Macromolecules 1987, *20*, 443–445

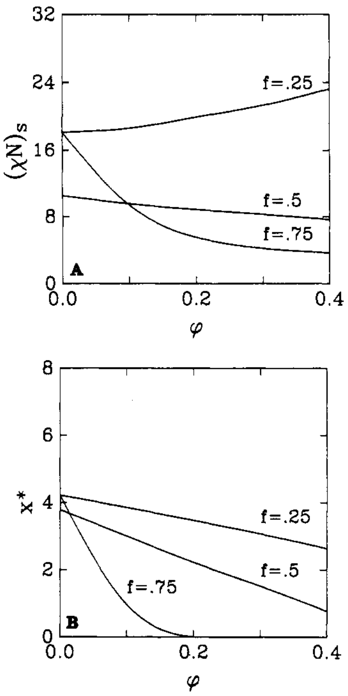

Figure 2. Block copolymer (A–B)–homopolymer (B) blend: (A) spinodal temperature $(\chi N)_s$; (B) x^* as a function of ϕ for $r = 1$ and $f = 0.25$, 0.5, and 0.75.

copolymers mixed with polystyrene or polybutadiene.

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Gelation and Solubilization of Aliphatic Polyamides in Tetrahydrofuran Using Lithium Perchlorate

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Mixtures of nylon 6 and inorganic salts, mainly metal halides such as LiCl, KI, and KBr, have been extensively studied over the past decade (see, for example, ref 1). In these efforts, the emphasis has been on the changes in the physical properties of nylon 6 arising from the solubility of these salts in nylon 6 even in the absence of any liquid diluent. Further, nylon 6 and other nylon type polyamides have been shown to be soluble in $CaCl_2$–methanol solutions.[2,3] We now report the swelling and eventual dissolution of aliphatic polyamides (nylons) in tetrahydrofuran (THF) in the presence of $LiClO_4$. The possibility of using the $LiClO_4$ complex of nylon 6 as a solid electrolyte and of drawing a fiber from nylon 6 gel were the motives behind this study.

Nylon 6 films (Type 77A) produced commercially by Allied Corp. were used in all our experiments ($[\eta] = 1.33$ dL/g, $M_n = 20\,000$, $M_w/M_n \approx 2$). Nylon 6,9 was obtained from Aldrich Chemical Co., nylon 6,10, nylon 11, and nylon 6,12 were purchased from Polysciences, Inc., nylon 12 was purchased from Emser Industries, and nylon 3 was obtained from H. K. Reimschuessel (Allied). X-ray diffraction (XRD) patterns were obtained at room temperature on a Philips automated powder diffractometer in the parafocus mode using Cu Kα radiation. Viscosities were determined with a capillary viscometer, using both *m*-cresol (a standard solvent) and the THF/$LiClO_4$ solution as solvents. Differential scanning calorimeter scans (DSC) were obtained on a Du Pont 9900 DSC apparatus. Infrared spectra were obtained on a Perkin-Elmer 953 spectrometer both in the ATR mode on a thick film and in the transmission mode on thin films sandwiched between KBr plates.

Polyamides do not dissolve in THF and it also was found that nylon 6 films changed very little when immersed in a solution of 0.25 M $LiClO_4$ in THF. At a salt concentration of 0.5 M, the nylon 6 film became whitish, at 0.75 M $LiClO_4$ the film lost its shape, and at 1.0 M $LiClO_4$ the film became a gel and did not dissolve in the solvent. The gel exhibited an ionic conductivity similar to that of the $LiClO_4$/THF solution, and this conductivity disappeared as the gel was dried. At a salt concentration of 1.5 M or higher, nylon 6 dissolved. At least 18 wt % of nylon 6 could be dissolved in a 2.0 M $LiClO_4$/THF solution (ca. 12 wt % in *m*-cresol). We also found that other nylons dissolved in THF at the following approximate concentrations of $LiClO_4$: nylon 3 at 2 M, nylon 6,6 at 4 M, nylon 6,9 at 2.5 M, and nylon 6,10 at 2.0 M. However, nylons with 10 or more CH_2 units, nylon 6,11 and nylon 11, dissolved very slowly over a period of several days in ~6 M $LiClO_4$/THF solution, and nylon 12 did not dissolve even in saturated (6–8 M) $LiClO_4$/THF solutions. We limited our detailed investigation to nylon 6.

