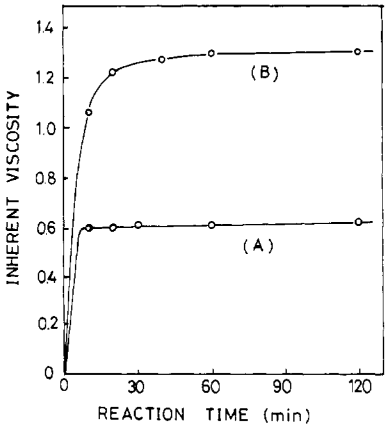

Figure 2. Polycondensation of **3** or **5** with ODA in NMP at 15 °C: (A) reaction of **3**; (B) reaction of **5**.

Table III
Polycondensation of Active Diamides with Diamines

active diamide	diamine	reaction conditions[a] solvent	time, days	polymer type	yield, %	η_{inh},[b] dL/g
5	ODA	NMP	1	**9a**	99	1.5
5	ODA	HMPA	1	**9a**	99	1.6
5	MDA	NMP	1	**9b**	99	1.2
5	MDA	HMPA	2	**9b**	99	1.2
5	HMDA	NMP	2	**9c**	72	0.44
5	HMDA	HMPA	2	**9c**	95	0.71
6	ODA	NMP	2	**10a**	98	0.67
6	ODA	HMPA	2	**10a**	96	1.0
6	MDA	NMP	1	**10b**	99	0.62
6	MDA	HMPA	2	**10b**	94	0.78
6	HMDA	NMP	1	**10c**	92	0.58
6	HMDA	HMPA	2	**10c**	99	0.54

[a] Polycondensation was carried out with 1.25 mmol of each monomer in 3 mL of solvent at 15 °C. [b] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 °C.

densation of active diamide **5** with ODA in NMP at room temperature is shown in terms of the inherent viscosity in Figure 2. Surprisingly, polycondensation was almost complete within 30 min and gave polyamide with an inherent viscosity greater than 1.0 dL/g. Table III indicates that polyamides were produced in quantitative yields with inherent viscosities of 0.5–1.7 dL/g.

The polymers obtained were identified as polyamides by comparing their infrared spectra with those of the authentic polyamides. Elemental analyses of the polymers also supported the formation of polyamides.

As expected, new active diesters and diamides derived from MB showed outstanding reactivity toward diamines and produced high molecular weight polyamides under mild conditions.

Acknowledgment. We are indebted to Mr. Sadao Kato for the performance of the elemental analyses.

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Adducts of Polyamides with Perfluoro Diacids

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ABSTRACT: Perfluoro diacids combine with matched aliphatic or aromatic polyamides to form highly crystalline stoichiometric adducts. Formation is associated with an approximate equivalence between the lengths of the extended diacids and the repeat unit of the polymeric chain. The interaction between the polyamides and diacids appears to be by means of hydrogen bonds. A proposed model suggests that the adducts precipitate out of solution once a sufficient number of intermolecular bonds are formed for the adduct aggregate to surpass a critical size for precipitation. Viscosity data support this model. Fluorinated monoacids and unfluorinated diacids do not form complexes, while excess urea blocks the formation of adducts with perfluoro diacids. Linear oligomers of ϵ-caprolactam of DP ≃ 25 and over combine with perfluoroglutaric acid to yield products similar to that obtained from nylon-6. Shorter linear oligomers did not form crystalline adducts.

Introduction

Synthetic macromolecules rarely interact stoichiometrically with small molecules to form ordered arrays.[1] In contrast, biological systems frequently exhibit specific inter- and intramolecular interactions, often involving hydrogen bonding, leading to well-defined tertiary structures.[2]

We here report the formation of highly crystalline adducts of synthetic aliphatic and aromatic polyamides with perfluoro diacids.

