylon-6 network in highly preferential amounts. In the intervening composition range, TFE is slightly preferred over either chloroalkane. In no case is the preference to the exclusion of the chloroalkane.

DISCUSSION

For a homogeneous mixture of two liquids at constant temperature T and pressure P , the Gibbs excess free energy of mixing ΔG_m is defined by

$$\Delta G_m = \Delta H_m - T\Delta S_m = \Delta E_m + P\Delta V_m - T\Delta S_m \quad (10)$$

where ΔH_m is the excess enthalpy of mixing, ΔE_m the excess internal energy of mixing, ΔV_m the excess volume of mixing, and ΔS_m the excess entropy

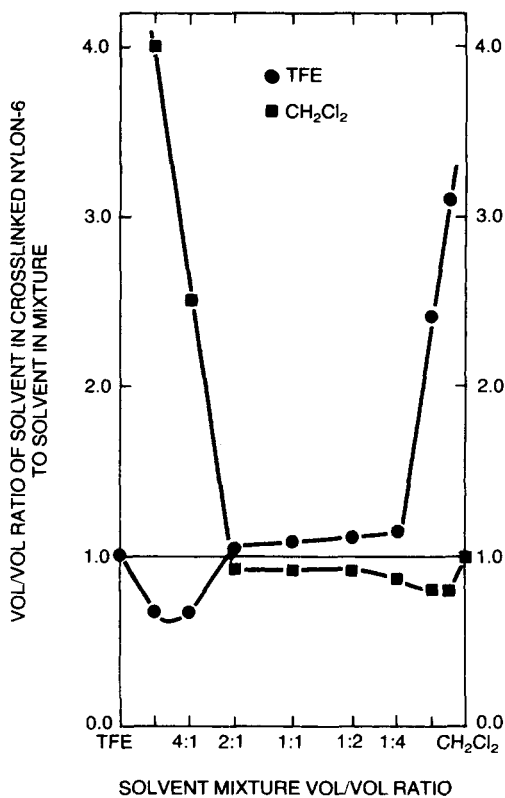


Fig. 9. Same as in Figure 8, but with TFE/CH₂Cl₂ immersion mixture: (●) TFE; (■) CH₂Cl₂.

of mixing. When two liquids spontaneously mix and reach a state of equilibrium, as was the case for our solvent mixtures TFE/CHCl₃, TFE/CH₂Cl₂, and TFE/CH₂Cl-CH₂Cl, the mixture is invested with a Gibbs free energy G lower than the sum of the free energies of the parent solvents. Thus, for the specified solvent mixtures,

$$\Delta G_m < 0 \quad (11)$$

We also know that, upon mixing and equilibrating, the volume of the mixtures increases significantly. Hence,

$$\Delta V_m > 0 \quad (12)$$

From the initial cooling upon mixing, and subsequent warming up to room temperature, we learn that the mixtures absorb heat from the environment; i.e., the mixing process is endothermic. Thus,

$$\Delta H_m > 0 \quad (13)$$

From the positive ΔH_m and ΔV_m and the negative ΔG_m we conclude that ΔS_m , in eq. (10), must be positive. The behavior of our solvent mixtures is,

thus, in agreement with the typical behavior observed in mixing two non-polar liquids.¹⁵ Furthermore, the observed volume expansion indicates that unfavorable energetic interactions take place¹⁵ between TFE and the chloroalkanes studied in this work. At first glance, the increased volume of the TFE-rich mixtures, with its attendant "free volume" increase, could be invoked to explain the excellent solubility and high dissolution rates of aliphatic polyamides in such solvent mixtures. However, in the chloroalkane-rich part of the solvent composition range, the excess volume of mixing is comparable to that of the TFE-rich region; yet the solvent power of the former mixtures is much smaller than that of the TFE-rich ones. Thus, a one-parameter, "free volume" approach to the solvent quality of TFE/chloroalkane mixtures fails to explain the observations.

