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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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R. S. Stein^a; M. Sethumadhavan^a; R. A. Gaudiana^b; T. Adams^b; D. Guarrera^b; S. K. Roy^b

^a Polymer Research Institute The University of Massachusetts, Amherst, Massachusetts ^b Materials Research Laboratory, Polaroid Corporation, Cambridge, Massachusetts

To cite this Article Stein, R. S. , Sethumadhavan, M. , Gaudiana, R. A. , Adams, T. , Guarrera, D. and Roy, S. K.(1992) 'Molecular Composites Comprising Rodlike Polyamides and Vinyl Polymers', Journal of Macromolecular Science, Part A, 29: 7, 517 – 531

To link to this Article: DOI: 10.1080/10101329208052179

URL: <http://dx.doi.org/10.1080/10101329208052179>

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MOLECULAR COMPOSITES COMPRISING RODLIKE POLYAMIDES AND VINYL POLYMERS

R. S. STEIN and M. SETHUMADHAVAN

Polymer Research Institute
The University of Massachusetts
Amherst, Massachusetts 01003

R. A. GAUDIANA,* T. ADAMS, D. GUARRERA, and S. K. ROY

Materials Research Laboratory
Polaroid Corporation
750M-5C
Cambridge, Massachusetts 02139

ABSTRACT

At present we have strong evidence that several members of a series of wholly-aromatic, para-linked, rodlike polyamides, polyesters, and polyesteramides form molecular composites with certain flexible-chain, thermoplastic polymers over a wide range of compositions. This paper reports on the initial results of an investigation of intermolecular interactions using spectroscopy and various scattering techniques as well as characterization of some of the mechanical and optical properties of these materials. The composites are made by two techniques: 1) photopolymerization of a homogeneous solution of a rodlike polymer in a monomer containing a photoinitiator; 2) solvent evaporation from homogeneous solutions of very limited combinations of solvent, rodlike polymers and flexible polymers. While both of these techniques produce optically clear, nonscattering films of various thicknesses over the entire compositional range, e.g., 1–99 wt% of rodlike polymer, the latter is generally more convenient and has been used extensively in this study.

Optical and electron microscopy, wide angle light scattering, and spectroscopic and thermal analysis support the view that these polymer combinations are truly molecularly dispersed.

INTRODUCTION

For the past several years our laboratories have been engaged in a joint project aimed at producing molecular composites exhibiting superior mechanical and optical properties.

Molecular composites are dispersions of stiff molecules in a matrix of flexible chains. Attempts to make these by casting from a mutual solvent usually lead to phase-separated systems. This is to be expected on the basis of theories of Onsager [1] and Flory [2, 3] which predict that it is not possible to achieve a molecular dispersion of the rods in coils due to unfavorable entropic interactions.

Our interest in molecular composites is based on the anticipated unique set of optical, thermal, and mechanical [4] properties which might result from systems of this type. For example, in regard to mechanical properties, composite theory suggests that the modulus, E , of a filled system is related to that of the unfilled system, E_0 , by the equation

$$E = E_0[1 + A(f)\Phi \dots]$$

where A = reinforcing ability of the filler

f = aspect ratio (L/D)

Φ = volume fraction of filler

Continuum theory expresses $A(f)$ as an increasing function of the aspect ratio which suggests that, if this theory can be extrapolated to molecular dimensions, stiff, rodlike molecules should very effectively enhance the modulus and strength of the composite. However, there is reason to believe that as the filler particles approach molecular dimensions, their stiffness is diminished and they become "floppy rods." It is of great theoretical and practical importance to determine whether or not continuum theory applies to the molecular level.

Some of the benefits of molecular composites might be most dramatically manifested in highly oriented systems. For example, in addition to mechanical properties, oriented molecular composites would find applications in high value added devices which utilize optical properties such as birefringence, dichroism, and nonlinear optics. Since heat conduction occurs more efficiently intramolecularly (through bonds) than intermolecularly (across van der Waals distances), it is likely that orientation of the rodlike molecules in a composite would impart anisotropic thermal conductivity to molded parts which might find application in microelectronics.