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Table I
Formation of Stoichiometric Crystalline Polyamide/Diacid Adducts[a–c]

polymer	perfluoro-succinic acid	perfluoro-glutaric acid	perfluoroadipic acid
nylon-6	WK	HR	WK
nylon-66	—	WK	YR
1:1 nylon-6 + nylon-66	NT	WK	NT
nylon-11	—	—	—
nylon-12	—	—	—
nylon-69	—	—	—
nylon-6/T	—	—	—
poly(*p*-benzamide)	NT	HR	NT
poly(*p*-phenylene terephthalamide)	NT	HR	NT
poly(*p*-benzanilidene terephthalamide)	NT	HR	NT

[a] HR, a crystalline adduct fromed within hours; WK, a crystalline adduct formed within one week; YR, a crystalline adduct formed within 1 year; —, no crystalline adduct was formed; NT, not tried. [b] All at polymer concentration within the 7.5–12% interval. [c] The formation of aliphatic adducts occurred at about the same rate in trifluoroethanol and *m*-cresol.

Experimental Section

Aliphatic polyamides were obtained from chemical supply houses or prepared in our laboratory. The aromatic polyamides poly(*p*-benzamide), poly(*p*-phenylene terephthalamide), and poly(*p*-benzanilidene terephthalamide) (from 4,4′-diaminobenzanilide and terephthalic acid) were prepared according to the procedure of Yamazaki et al.[3]

Typical preparation procedures of the adducts are given below.

Procedure 1. In a stoppered glass vessel equipped with a magnetic stirrer, 10.0 g of nylon-6 was dissolved in 80 mL of trifluoroethanol with gentle warming (≤50 °C). To the solution was added 10.7 g of perfluoroglutaric acid (1 diacid molecule/2 amide residues). Within minutes the diacid dissolved. The solution was allowed to cool to room temperature. After less than 1 h a voluminous precipitate formed. The trifluoroethanol was then either filtered off or removed under vacuum at 70 °C. This procedure was performed with other aliphatic polyamides in trifluoroethanol and with other diacids; see Table I.

Procedure 2. A solution of about 5% poly(*p*-benzamide) in dimethylacetamide (DMAc) containing 5% LiCl was prepared in a stoppered glass vessel by heating to 130 °C. Perfluoroglutaric acid was added to this solution in the ratio of 1 diacid molecule/2 amide residues. An adduct quickly precipitated. The hot solution was filtered and the solids were washed several times with DMAc. Drying was at 135 °C under vacuum. This procedure was used for the preparation of all adducts from aromatic polyamides.

Procedure 3. A solution of about 15% (w/v) oligomer was prepared by dissolving it at about 60 °C in trifluoroethanol. A 15% solution of the perfluoroglutaric acid in trifluoroethanol was added to yield a stoichiometry of 1 acid residue/amide unit. Each clear solution, of about 7.5% polymer concentration, was kept at about 50 °C for 15 min and then left at room temperature. After being observed for 1 week and reaching an apparent equilibrium, the systems were stripped from solvent under high vacuum, visually observed, and studied by X-ray diffraction. The results are presented in Table II.

Infrared (IR) spectra were obtained with a Perkin-Elmer spectrophotometer Model 283B. Wide-angle X-ray diffraction (WAXD) patterns were generated by a Norelco diffractometer operating in parafocus geometry with monochromatized copper radiation. For both measurements, the polymer adducts were pulverized in liquid nitrogen and examined at room temperature. Solution viscosities were measured at 25 °C in Cannon-Ubbelohde internal dilution glass viscometers and with a Nametre direct-readout viscometer.

Upon immersion in water, the crystalline adducts were destroyed and the polymer was regenerated. The resulting solutions were titrated and in all cases showed a stoichiometry of 1 diacid molecule/2 polymeric amide groups. The intrinsic viscosity of the starting and regenerated polymers was measured and, for the high molecular weight aliphatic polyamides, showed practically no reduction. Thus, hydrolysis plays no significant role in the adduct formation.

Differential scanning calorimetry (DSC) scans were performed with a DuPont 990 DSC instrument at a heating rate of 20 K/min under an argon atmosphere. Cross-polarized light, hot-stage microscopy was performed with a Reichert microscope operating at 100× magnification. The hot stage was calibrated by comparison with the melting points of standards and with DSC results.