An estimate of ΔE_m may be obtained¹⁵ from

$$\Delta E_m = Vv_1v_2(\delta_1 - \delta_2)^2 \quad (14)$$

where V is the volume of the mixture, v_1 and v_2 are the volume fractions of the two components, and δ_1 and δ_2 their solubility parameters. The molar volume of TFE is 77.64 cm³ and that of chloroform is 80.03 cm³. For one mole of a 1:1 v/v mixture of TFE/CHCl₃ we use the solubility parameters calculated above and obtain a value of $\Delta E_m = 13.9$ cal/mol. From eq. (10),

$$\Delta E_m = \Delta H_m - P\Delta V_m \quad (15)$$

and for TFE/CHCl₃ and TFE/CH₂Cl₂, ΔV_m at 1:1 v/v is about 1% of the volume of the system. This indicates that ΔH_m is slightly larger than ΔE_m , but, because of the usually large changes in pressure with temperature at constant volume, significant differences between ΔE_m and ΔH_m are possible.¹⁵

Using the solubility parameters given in the Results section, three interaction parameters, χ_{12} , χ_{13} , and χ_{23} , were calculated as was shown by Scott for a solvent/nonsolvent/polymer system.¹⁶ The calculations produced the physically meaningless values of $\chi_{12} = 0.096$, $\chi_{13} = 1.78$ and $\chi_{23} = 2.14$. Here χ_{12} is the interaction parameter between TFE and chloroform, χ_{13} is the interaction parameter between TFE and nylon-6, and χ_{23} is the interaction parameter between chloroform and nylon-6. In the following, χ_{12} and χ_{23} will represent the interaction parameter between either chloroalkane and TFE, and the interaction parameter between either chloroalkane and nylon-6, respectively.

Because of the substantial, yet incomplete, solubility of nylon-6 in TFE, the expected magnitude of χ_{13} should be in the interval $0 < \chi_{13} < \frac{1}{2}$. For complete miscibility of TFE and either chloroalkane, χ_{12} must be smaller than 2.0.⁴ At the same time, the volume expansion of the solvent mixtures indicates a very unfavorable tendency to form contact pairs, resulting in a rather large χ_{12} yet smaller than 2.0. In reporting the studies with cross-linked nylon-6 immersed in TFE/CHCl₃ mixtures, it was mentioned that the network soaked up a small amount of chloroform when immersed in this solvent. This indicates to us that while CHCl₃ is a nonsolvent for nylon-6, some interaction between the amorphous polymer and chloroform is

present, and $0.5 < \chi_{23} < 2.0$. When immersed in methylene chloride, the crosslinked network imbibes less solvent than in the case of chloroform, only about 5 vol %, indicating that for nylon-6/ CH_2Cl_2 χ_{23} is larger than for nylon-6/ CHCl_3 , but still smaller than 2.0.

It has been known for years that the degree of swelling of a lightly crosslinked network strongly depends on the "quality" of the solvent, or, in other words, on the solvent-polymer interaction parameter χ .⁴ It is also well known that parameters of semidilute (or semiconcentrated) solutions, such as osmotic pressure^{4,17-19} or macromolecular chain expansion,^{20,21} depend on the concentration c in the same manner as the elastic modulus of a crosslinked network. Thus, it is fair to draw conclusions from the swelling behavior of a lightly crosslinked network on the solvent-polymer interactions of its uncrosslinked analogue. Such an approach was adopted by Krigbaum and Carpenter in their treatment of phase equilibria in systems containing one polymer and two nonpolar liquids.²² Defining the composition ratio R as

$$R = (\phi_1/\phi_2)/(v_1/v_2) \quad (16)$$

where v_1 and v_2 are the volume fractions of liquids 1 and 2 in the binary, immersion, phase and ϕ_1 and ϕ_2 are the volume fractions of the corresponding liquids in the ternary, swollen network phase, they divide the phase behavior into three categories. For the case where the molar volume of the two liquids is the same, $V_1 = V_2$, or very close to it as is the case with TFE and CHCl_3 , $V_1/V_2 = l = 0.970$, and all χ positive, the first category is $\chi_{13} < \chi_{12} < l\chi_{23}$. In this category the formation of contacts between the polymer and liquid 2 are least favorable. Departures of R from unity are rather large and will increase as v_1 increases. The second category is $\chi_{12} < \chi_{13} < l\chi_{23}$, and it differs from category 1 in that here the interaction between the two liquids is most favored. Hence, departures of R from unity will be similar to those in category 1, but not as large. In the third category,