Viscosity measurements were done to follow the changes in the molecular weight and the conformation of nylon 6 in solution. The intrinsic viscosity of a sample of nylon 6 in *m*-cresol was 1.33 dL/g. The intrinsic viscosity of nylon 6 in THF with 2.0 M $LiClO_4$ was 0.88 dL/g. The lower intrinsic viscosity in $LiClO_4$/THF as compared to that in *m*-cresol suggests a smaller spatial extension of nylon 6 in $LiClO_4$/THF. The viscosities of nylon 6 reprecipitated from the gel and from the solution ($LiClO_4$/THF) as measured in *m*-cresol are similar to that of the original nylon 6 (1.38 vs. 1.32 dL/g; thus in fact slightly higher), suggesting that nylon 6 was not degraded in the $LiClO_4$/THF solvent.

X-ray diffraction scans of nylon 6 variously treated with $LiClO_4$/THF solutions are shown in Figure 1. The gel freshly prepared by immersing nylon 6 in 1.0 M $LiClO_4$/THF for ~15 h was amorphous (Figure 1a). Drying the gel under vacuum at 22 °C crystallized $LiClO_4{\cdot}3H_2O$ but nylon 6 apparently was still complexed with Li^+ and ClO_4^- ions and thus remained amorphous (Figure 1b). The

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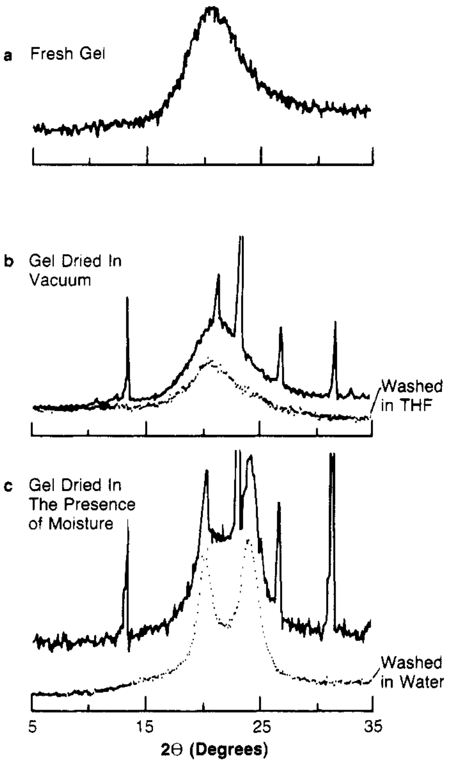

Figure 1. X-ray diffraction scans of nylon 6 in 1.0 M $LiClO_4$/THF: (a) fresh gel; (b) gel dried under vacuum before (full line) and after (dotted curve) washing for ~2 h in THF; (c) gel dried in the presence of moisture before (full line) and after (dotted curve) washing the $LiClO_4$ in sample b with water.

crystals of $LiClO_4{\cdot}3H_2O$ could be washed off by immersing ~2 h in THF, and the resulting specimen was dried under vacuum at 22 °C to give an amorphous nylon 6–$LiClO_4$ complex (Figure 1b, dotted curve). Separation of nylon 6 (α-crystalline form) and $LiClO_4$ ($LiClO_4{\cdot}3H_2O$ crystals) occurred when the gel was dried in the presence of moisture (Figure 1c). Both the fresh and the dried gel and the precipitate obtained from solutions in $LiClO_4$ (>1.5 M)/THF by adding water showed only the α form of nylon 6 after a thorough washing in water or THF followed by drying (Figure 1c, dotted curve). The vacuum-dried gel is elastic, and its toughness appears to decrease with an increase in $LiClO_4$ concentration. The gel could be drawn into a fiber and, as ascertained from the XRD photographs, this orientation was preserved in the α form obtained after washing with water.

Infrared spectra of the dried gel are shown in Figure 2. The amide I and amide II bands and especially the N–H stretch (3300 cm^{-1}) are visible in the spectra, suggesting that the hydrogen bonds are not completely destroyed. There are some "free" or non-hydrogen-bonded N–H frequencies in the 3375–3588-cm^{-1} region. The fraction of the "free" N–H groups is probably at least an order of magnitude higher than that indicated by the ratio of the "free" and hydrogen-bonded N–H absorbances.[4] The intensities of these N–H bonds vary with the state of the complex and are different for a fresh gel, dried gel, or an aged complex.

The DSC scan of a partially dried gel (no crystallization of $LiClO_4$) at 1.0 M $LiClO_4$ showed two amorphous relaxations at −79 and at −11 °C (glass transition temperatures, T_g's). Only one T_g was observed at −14 °C in the DSC scan of a sample before it was dried. While the T_g near −12 °C may be due to the plasticization effect of THF, the T_g at −79 °C is probably associated with the nylon 6–$LiClO_4$ complex. A gel dried under ambient conditions (i.e., in the presence of moisture; see XRD scan in Figure 1c) has a T_g of 48 °C (cf. 33 °C for the uncomplexed starting film), consistent with the XRD observation that nylon 6 has phase separated and crystallized into the α form.