Results and Discussion

The results of our experiments are presented in Tables I and II. All adducts of a high molecular weight polyamide and a perfluoro diacid were more crystalline than the parent polyamide. Levels of crystallinity were estimated from WAXD patterns by using the Hermans and Weidinger procedure.[4] The stoichiometry was uniformly 1 acid residue/polymeric amide residue (two polymeric amide

Table II
Reaction of Linear Oligomers of Nylon-6 with Perfluoroglutaric Acid[a]

oligomer	length, Å	results after 24 h	results after 48 h	results after 72 h	results after 7 days	results after stripping of solvent	X-ray results on solvent-stripped sample
DP = 2–5	17–43	clear soln, no adduct	same	same	same	viscous fluid	amorphous fluid
DP = 18	155	clear soln, no adduct	very small amount of haze	same	same	semisolid (tacky)	50:50 crystalline adduct/amorphous solid
DP = 26	224	a little adduct	more adduct, not yet slush	same	same	solid with some transparent areas	90:10 crystalline adduct/amorphous solid
DP = 36	310	mostly adduct, slush	more adduct, heavy slush	more adduct, heavier slush	same	solid	crystalline adduct
DP = 75	645	all adduct, solid	same	same	same	solid	crystalline adduct
nylon-6 (8207), $M = 19\,000$		all adduct	same	same	same	solid	crystalline adduct
DP = 170	1460	solid					

[a] All at oligomer concentration of 7.5%.

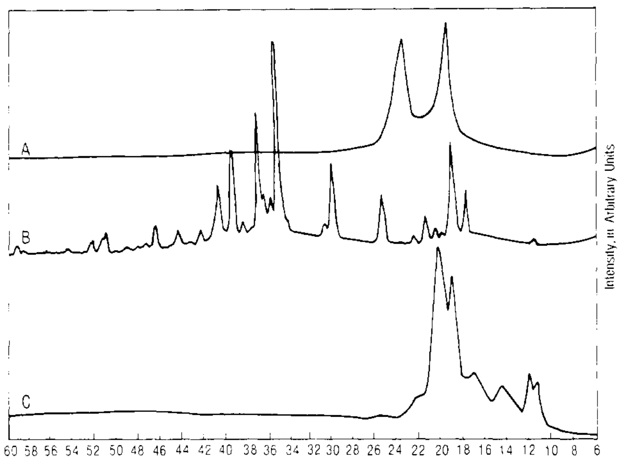

Figure 1. WAXD patterns of (A) well-annealed nylon-6, (B) perfluoroglutaric acid, and (C) nylon-6/perfluoroglutaric acid adduct.

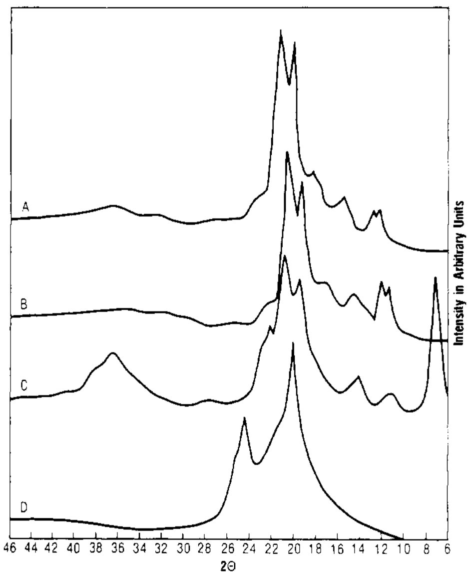

Figure 2. WAXD patterns of (A) nylon-6/perfluorosuccinic acid adduct, (B) nylon-6/perfluoroglutaric acid adduct, (C) nylon-6/perfluoroadipic acid adduct, and (D) nylon-6.

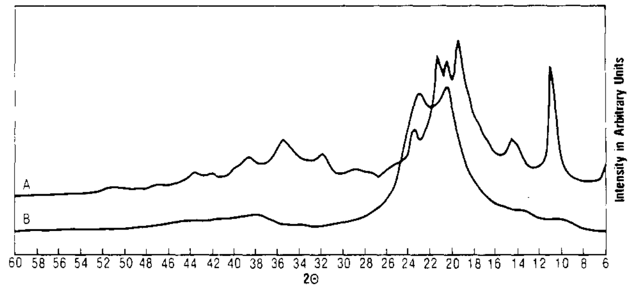

Figure 3. WAXD patterns of (A) nylon-66/perfluoroglutaric acid adduct and (B) nylon-66.