The motivation for this research is the discovery of a class of semiflexible, wholly-aromatic, para-linked polyamides, polyesters, and polyesteramides which are noncrystalline and extremely soluble in common organic solvents [5]. The strategy followed in the initial phase of this earlier research was the preparation of homogeneous solutions of a rodlike polymer with a flexible chain polymer in a low boiling solvent. It was hoped that the polymers would remain completely dispersed after the solvent was removed by evaporation and yield a homogeneous polymer

blend. Unfortunately, phase separation occurred at very low concentrations of rodlike polymer in flexible chain polymer, and vice versa, as demonstrated by light-scattering and neutron-scattering techniques used for defining the state of dispersion of these blends. These earlier studies defined phase diagrams for the rod/coil/solvent system [6, 7] and confirmed the theoretical predictions of Onsager and Flory that the range of mutual solubility is very limited, resulting in a strong driving force toward undesirable aggregation of rods.

Attempts have been made and are in progress in our laboratories and other research groups worldwide to find techniques for minimizing or eliminating this aggregation and for optimizing the stability of the dispersion of the rod/coil composites. These involve:

1. Selecting solvents and rodlike and coil molecules with specific interactions to enhance enthalpy of mixing.
2. Increasing the flexibility of the rods in an effort to increase their entropic mixing.
3. Grafting of flexible chains on the backbone of the rods so as to prevent entropy driven demixing.
4. Controlling kinetics of aggregation.

As mentioned previously, our initial attempts to obtain molecular composites by means of Method 1 merely confirmed Flory's theory of rod/coil thermodynamics. However, a very recent paper describes a successful attempt to enhance enthalpic interactions between rodlike and flexible chain polymers. A nearly complete molecular dispersion of 50 wt% of poly(*p*-phenylene benzobisthiazole) and poly(2-acrylamido-2-methyl-propanesulfonate) was obtained in the form of films and fibers by coagulating a methane sulfonic acid solution of the polymers in water. Strong coulombic interactions between protonated thiazole rings and pendant sulfonate groups prevented phase separation [8].

Although Method 2 has met with some success in other laboratories [9] due to the fact that increasing the flexibility of the rods enhances solubility and increases entropic mixing, more flexibility should limit the reinforcing effectiveness of the rods, and we have chosen not to investigate this approach. In regard to Method 3, the synthetic difficulty encountered in attempting to graft or grow flexible chains directly on the backbone of a rodlike polymer is far greater than originally anticipated, and this approach has met with only limited success in our laboratories and has been temporarily discontinued. However, a strategy which incorporates a hydroquinone-endcapped, low molecular weight polystyrene [10a] or polymethyl methacrylate [10b] as a comonomer in the synthesis of an aromatic polyester has been successfully demonstrated.

About 18 months ago we began research on a simpler strategy to attaining the goal of molecular composites, namely, the control of aggregation kinetics rather than thermodynamics of mixing (Method 4).

A recent development bearing on this proposal is a Ph.D. Thesis completed at the University of Massachusetts by O. Aoki [11] which dealt with semi-interpenetrating network blends. This is an extension of previous work on phase equilibria [12] and separation [13] of polystyrene/poly(vinylmethyl ether) (PS/PVME) blends. The blends exhibit a lower critical solution temperature (LCST) which means that they are miscible at low temperature but phase separate upon

heating. Phase separation can be detected most accurately through the observation of the cloud point (T_{cl}) by light scattering. It was observed that miscibility decreases, i.e., the cloud point is found at a lower temperature, with increasing molecular weight of the composite materials.

In the work of Aoki, PVME was dissolved in a mixture of styrene and divinyl benzene monomers which were then photochemically polymerized so as to form a polystyrene network surrounding the PVME linear polymer. This was done at a temperature corresponding to the miscible region so as to form a molecularly dispersed semi-interpenetrating network (SIN) blend. The temperature was then increased and light-scattering measurements were done in order to observe the cloud point of phase separation. It was expected that the network polymer would exhibit lower miscibility than the linear polymer due to the lower entropy of mixing and that T_{cl} would be observed at a lower temperature. Quite unexpectedly, no perceptible scattering was observed upon heating these SIN blends. More detailed analysis of the scattering revealed that T_{cl} did occur at lower temperature but that scattering was significantly reduced relative to that observed for a mixture of the linear polymers. Furthermore, the scattering observed above T_{cl} decreased with increasing degree of crosslinking of the network. This observation led to the conclusion that crosslinking retards phase separation and reduces the compositional differences between the separating phases, thus minimizing refractive index differences and light scattering. It is also apparent that crosslinking restrains complete separation of the components at the cloud point.