$$\begin{aligned} \chi_{13} < l\chi_{23} < \chi_{12} \text{ and } R > 1 \text{ when } \chi_{12}(v_1 - v_2) < (l\chi_{23} - \chi_{13}) \\ R < 1 \text{ when } \chi_{12}(v_1 - v_2) > (l\chi_{23} - \chi_{13}) \end{aligned} \quad (17)$$

For this category "the formation of contact pairs between molecules of the two liquids is discouraged. The presence of either liquid in the ternary phase will be relatively more favored when its volume fraction in the binary phase is small."²² A glance at our Figure 8 indicates that this is the case for the system of crosslinked nylon-6/TFE/ CHCl_3 . The preferential solvation of the minor solvent component, shown in Figure 8, seems to be the reason for the appearance of a region of nylon-6 solubility in the 1:9 TFE/ CHCl_3 mixture shown in Figure 3. In this case the polymer preferentially interacts with the TFE to such an extent that it becomes completely solubilized in the solvent mixture. Mixtures somewhat richer in TFE do not show such level of preference, leading to a reduction in the amount of polymer soluble in them, as can be seen for the 1:4 and 1:2 TFE/ CHCl_3 mixtures in Figure 3.

Taking into consideration all the above data, we can set magnitude ranges in which the various interaction parameters are expected to reside. For nylon-6/TFE/CHCl₃ and for nylong-6/TFE/CH₂Cl₂;

$$0 < \chi_{13} < < \frac{1}{2} < \chi_{23} < \chi_{12} < 2.0 \quad (18)$$

Comparison of our Figure 3 with Figure 7.5 of Tompa¹³ affords us a crude estimate of χ_{12} to be in the interval $1.5 \simeq \chi_{12} < 2.0$. The value of χ_{13} at 25°C was determined by Mattiussi et al.³ to be 0.094. As will be shown in the next paragraph, our viscosity data lead to $\chi_{13} = 0.090$. At the temperature of 21–22°C, where our experiments on ternary phase relationships and network swelling were conducted, the value of χ_{13} should be close to this value. This is, of course, in the range of expectation indicated in inequality 18.

Using the intrinsic viscosity values for nylon-6 grade 8207 indicated in Figures 1 and 2, the molar volumes of the TFE/CHCl₃ and TFE/CH₂Cl₂ obtained during the solvent mixing studies, and a specific volume of 0.9 cm³/g for the polymer, we followed Mattiussi et al.³ in applying the Stockmayer–Fixman theory to several of the solvent mixtures employed in the ternary phase diagrams in Figures 3 and 4, and obtained apparent solvent/polymer interaction parameters χ_a values as indicated in Table III. Because a single solvent approximation was applied to the mixtures, the χ_a of the mixtures with the polymer is considered to be an apparent interaction parameter. However, in the case of nylong-6/TFE, the interaction parameter χ_a is χ_{13} . The value of 0.09 determined by us is very close to the value obtained by Mattiussi et al.,³ lending credibility to the other χ_a values in Table III. At present we have insufficient data to obtain χ_a values for the systems described in Figures 5 and 6.

Returning to Figure 7, we notice that in pure TFE the crosslinked nylon-6 network contained slightly over 800% solvent. This translates to a network swelling ratio of 9.01, as defined by Flory.^{4,5} Using this value together with $\chi_{13} = 0.090$, $M_n \simeq 19,000$, and network density of 1.1 g/cm³, one can calculate a molecular weight between crosslinks of $M_c \simeq 10,450$. This value is lower than the value of $M_c \simeq 13,300$ obtained in the Experimental section