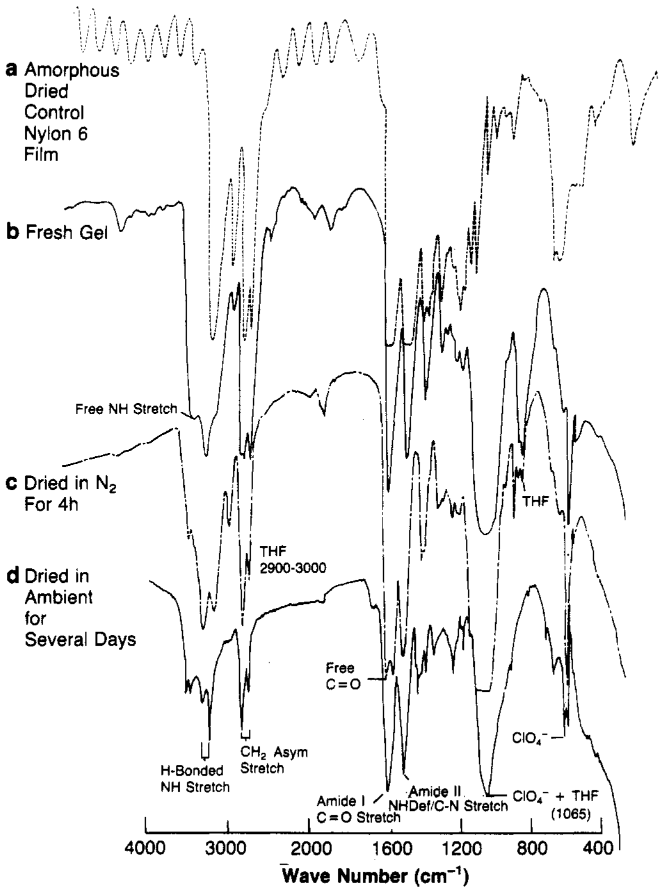

Figure 2. Infrared spectra of nylon 6 films cast from 1.0 M $LiClO_4$/THF gel: (a) typical spectra from uncomplexed, unannealed nylon 6 film; (b) fresh gel; (c) dried for ~4 h; (d) dried for several days.

Elemental analysis was carried out on gels to determine the molar concentrations of $LiClO_4$, THF, and nylon 6. Nylon 6 was gelled for ~16 h in 1 M $LiClO_4$/THF and dried under vacuum at 22 °C to remove excess THF. $LiClO_4$ crystallized during this drying was washed off with THF for ~30 min (if less than ~30 min, then all free $LiClO_4$ could not be removed, and if more than ~30 min, then nylon 6 would crystallize into the α form), the sample was again dried under vacuum at 22 °C to remove excess THF, and this amorphous gel was analyzed. Since any further washing of this gel in THF leads to the crystallization of the α form, the concentration of $LiClO_4$ in this gel is the minimum necessary to keep nylon 6 amorphous. Elemental analysis of such a gel gave the following result: nylon 6 + $(THF)_{0.5}$ + $(LiClO_4)_{0.5}$ + $(H_2O)_2$. The two molecules of water were probably absorbed from the atmosphere between the time the gel was prepared and analyzed.

It is likely that Li^+ and ClO_4^- ions interact with the CO^- and NH^+ groups, respectively, of nylon 6, thus preventing the formation of the interchain NH–OC hydrogen bonds and therefore swelling nylon 6 in THF at low salt concentrations and solubilizing it at higher salt concentrations. This mechanism differs from the one in which LiCl in dimethylacetamide (DMA) is known to solubilize aromatic polyamides. For example, Panar and Beste[5] suggest that the positively charged DMA–Li^+ species solvates the negatively charged poly(1,4-benzamide)–Cl^- complex, and the resulting neutral entity is soluble in DMA. In dried specimens, the nylon 6–$LiClO_4$ complex remains amorphous probably because CO–NH links, i.e., hydrogen bonds, are energetically less favored than NH–ClO_4^- and CO–Li^+ links. The "free" N–H stretch vibrations in the 3375–3588-cm^{-1} region support such a mechanism. Although at high salt concentrations each of the CO and NH groups may interact with separate Li^+ and ClO_4^- ions, at the limiting salt concentration in a gel, elemental analysis has shown that two amide groups are associated with one Li^+ and one ClO_4^- ion. Therefore, a single ion may coordinate with more than one amide group, and the resulting pseudo-cross-linked structures may give the complex the texture of a gel. Upon the addition of water or excess THF to the solution of nylon 6 in THF/$LiClO_4$ (or to the gel or to the amorphous dry complex), Li^+ and ClO_4^- ions are preferentially solvated by water molecules or by THF. Nylon 6 now readily forms hydrogen bonds within its own species and thus crystallizes into the α form.