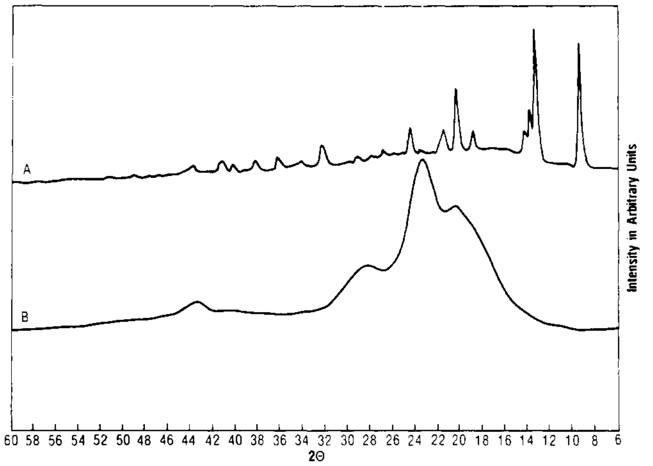

Figure 4. WAXD patterns of (A) poly(*p*-benzamide)/perfluoroglutaric acid adduct and (B) poly(*p*-benzamide).

functions for each diacid molecule). In no case was a crystalline adduct formed from a polyamide and a perfluorinated monoacid such as trifluoroacetic acid, heptafluorobutyric acid, or perfluorooctanoic acid or a nonfluorinated diacid such as glutaric acid. Also, no crystalline adducts were formed from a polyamide and lithium, sodium, or potassium perfluoroglutarate, $LiBF_4$, and KBF_4. No adducts were formed from polyamides and diester or diamide derivatives of perfluoroglutaric acid prepared in our laboratories.

Visual observations indicated that the rate of adduct formation was concentration dependent. Thus, at a concentration of 10 ± 2% the nylon-6/perfluoroglutaric acid adduct formed at room temperature within 1 h. At 2% concentration it required about 24 h and at 1% about 1 week. In the cases of adduct formation between perfluoro diacids and polymeric or oligomeric aliphatic polyamides, an increase in temperature resulted in slower adduct formation.

In Figure 1 the WAXD pattern of a nylon-6 sample of $M_n = 19\,000$ annealed for 16 h at 130 °C (A) is compared with the patterns of perfluoroglutaric acid (B) and the nylon-6/perfluoroglutaric acid adduct dried for 16 h at 70 °C (C). The unique structure of the adduct and its high crystallinity relative to that of the parent polymer are evident.

Figure 2 shows the WAXD patterns of nylon-6 and three adducts. The most important feature is the clear distinction between patterns A–C, of nylon-6/perfluoro diacid adducts, and pattern D, of the uncomplexed polymer. The patterns of the perfluorosuccinic acid and the perfluoroglutaric acid adducts, curves A and B, respectively, are remarkably similar to one another. The pattern of the perfluoroadipic acid/nylon-6 adduct (curve C) is significantly different from curves A and B. Curve D arises from nylon-6 that was subjected to dissolution, solvent stripping, and vacuum drying at 70 °C, a treatment similar to the one accorded to the adducts. When any of the above adducts was decomposed with water, the residual solid nylon-6 exhibited a WAXD pattern similar to curve D. In no case were diffraction patterns of the free perfluoro diacids observed in the samples of the polymeric adducts.

As indicated in Table I, the formation of the perfluoroglutaric acid/nylon-6 adduct occurred far more rapidly than the formation of the perfluorosuccinic acid and perfluoroadipic acid adducts under the same temperature and concentration conditions. With nylon-66, the perfluoroglutaric acid adduct formed in 1 week, the adduct with perfluoroadipic acid required more than 6 months, and no adduct was produced with perfluorosuccinic acid. Figure 3 shows the WAXD patterns of the perfluoroglutaric acid/nylon-66 adduct (A) and of nylon-66 that underwent the same dissolution and thermal treatment as the adduct (B).