TABLE III
Nylon-6/Solvent Mixture Apparent Interaction Parameters^a

Solvent mixture	Solvent molar volume (cm ³ /mol)	Nylon-6 grade 8207 Intrinsic viscosity	Apparent interaction parameter χ_a
TFE	77.64	1.36	+0.090
1:1 TFE/CHCl ₃	79.535	1.37	+0.075
2:1 TFE/CHCl ₃	79.063	1.67	-0.138
4:1 TFE/CHCl ₃	78.352	1.62	-0.035
1:1 TFE/CH ₂ Cl ₂	71.94	1.45	+0.082
2:1 TFE/CH ₂ Cl ₂	73.64	1.53	+0.037
4:1 TFE/CH ₂ Cl ₂	75.17	1.50	+0.040

^a For TFE, χ_a is χ_{13} .

on the basis of reaction only at chain ends. At present we have no credible explanation for the difference in the M_c values. This difference does not affect in any way the conclusions arrived at in this work.

When a polymeric solute is placed in osmotic equilibrium with a mixture of two solvents, or when a lightly crosslinked polymeric network is immersed in such a binary mixture, a redistribution of solvent molecules between the two phases takes place. "The resulting difference in solvent composition between the two phases at thermodynamic equilibrium is termed preferential or selective solvent sorption (solvation)."²³ Two theories were developed over the years to explain the phenomenon of preferential solvation, neither of which proved to be successful in reproducing the experimental results of all ternary systems studied. One theory is an elaboration²⁴⁻²⁹ of the classical Flory-Huggins (FH) lattice model theory. This theory suffers from deficiencies³⁰ necessitating a different approach to the problem of ternary systems. The second (PFP) theory, developed by Flory³⁰ and by Patterson and Delmas,³¹ is based on ideas advanced by Prigogine.³² They state that the thermodynamic properties of a ternary polymeric solution result from two contributions: one from the contact energy between polymer segments and solvent molecules, and the second from the free volume dissimilarity between polymer chains and low molecular weight simple liquids. In addition to the free volume difference, the polymer-solvent interactions are assumed in the latter theory to take place on the molecular surfaces, emphasizing molecular surface ratios instead of the molecular volume ratios considered in the FH theory. In a later paper, Pouchly and Patterson³³ compared experimentally determined with theoretically calculated heats of solution and intrinsic viscosities. They clearly show that the FH lattice model theory produces values which strongly deviate in size and in sign from the experimental values. The PFP theory results in qualitative agreement with experiment, but may give values orders of magnitude different from the observed ones.³⁴ Although our results, especially those in Figures 7-9, are in qualitative agreement with the Krigbaum-Carpenter expectations²² based on the Flory-Huggins theory of polymer solutions, we decided not to attempt a quantitative fit of our data with either the FH or the PFP theory. This is due to the general inability of either theory to generate calculated values in close agreement with experiment, and to the very complicated nature of the phase diagrams obtained in our study (in Figs. 3, 4, and 6, in particular).

It should be noted that studies on the ternary systems of polyvinylpyrrolidone (PVP) dissolved in TFE/ CHCl_3 and in TFE/ $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ were reported in the literature about a decade ago.³⁵⁻³⁹ In contradistinction to the nylons investigated in the present study, TFE is the poor solvent for PVP while the chloroalkanes are the better ones. Furthermore, the solubility of PVP in TFE/ CHCl_3 mixture is poorer than in either solvent alone.³⁵ Despite these differences, some similarities between nylon-6/TFE/ CHCl_3 and PVP/TFE/ CHCl_3 do exist. Prominent among them is the appearance of a small biphasic interval in the PVP/TFE/ CHCl_3 ternary phase diagram,^{35,36} the phenomenon of preferential solvation³⁷⁻³⁹ and similarities in IR band position shifts with the composition of TFE-containing solvent mixtures.^{38,39}

To qualitatively sum it up: In our systems, each solvent prefers to interact with the polymer in order to minimize contacts with the other solvent. This preferred interaction is especially noticeable when a solvent is present in the system in relatively small amounts. It is probably the cause for the unique solubility characteristics of the aliphatic polyamides in the TFE/ CHCl_3 and TFE/ CH_2Cl_2 mixtures.

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