This observation led to the idea that a similar strategy, i.e., prevention of aggregation via a rapid buildup in viscosity and stabilization via crosslinking, might avoid rod/coil separation in rod/flexible coil system and generate a molecular composite. Although we originally thought that this idea represented a unique approach toward the attainment of this goal, we soon discovered a patent and paper by Kozakiewicz and coworkers [9] which describe improved mechanical properties of a molecular composite comprising cellulose acetate as the rodlike component and a variety of monomeric vinyl solvents which were photopolymerized to flexible chain polymers. More recently, a European patent application described the sequential *in-situ* polymerization of a rodlike azomethemine polymer in molten caprolactam followed by the *in-situ* polymerization of the latter which forms nylon 6; the composite is reported to have significantly improved mechanical properties [14]. In another recent paper, films containing various ratios of a liquid crystalline polymer, e.g., a main-chain, rigid-flexible type with a very short mesogen length, and a trifunctional acrylate were photopolymerized. The LC phase behavior in the resulting semi-IPN (type II) was retained although phase transitions were depressed, indicating some degree of intimate mixing [15].

The reported success of Kazakiewicz's work encouraged us to pursue composites consisting of para-linked, wholly-aromatic polyamides since they represent a polymer class which exhibits considerably enhanced rodlike character compared to the cellulose. In addition, we anticipated that many of the substituted, biphenylene polyamides would be soluble in combinations of vinyl monomers which would prove to exhibit very useful physical and optical properties. The present paper describes the *in-situ* of "kinetic" approach to molecular composites of rodlike and flexible chain polymers and some of the properties of the resulting mixtures. The method of preparation and the determination of properties of homogeneous blends of two of the rodlike polyamides, which were obtained by dissolution in a common

solvent followed by evaporation, are also described. These blends are of particular interest due to the fact that they cover the entire compositional range, and they are the first examples of homogeneous mixtures of wholly-aromatic polyamides in flexible matrices in which the enthalpy of mixing dominates the entropy of demixing, leading to thermodynamic stability.

EXPERIMENTAL

Photochemically Generated Composites

A high molecular weight ($M_w \approx 10\text{--}20 \times 10^3$), rodlike polymer, such as Polyamide I (see previous for structure), was dissolved (≤ 50 mol%) in a photopolymerizable monomer which contained a benzoin ether photoinitiator (1–5 mol% based on vinyl monomer) such as 2,2-dimethoxy-2-phenylacetophenone (Aldrich Chemical Co. or E. M. Chemicals, Darocure 1173); the photoinitiator did not require purification. Monomers used thus far are 4-vinylpyridine (4-VP), *N*-vinylpyrrolidone (NVP), and vinyl methyl ketone (MVK); the former yellows on standing and was distilled prior to use. At higher concentrations of rodlike polymer, e.g., >20 wt%, solution viscosities were so high that they could not be stirred. To aid dissolution, a solvent such as THF was added and subsequently evaporated prior to polymerization; during evaporation, small but undetermined amounts of the monomers also evaporated, which makes the actual rodlike polymer concentrations slightly higher than reported. A 250-W medium pressure Hanovia lamp placed in a water-cooled quartz cavity was used as a UV source. The polymer solutions were sandwiched between two glass microscope slides or, when large samples were required, they were poured into cuvettes. The solutions were subsequently irradiated for 10 to 30 minutes or several hours, respectively, under a blanket of nitrogen at room temperature. When the microscope slides were pried apart or the cuvettes broken open, strong, optically nonscattering films or pieces were obtained.

Monomer conversions for the *in-situ* procedure were probably low and variable as evidenced by the T_g values for a photopolymerized sample compared to a commercial sample of P4VP (MW = 300,000), 109 vs 138°C, respectively.

Blends

Nonscattering, two component polymer blends were made by dissolving a polyamide and a flexible chain polymer in a solvent at room or slightly elevated temperature. The homogeneous solutions were cast onto glass plates; the solvent was evaporated in an oven at a temperature close to the boiling point of the solvent. Very specific combinations of polymers, solvent, and evaporation rate generated completely nonscattering films which were identical to the two component polymer mixtures prepared by the previously described *in-situ* method (see above).