Aromatic polyamides are insoluble in trifluoroethanol. Their adducts with perfluoroglutaric acid were prepared, therefore, according to procedure 2 above. Figure 4 shows the WAXD patterns of the poly(*p*-benzamide)/perfluoroglutaric acid adduct (A) and of the parent polymer poly(*p*-benzamide) (B) that was subjected to the same

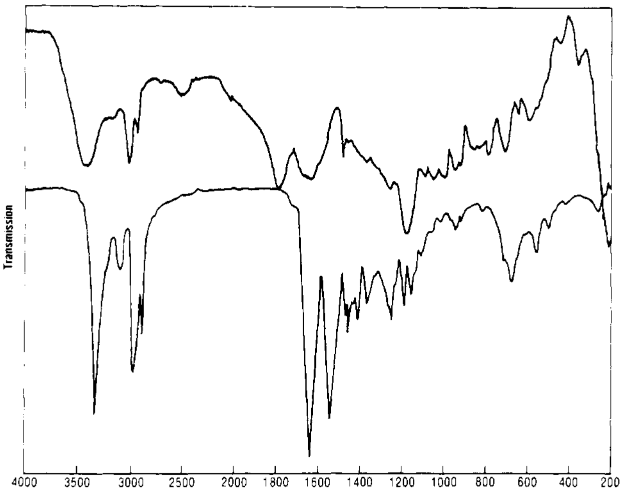

Figure 5. Infrared spectra of nylon-6/perfluoroglutaric acid adduct (top) and crystalline nylon-6 (bottom).

dissolution, solvent removal, and heat treatment as the adduct.

The melting characteristics of the polymeric adducts are of interest. DSC and microscopy indicate that the melting temperatures, T_m, of nylon-6/perfluorosuccinic acid adduct and nylon-6/perfluoroglutaric acid adduct are 108 and 111 °C, respectively. The T_m of nylon-66/perfluoroglutaric acid adduct is 75 °C. In all instances highly mobile, water-clear melts were formed. On slow cooling, the melts formed clear glasses. After several days at room temperature, microscopy showed a low level of crystallinity, indicating a slow rate of crystallization from the glass, similar in nature to the slow crystallization from the glass of the parent polyamide. When the adducts of poly(*p*-benzamide)/perfluoroglutaric acid and poly(*p*-benzanilidene terephthalamide)/perfluoroglutaric acid were heated, both softened at about 280 °C. At this temperature significant discoloration occurred, indicating possible degradation. An unequivocal determination of melting points was not possible.

An indication of the high levels of crystallinity and crystal perfection in the adducts can be gathered from the narrowness of their melting peaks in the DSC instrument. Thus, for instance, the width at half-height of the melting peak of perfluoroglutaric acid/nylon-6 adduct is 12 K while that of the parent nylon-6, annealed at 130 °C for 16 h, is 13 K.

In Figure 5 the IR spectra of perfluoroglutaric acid/nylon-6 adduct and crystalline nylon-6 are plotted. The intense band of nylon-6 at 1640 cm^{-1} (amide I) is substantially weaker, if at all present, in the adduct. The absorption at 1560 cm^{-1} (amide II) is not found in the adduct. A comparison of the spectrum of the adduct with that of neat perfluoroglutaric acid indicates that the intense absorptions of the adduct at 1760 and 1170 cm^{-1} correspond to the strongest bands in the perfluoroglutaric acid, the carbonyl and the C–F stretching vibrations, respectively.

The IR spectrum of the poly(*p*-benzamide)/perfluoroglutaric acid adduct (Figure 6, top) is different from that of the pure polymer (Figure 6, bottom). These spectra indicate that the carbonyl stretching band of the perfluoroglutaric acid in the adduct appears close to 1700 cm^{-1}, 60 cm^{-1} below that of the uncomplexed acid. For the perfluoro diacids in their ionized state, an intense doublet at lower frequency is expected, similar to that observed in perfluoro monoacids upon conversion from the protonated acid to the ionized state.[1c] Thus, one concludes that in the polymeric adducts studied in this work, the perfluoro diacids exist as protonated rather than ionized acids.

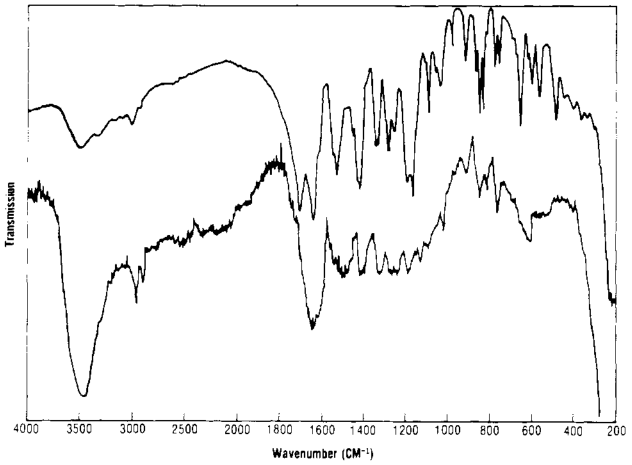

Figure 6. Infrared spectra of poly(*p*-benzamide)/perfluoroglutaric acid (top) and poly(*p*-benzamide) (bottom).

