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Communications to the Editor

Ordered, Stoichiometric Adducts of Polyamides with Perfluoro Diacids

Synthetic macromolecules rarely interact stoichiometrically with small molecules to form an ordered array.[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 (~70%) adducts of polyamides with perfluoro diacids. An example is poly(ϵ-caprolactam) (nylon-6) with perfluoroglutaric acid. The stoichiometry is 2 amide functions for each diacid molecule or 1:1 for each variety of carbonyl. The diacids were chosen so that in their extended form the spacing between the carboxyl groups approximates that between consecutive amide functions of the polymer. Adducts with relatively sharp X-ray patterns and well-defined melting points are obtained. The diacid can be removed by dissolution, leaving a porous solid with a crystallinity approximating that of the original polyamide.

Experimentally, the complex of poly(ϵ-caprolactam) and perfluoroglutaric acid was prepared by adding diacid to a solution of polymer in trifluoroethanol at <50 °C. After standing at ~20 °C for 1 h, the adduct was separated. X-ray diffraction patterns (Figure 1C) showed sharp lines indicating a high degree of crystallinity, perhaps 70–80%. The pattern was distinct from those of the crystalline diacid (Figure 1B) and from the substantially less crystalline (~40%) polyamide (Figure 1A). Clearly a new organization at the molecular level was present. Differential scanning calorimetry and microscopy indicated that the complex melted at 111 °C, forming a highly mobile, water-clear melt. On cooling, a clear glass was produced. This began to crystallize after several days at ~20 °C.

The importance of a match of extended chain separations between the carboxyls of the diacid and the amide of the polymer appears when other adducts are considered. Thus nylon-6 complexed with perfluorosuccinic and -adipic acids as well as with perfluoroglutaric acid (these adducts required 1 week to form, in contrast to the 1 h required with perfluoroglutaric acid) but nylons-11 and -12 did not. Longer perfluoroacids may well lead to adducts. A three-component complex was produced with nylon-6 in which the perfluoro acids were half adipic and half succinic, a system with several alternatives for the relative positioning of the diacid components. In this case, the complexation was complete within 1 h, 2 orders of magnitude more rapidly than with either acid alone. Equimolar amounts of perfluoroadipic or -succinic acid with perfluoroglutaric acid gave only small amounts of the glutaric adduct.

Negative results were obtained with perfluoro monoacids of length similar to that of the diacid and with the corresponding nonfluorinated diacids. This last observation may be due to the greater ease of rotation about protonated carbon–carbon single bonds.[3] This greater rotational freedom in solution for these acids may lead to a reduced tendency to assume the fixed structures expected in the solid complex. The lower acidity of the protonated acid, giving weaker hydrogen bonds with amide functionalities, could also contribute, but hydrogen bonding to the polar solvent should reduce the energy differences between solution and the solid adduct.

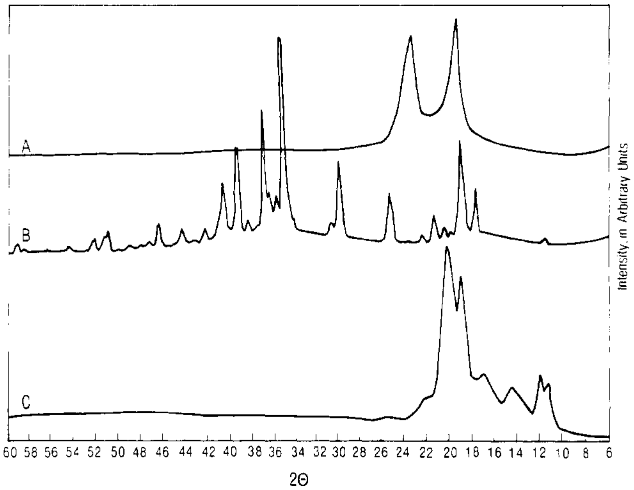

Figure 1. X-ray powder patterns: (A) nylon-6; (B) perfluoroglutaric acid; (C) adduct of perfluoroglutaric acid and nylon-6. Cu Kα (0.154 nm) radiation, T ~ 20 °C.

Infrared spectra indicated that there were substantial changes in the nylon-6 absorptions at 1640 and 1560 cm^{-1}, pointing to new interactions of the amide function, probably with the carbonyls and hydroxy groups of perfluoroglutaric acid. The carbonyl stretch in perfluoroglutaric acid at 1710 cm^{-1} shifted in the adduct to 1700 cm^{-1}. A larger change to lower frequencies would be expected for ionization of the acid. Thus the perfluoro acid exists in the adduct as hydrogen bond free acid and not as a salt.

Attempts were made to form adducts with the dilithium, disodium, and dipotassium salts of perfluoroglutaric acid and poly(ϵ-caprolactam). The last two remained as a separate phase embedded in the polymer. The lithium salt converted the polymer into an amorphous structure with no evidence of crystallinity. Such destruction of crystallinity in polyamides by lithium salts has been observed previously.[4] The origin is probably the strong bond of the cation to the carbonyl oxygens.

Experiments were also performed in which the average length of the polyamide chain was varied. It was found that with degrees of polymerization of less than 25, no adduct was formed. Only with longer chains was a crystalline adduct and with the characteristic X-ray pattern obtained. Presumably, the reduced entropy associated with higher degrees of polymerization assisted adduct formation.

It was also found that the cyclic dimer of ϵ-caprolactam was able to form an adduct with perfluoroglutaric acid. Here the 1:1 molecular complex forms well-defined crystals.

Adducts were also formed with other polyamides. Complexes of nylon-66 with perfluoroglutaric acid formed in 1 week, and with perfluoroadipic acid in about 6 months. No complex was produced with perfluorosuccinic acid.