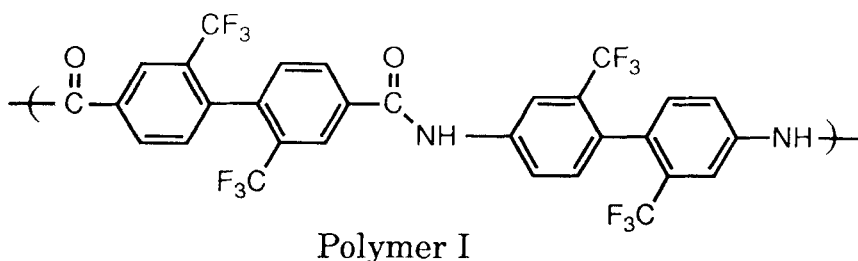
Characterization

Films from both procedures were used as obtained for spectroscopic and scattering studies. When heated to a temperature ($>10^\circ\text{C}$) above the softening point, the larger pieces could be pressed into films by means of a hot press or highly birefringent fibers could be drawn from them.

Differential scanning calorimetry (DSC) data were obtained by means of a Perkin-Elmer DSC-7; data points were taken after one complete heating/cooling cycle at a rate of 10°C/min under a nitrogen atmosphere. Tables 1 and 2 summarize the data for samples obtained by the *in-situ* and blend procedures. Dynamic mechanical analysis (DMA) was performed on an Autovibron (IMASS, Hingham, Massachusetts) operating at 11 Hz over a temperature range of -150 to $+200$ °C at a heating rate of 2°C/min. Typical sample dimensions were $4 \times 0.3 \times 0.001$ cm. A correction for end grips was not made since only relative measurements were required at this point in the study. A detailed analysis of the frequency response of these polymers as a function of temperature is planned. Figures 1a, 1b, 2a, and 2b show plots of both storage modulus and loss tangent ($\tan \delta$) as a function of temperature for Polyamides I and II in P4VP and PNVP, respectively. The curves have been shifted by half a decade along the ordinate for ease of comparison.

RESULTS AND DISCUSSION

In the procedure we are currently using, a high molecular weight, rodlike polyamide (persistence length: 200–300Å) (Polymer I) is dissolved in a liquid monomer of a flexible chain polymer, e.g., 4-vinylpyridine (vinylpyrrolidone or methyl vinyl ketone has also been used successfully) along with a benzoin ether as photoinitiator.



A polyfunctional monomer may be optionally added to serve as a crosslinker, but this was found to be unnecessary for the compositions described in this paper. Certain analogous polyesters or polyesteramides may also be used in place of the polyamide. The homogeneous solution is then photochemically polymerized to generate a matrix in the form of a film or small block which is completely nonscattering to the eye. When heated to their softening points, most composite combinations can be pressed into films, and fibers may be pulled from the bulk. Rodlike polymer/monomer combinations which have generated nonscattering films using this procedure are: Polymer I (≤ 47.1 wt%) in *N*-vinylpyrrolidone, (≤ 44.2 wt%) in 4-vinylpyridine, and (< 22.5 wt%) in methyl vinyl ketone.

Table 1 contains the softening points (TMA) and T_g data (DSC) for a range of composite compositions of Polymer I and poly-4-vinylpyridine, obtained from photopolymerization of the monomer as described above, as well as the corresponding data for the blends (values in brackets) of Polymer I and poly-4-vinylpyridine (P4VP)—see below for details of blends. DSC analysis of the homogeneous mixture containing 10% of Polymer I indicates that the T_g is identical to that of poly-4-vinylpyridine synthesized separately by the same procedure in the absence of Poly-

TABLE 1. Thermal Data for Composites of Polymer I with 4-Vinylpyridine and Poly-4-Vinylpyridine^a

	I (100%) ^b	I (75%)	I (50%)	I (25%)	I (10%)	P4VP (100%)
DSC ^c	ND ^d	—	—	ND	109	109
	"	[208] ^a	[187]	[152]	—	138 ^e
TMA ^c	179	—	—	90, 218	109, 193	84
	"	[174]	[167]	[123]	—	126 ^e

^aValues in brackets are obtained from blends (solvent pyridine).

^bAll composition values are given in weight percent.

^c10°C/min second heat; all temperatures are in °C.

^dNot detectable.