The results presented above indicate that in order to participate in a crystalline adducts, the perfluorinated diacid should be in its protonated form. The bonds formed with the polyamide are expected to be hydrogen bonds. The necessary presence of the acid hydrogen indicates that both the O—H···O=C—N—H and the =N—H···O=C—OH hydrogen bonds participate in adduct formation. The observations of Leiserowitz and Nader[5] on low molecular weight amide/dicarboxylic acid complexes show that the former hydrogen bond is remarkably short (0.250 nm) and thus likely to be a major contributor to the stability of the structures.

Models demonstrate that the fully extended perfluoroglutaric acid has about the same length as the caproamide repeat unit in nylon-6. The fit of a caproamide residue with perfluorosuccinic or perfluoroadipic acid is poorer. This is reflected in the low rates of formation of the perfluorosuccinic acid and perfluoroadipic acid adducts with nylon-6, as compared with the nylon-6/perfluoroglutaric acid adduct. The match of perfluoroglutaric acid with the alternating moieties along the nylon-66 chain was not as close as that of nylon-6; this resulted in the reduced ability of nylon-66 to form adducts with the perfluoro diacid. The match of the other two diacids with nylon-66 was even worse, a fact reflected in the drastic reduction in the rate of adduct formation. No fit exists between the perfluorinated diacids and repeat units in any of the other aliphatic polyamides in Table I. The inability of nylon-69, nylon-11, and nylon-12 to form stoichiometric crystalline adducts with the perfluorinated diacids investigated in this work then follows.

The length of the extended perfluoroglutaric acid approximates well the distance between two consecutive amide residues in the aromatic polyamides investigated. The very rapid adduct formation experimentally observed is in agreement with the expectation from such a fit.

Because the adducts formed only in cases where there was a reasonable match between the lengths of the diacid and the polymer repeat unit, it is our tentative conclusion that once the adducts are formed and precipitate out of solution, most diacid molecules lie parallel to the polymer chains in the adduct, with each diacid forming four hydrogen bonds with two consecutive amide groups in each of two adjacent polymer chains.

In order to determine whether prior to precipitation the process of adduct formation is wholly intramolecular with

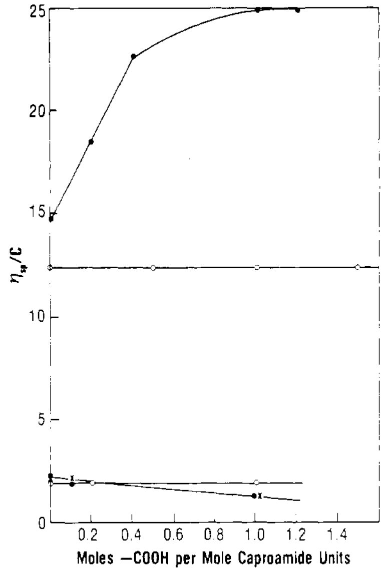

Figure 7. Reduced viscosity as a function of acid:amide ratio. Top curves: (●) 10% nylon-6 + perfluoroglutaric acid; (○) 8% nylon-6 + trifluoroacetic acid. Bottom curves: (●) 1% nylon-6 + perfluoroglutaric acid, two runs; (○) 9% nylon-6 + trifluoroacetic acid.

respect to the parent polyamide or involves intra- as well as intermolecular association, viscosity measurements were conducted on solutions of nylon-6 of $M_n = 19\,000$ in trifluoroethanol to which increasing amounts of perfluoroglutaric or trifluoroacetic acid were added. The viscosities were measured within 10 min from the addition of the acid. In this manner it was ensured that no adduct might precipitate before the measurements were completed. The results for polymer solutions of the order of 1 and 10% (w/v) concentration are shown in Figure 7. It is obvious that the addition of trifluoroacetic acid in quantities up to 1.5 times the molar amount of caproamide units did not affect measurably the reduced viscosity of the polymer. When the trifluoroacetic acid was replaced by perfluoroglutaric acid, the reduced viscosity of the ~1% solution slightly decreased with increasing amounts of diacid. In the concentrated (~10%) solution, the reduced viscosity sharply increased with addition of perfluoroglutaric acid, up to 1:1 ratio of acid to amide residues.