When 10% solutions of the aromatic polyamides poly(*p*-phenylene terephthalamide), poly(*p*-benzamide), and poly(*p*-benzanilydene terephthalamide) in DMAC/5% LiCl at ~130 °C were mixed with perfluoroglutaric acid, stoichiometric adducts instantaneously precipitated. At,

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and below, the temperature of precipitation, these adducts were not liquid crystalline. As is true for the uncomplexed polymers, the adducts did not exhibit well-defined melting points. Instead, the last two produced softened systems at ~280 °C. Gradual decomposition of these polymers was noted when they were kept at ~280 °C, leading us not to test the modest molecular weight poly(*p*-phenylene terephthalamide) we had on hand. In all cases, the diacid could be removed from the adducts by dissolution.

The structures which are most reasonable for these adducts have the common features of a diacid forming a total of four hydrogen bonds with two parallel, oppositely oriented polyamide chains. Detailed crystal structures and understanding of the molecular packing will have to wait better-formed samples. Two points are likely to be of particular interest. Models indicate that the carbonyl–hydroxyl pair may adopt a cis orientation in the adduct, unlike the conformation found in acid-monomeric amide complexes.[5] The open spaces introduced between consecutive diacids in a plane may imply perpendicular arrays of complexed polyamide and diacid in the crystalline adduct.

References and Notes

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On the Material Time Constant Characterizing the Nonlinear Viscoelasticity of Entangled Polymeric Systems

In previous papers,[1,2] we have seen that the nonlinear behavior of concentrated polymer solutions can be well described by the Doi–Edwards theory[3] at times longer than a certain value τ_k, empirically determined for each solution, in the stress relaxation process. It has also be shown on the basis of a few available data that the quantity τ_k is related to the number of entanglements per molecule, M/M_e, through the simple relation[1]

$$\tau_1^0/\tau_k \simeq M/M_e \tag{1}$$

where τ_1^0 is the maximum relaxation time for the stress relaxation. In eq 1, M represents the molecular weight and M_e the molecular weight of the polymer chain between entanglements. Here we study τ_k over wide ranges of molecular weight and concentration and try to find its molecular-theoretical interpretation in view of the Doi–Edwards theory.

The Doi–Edwards theory is based on the tube model of de Gennes for entangled polymeric systems[4] and involves two characteristic times first proposed by de Gennes. One denoted as T_{eq} is the equilibration time of the fluctuation of contour length of a polymer chain confined in a tube. The other, T_d, represents the time for a chain to change shape completely through disengaging from a tube in which it is initially confined. In the Doi–Edwards version of the theory,[3,5] the quantitites T_{eq} and T_d are proportional to the second and the third power, respectively, of the number of entanglements per molecule. It is predicted that the stress at times sufficiently longer than T_{eq} following the application of stepwise strain should be factored into a function of time and one of magnitude of strain. The theory predicts also that the maximum relaxation time of the stress, τ_1^0, should be equal to T_d.

For stepwise shear deformations of polystyrene solutions, each of the stress components, i.e., the shear and normal stresses, could be factored into a function of time t and one of the magnitude of shear γ at times longer than a certain value τ_k determined for each solution.[1,2] The function representing the strain dependence of each stress component was in close agreement with that given by the Doi–Edwards theory. Equation 1 approximately represented the effects of molecular weight and concentration on τ_k evaluated from the then available data; the quantity M_e was evaluated from the relation

$$cM_e = 2 \times 10^4 \text{ g cm}^{-3} \tag{2}$$

where c is the concentration. One may suppose that eq 1 is in accord with the prediction of the Doi–Edwards theory that $T_d/T_{eq} \propto M/M_e$ under the plausible assumption that τ_k is a measure of the time sufficiently longer than T_{eq} and is a constant multiple of T_{eq}.

On the other hand, it is well-known that the maximum relaxation time τ_1^0 of polymer concentrates is approximately proportional to $M^{3.5}$ instead of $M^{3.0}$, the theoretical prediction. Thus we will be led to the relation

$$\tau_1^0/\tau_k \propto (M/M_e)^{1.5} \tag{3}$$

in place of eq 1, if we assume that T_{eq} is still proportional to $(M/M_e)^2$ and that τ_k is a constant multiple of T_{eq}. The tentative relation (1) is inconsistent with these assumptions. Incidentally the line below eq 16 of ref 1 is in error. It should be corrected as "Equations 4 and 5 lead to ...".

In order to investigate the detailed properties of τ_k, we measured the shear stress in a stepwise shear strain for a few polystyrene solutions. The polystyrene samples were the standard polystyrenes from Pressure Chemical Co. Molecular weights of the polymers, M, were 9.50×10^5 (lot no. 61208), 6.70×10^5 (no. 13a), and 2.33×10^5 (no. 50124). The solvent was a chlorinated biphenyl, Aroclor 1248, from Monsanto Chemical Co. Seven solutions were tested. The concentrations c are listed in Table I together with the methods of stress measurements and the results on τ_1^0/τ_k. For solutions of relatively low viscosities, the shear stress was measured with a relaxommeter of the cone-and-plate type,[6] represented by CP in Table I. For solutions of high viscosities, the stress was measured with a tensile tester,[7] represented by TT in Table I. In this case the sample was held between two parallel glass plates and the two plates were pulled in opposite directions with the tensile tester. Measurements were performed for magnitudes of shear γ ranging from 0.5 to 4. All the measurements were performed at 30 °C. The ratio τ_1^0/τ_k was determined through comparison of the shape of curves for various γ values on