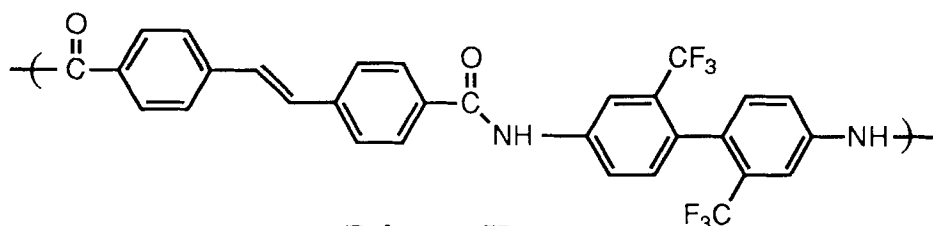
^eCommercial sample MW ≈ 300K.

mer I; a T_g of the 25 wt% rodlike polymer mixture could not be found. DSC analysis of blends of I and P4VP indicate that the T_g 's (values in brackets) are between those of the two individual polymers. TMA analysis of the composites exhibits softening points which do not correspond to either of the individual components, but the softening points of the blends lie between the two individual components. The discrepancy in the data between the blends and the composites probably reflects the lack of control of molecular weight during photopolymerization. TGA analysis indicates that neither the composites nor the blends have any unreacted monomers or solvent, and that the decomposition temperature is equal to or slightly above that of the flexible polymer.

Surprisingly, these homogeneous rod/coil composites can be subjected to extended periods of heating without exhibiting phase separation. For example, samples stored at 120°C do not exhibit any change in appearance, i.e., they remain nonscattering, even after 20 days.

These observations suggest that aggregation of the rods is prevented because the network-forming polymerization occurs more rapidly than aggregation. In other words, the rate of increase in viscosity exceeds the diffusion rate of the rods.

In addition to molecular composites comprising Polymer I and certain polyesters and polyesteramides, the structures of which can be found in a recent communication [16], and since we are interested in increasing the refractive index of molded lenses, we investigated another rodlike polyamide (Polymer II) which has a very high isotropic refractive index, e.g., 1.89; Polymer I has an index of approximately 1.67 and P4VP has an index of 1.59.



Polymer II

If a monomer could be found which would allow the formation of nonscattering

films containing Polymer II, then this might ultimately lead to high index lenses and, due to the large mismatch in index, would lead additional credence to our hypothesis regarding the molecular nature of these composites. Unfortunately, we have not yet found a monomer for Polymer II.

However, during the course of this investigation, it was deemed necessary for comparison purposes to prepare blends of Polyamide I with poly-4-vinylpyridine and separately polyvinylpyrrolidone (PNVP) using a mutual solvent. Considering the results of our previous 2-year effort, we unexpectedly discovered that certain very specific combinations of Polymer I, flexible chain polymer, and solvent gave completely nonscattering films after solvent evaporation (Method 1). One such combination is Polymer I, P4VP, and pyridine. By using this combination we were able to conveniently make and investigate the *entire compositional range from 1 to 99%* of Polymer I. Other solvent/polymer combinations include Polymer I with PNVP from NMP and PNVP from pyridine [16]. In addition, at the present time we have found one rod/coil/solvent combination for Polymer II, e.g., II, PNVP, and TMU, and in analogy to the former example, after solvent removal this combination also gives completely nonscattering films over the entire compositional range.

TGA indicates the presence of less than 5 wt% residual solvent in these blends, and it can be readily removed by continued heating at low pressure without degradation of optical properties.

The DSC and TMA data for this blended composite are given in Table 2. No detectable transitions could be found by DSC, but in analogy to Polymer I blends, the softening points of all of the various compositions lie between those of the individual polymers.

The reinforcing ability of the rodlike polymer was examined by means of dynamical mechanical analysis (DMA) in the -150 to $+200^{\circ}\text{C}$ temperature range. The most surprising result from these experiments is the degree to which the useful temperature range of the flexible polymer has been extended with the addition of only 25 wt% of either of the rodlike polymers as demonstrated by the storage moduli versus temperature curves (Figs. 1a and 2a.) For example, the addition of 25 wt% of Polymer II (Fig. 2a) has shifted the glass-rubber transition of PNVP by approximately 40°C , and at 50 wt% rodlike polymer the blend shows no significant loss of modulus up to 200°C .

Similar results were obtained for composite blends with compositions ranging

TABLE 2. Thermal Data for Composite Blends of Polymer II with Poly-*N*-Vinylpyrrolidone^a

	II (100%) ^b	II (75%)	II (50%)	II (25%)	PNVP
DSC ^c	ND ^d	ND	ND	ND	86
TMA ^c	290	163	156	146	124

^aSolvent tetramethylurea.

^bWeight %.

^c $10^{\circ}\text{C}/\text{min}$, second heat; all temperatures are in $^{\circ}\text{C}$.