In both concentration regimes, the addition of a molar excess of urea fully eliminated the effects of the perfluoroglutaric acid on the solution viscosity.

No meaningful difference between the reduced viscosities of the resulting systems was observed upon the addition of trifluoroacetic acid or perfluoroglutaric acid to very dilute solutions of nylon-6 in trifluoroethanol (0.1–0.18% (w/v)). In solutions more dilute than these, a weak polyelectrolyte effect was observed in the presence of less than 1:1 molar amounts of either of these acids.

From data assembled by Kurata et al.[6] the radius of gyration of unperturbed nylon-6 of $M_n = 19\,000$ is calculated to be around 5.5 nm. From this, the concentration at which the polymeric coil (or the corresponding spheres) completely fills the available solution volume calculates to be about 4.5%. In our case the solvent is better than a Θ solvent and the concentration for complete space filling decreases. Our estimate is that the transition from dilute solution, in which polymer coils do not interpenetrate one another, to a concentrated solution, where interpenetration becomes evident, is in the 3–4% concentration interval. Importantly, even if our estimate is somewhat off, the ~1% polymer solutions above are definitely within the dilute regime and the ~10% solutions are deep in the concentrated region. The reduced viscosity curves thus reveal that in the dilute region the perfluoroglutaric acid forms intramolecular adducts with the nylon-6 in which some diacid molecules are associated with amide residues remotely placed along the chain. These diacid molecules thus pull the coil slightly closer than in their absence, as indicated by the decrease in reduced viscosity with the incremental addition of perfluoroglutaric acid. That only a small fraction of the diacid molecules serve to "bridge" together distant parts of the coil is gathered from the fact that the decrease in viscosity, although substantial, is not drastic. Because trifluoroacetic acid molecules cannot form such intramolecular "bridges" at any concentration, their addition does not affect the reduced viscosity. In the concentrated solution regime the same "bridge" formation by perfluoroglutaric acid molecules takes place. The fraction of diacid molecules participating in such bridges need not be very large, however. Because of the highly interpenetrated nature of the system, many of the bridges are intermolecular and not solely intramolecular. The intermolecular association results in the reduced viscosity rapidly increasing with added perfluoroglutaric acid, until all the amide residues are complexed. Further addition of diacid contributes no additional bridges, leaving the reduced viscosity unchanged.

Precipitation occurs once the complexes aggregate reaches a certain critical size, of which we have no estimate at present. The time it takes to reach this critical size is dependent on the polymer concentration and inversely dependent on the temperature, in agreement with observations. Because only a modest fraction of the diacid molecules participate in bridge formation, upon precipitation a rather ordered crystalline adduct is obtained in which most diacid molecules lie along the polymer chains, accounting for the necessary match between the diacid and polymer repeat unit length. Infrared scans showing the diacid in the solid adducts to be in its protonated form and the complete suppression by the addition of urea of the effects of perfluoroglutaric acid on the viscosity of nylon-6 solutions both indicate the interaction between the polyamide and perfluoro diacid to be hydrogen bonded in nature.

In order to determine the minimum degree of polymerization of nylon-6 required to form adducts, an attempt was made to complex perfluoroglutaric acid with several linear poly(ϵ-caprolactam) oligomers. From Table II, it is apparent that under the experimental conditions the very low molecular weight oligomers failed to produce crystalline adducts with perfluoroglutaric acid. As the length of the linear oligomer increased, a faster rate of formation and a larger quantity of crystalline adduct were observed, as well as a decreased amount of clear amorphous solid on the removal of solvent. The WAXD patterns of the perfluoroglutaric acid adducts with linear oligomers are presented in Figure 8. The patterns gradually shift with increasing degree of polymerization (DP) to those of nylon-6/perfluoroglutaric acid adduct (curve B in Figure 2). The crystal structure of the perfluoroglutaric acid adducts with the longer linear oligomers (Figure 8) is then the same as the structure of the high molecular weight nylon-6 adduct.