In conclusion, the gelation and solubilization of nylons in THF and the formation of an amorphous nylon 6–$LiClO_4$ complex upon drying are attributed to the interaction of Li^+ and ClO_4^- ions with the CO and NH groups of nylons. Removal of Li^+ and ClO_4^- ions either by solvation with water molecules or by THF leads to the crystallization of nylon 6 in the α form. Nylons are not degraded in the presence of $LiClO_4$, the gel can be drawn into a fiber, and nonbonded N–H groups are present even in dried complexes.

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Registry No. THF, 109-99-9; $LiClO_4$, 7791-03-9; nylon 6 (SRU), 25038-54-4; nylon 6,6 (SRU), 32131-17-2; nylon 3 (SRU), 24937-14-2; nylon 3 (homopolymer), 25513-34-2; nylon 6,9 (SRU), 28757-63-3; nylon 6,9 (copolymer), 27136-65-8; nylon 6,10 (SRU), 9008-66-6; nylon 6,10 (copolymer), 26123-27-3; nylon 6,11 (SRU), 50732-66-6; nylon 6,11 (copolymer), 27967-39-1; nylon 11 (homopolymer), 25587-80-8; nylon 11 (SRU), 25035-04-5.

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Simultaneity of Initiation and Propagation in Living Polymer Systems

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Polymerization free of termination and chain transfer is referred to as living polymerization. This kind of system is often encountered in ionic polymerizations, and provided that initiation is virtually instantaneous and propagation irreversible the resulting polymers are characterized by a Poisson molecular weight distribution; i.e., for high degrees of polymerization they have nearly uniform size. Slow initiation broadens molecular weight distribution, a disturbing effect observed, e.g., in anionic polymerization of vinyl and diene monomers initiated by organolithium compounds, especially *n*-butyllithium in hydrocarbon solvents.

It was suggested in several publications[1] and again in a recent monograph[2] that such a broadening may be prevented by means of the so-called "seeding technique" based on the following concept. A *small* fraction of the monomer to be polymerized is mixed with *all* the initiator to be used in the reaction. The mixture is left to react for a while, and thereafter the bulk of the monomer is added. It is believed that *all* the initiator, however slowly initiating the polymerization, will react *quantitatively* with the *small* amount of monomer supplied initially, provided that the mixture is allowed to react for a sufficiently long time. Then, on addition of the remaining monomer, the previously formed oligomers will propagate the polymerization of the added bulk of the monomer, yielding product of uniform size because the slow initiator was already consumed.

Contrary to the published claims, this technique cannot eliminate the undesired broadening of molecular weight distribution in virtually irreversible propagation. This is proved in the present paper, and the derived conclusions are confirmed by the experiments reported here. The misconception of this approach becomes obvious by considering first a simple kinetic scheme. Let an initiator I react with a monomer M in a bimolecular fashion with rate constant k_i. The resulting living polymers P* propagate, again in a bimolecular reaction, with propagation constant k_p, smaller than the initiation constant k_i. It will be shown that, whatever the concentration of the added monomer and however large is k_i, the initiator cannot be consumed *quantitatively* in irreversible polymerization ensuing in this system.

Simple Case. First-Order Initiation and Propagation

The kinetics of this system is described by three differential equations, $-\mathrm{d}I/\mathrm{d}t = k_iIM$, $-\mathrm{d}M/\mathrm{d}t = (k_iI + k_pP^*)M$, and $\mathrm{d}P^*/\mathrm{d}t = k_pIM$, with initial conditions at $t = 0$, $I = I_0$, $M = M_0$, and $P^* = 0$. The symbols I, M, and P^* denote the respective concentrations. It follows that

$$\mathrm{d}M/\mathrm{d}I = 1 + (k_p/k_i)(I_0 - I)/I$$

because $P^* = I_0 - I$, since each molecule of I forms one P* on reaction. Hence, M is a function of I and $I_0 - I$ only, being independent of M. Thus

$$M = M_0 + (1 - k_p/k_i)(I - I_0) + (k_p/k_i)I_0 \ln (I/I_0)$$

The amount I_r of the residual initiator left after all the monomer was polymerized is given by the solution of the equation

$$M_0 = (k_p/k_i - 1)(I_r - I_0) - (k_p/k_i)I_0 \ln (I_r/I_0)$$

Therefore, contrary to the expectation of some workers, the initiator cannot be used up *quantitatively*, whatever the initial concentration of the monomer, provided that initiation and propagation are irreversible.

These conclusions are clearly revealed by Figure 1. The curves M vs. I shown in this graph have identical shape for a constant I_0, being only displaced parallel to the M axis for various initial values of M_0. They are all approaching the M axis asymptotically as I tends to zero

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