The fact that the rate of adduct formation increases with molecular weight of the oligomeric component may simply be explained by noting that a decreasing number of macromolecules is required in order for the adduct aggregate to reach its critical size for precipitation. During the week the experiment with oligomers was in progress, the oligomer with DP = 2–5 formed no aggregate large

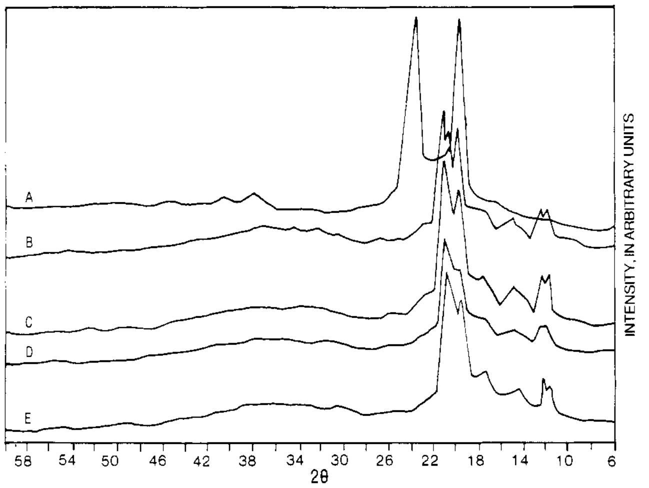

Figure 8. WAXD patterns of (A) linear oligomer of ϵ-caprolactam, DP = 18, (B) linear oligomer DP = 18/perfluoroglutaric acid adduct, (C) linear oligomer DP = 26/perfluoroglutaric acid adduct, (D) linear oligomer DP = 36/perfluoroglutaric acid adduct, and (E) linear oligomer DP = 75/perfluoroglutaric acid and adduct.

enough to precipitate, the oligomer with DP = 18 formed some, the one with DP = 26 formed more, and the higher oligomeric adducts precipitated completely.

As was mentioned above, intrinsic viscosities of high molecular weight aliphatic polyamides showed no significant reduction upon regeneration from the adducts. This indicates that in this case all macromolecules participated in the formation of adducts, with no segregation according to molecular weight. Because of the stoichiometry of the system, measured by titration, a simple occlusion of low molecular weight macromolecules in the precipitating adduct aggregates is unacceptable. A hypothetical explanation may be that the high molecular weight macromolecules in the polydisperse systems at hand serve with their associated diacid molecules as a matrix along which the lower molecular weight macromolecules (or oligomers) organize themselves. A similar capability of self-organization of oligomers along higher molecular weight molecules was recently reported in the literature.[7,8]

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Polydepsipeptides. 9. Synthesis of Sequential Polymers Containing Some Amino Acids Having Polar Side Chains and (*S*)-Lactic Acid

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ABSTRACT: Sequential polydepsipeptides having polar side chains were prepared by polycondensation of the active ester of the oligodepsipeptides. The N-protected oligodepsipeptides having polar side chains were synthesized by a new method using (*o*-nitrophenyl)sulfenyl N-carboxyl-α-amino acid anhydrides (Nps-NCAs) which were shown to react rapidly with the hydroxy group of (*S*)-lactic acid. The polymerization was carried out both by methods involving matrix-mediated thermal reactions and by condensation reactions in solution. Of the two, the solution polymerization yielded polymers in higher yields with high molecular masses ((2.3–12.9) × 10^4 daltons).

Introduction

Recent studies of polydepsipeptides have shown that these molecules exhibit conformational characteristics similar to corresponding polypeptides. Helix-to-coil transitions can be induced in these polymers both thermally and by changes of solvent.[2] Therefore, these macromolecules can serve as good model systems for the study of the helical structures of proteins and are specially well suited to study the role of hydrogen bonding in the stabilization of the helix.

To date our work has concentrated on amino acids and hydroxy acids with alkyl side chains (L- and D-alanine with (*S*)-lactic acid).[3,4] In this paper, we describe the first successful synthesis of polydepsipeptides having protected polar side chains. We have introduced a new method for the synthesis of the depsipeptide "monomers", which in-

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