^dNot detectable.

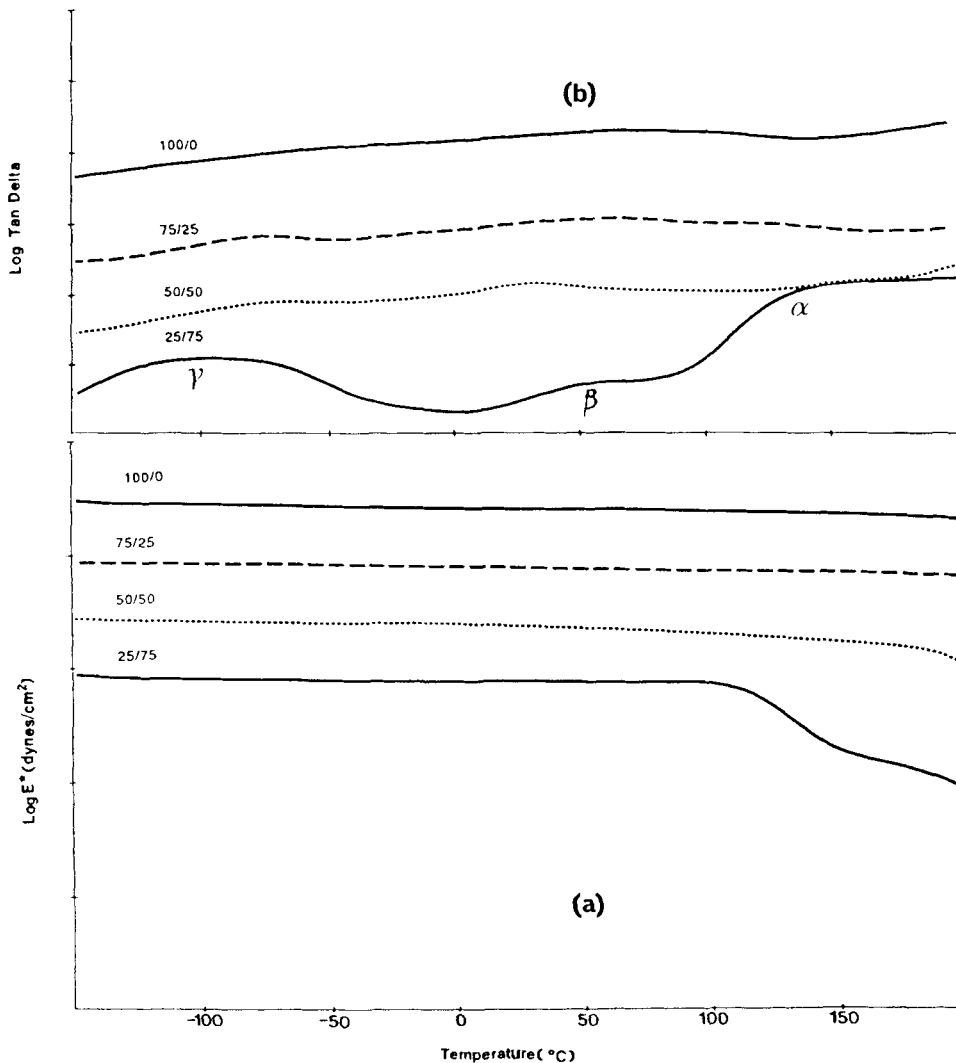


FIG. 1. (a) Storage modulus (E' , log scale) versus temperature ($^{\circ}\text{C}$) for composites of Polymer I and poly-4-vinylpyridine. (b) $\tan \delta$ versus temperature ($^{\circ}\text{C}$) for composites of Polymer I and poly-4-vinylpyridine.

from 25 to 75 wt% of Polymer I with P4VP. It should be noted that both solution-cast and melt-pressed samples of pure P4VP ($MW \approx 50K$) lack the required mechanical integrity for dynamic mechanical analysis and hence could not be measured. At the lowest rodlike concentration the softening point is about 120°C ; it shifts 60°C and greater than 80°C for 50 and 75 wt% rodlike polymer, respectively.

Three main relaxations, namely γ , β , and α , have been identified on the $\tan \delta$ curve for the flexible chain polymers. For amorphous polymers, the γ - and β -relaxations are attributed to local, short-range motions of the chains, while the α -relaxation is identified with the glass transition [17]. Figure 1(b) indicates that the γ - and

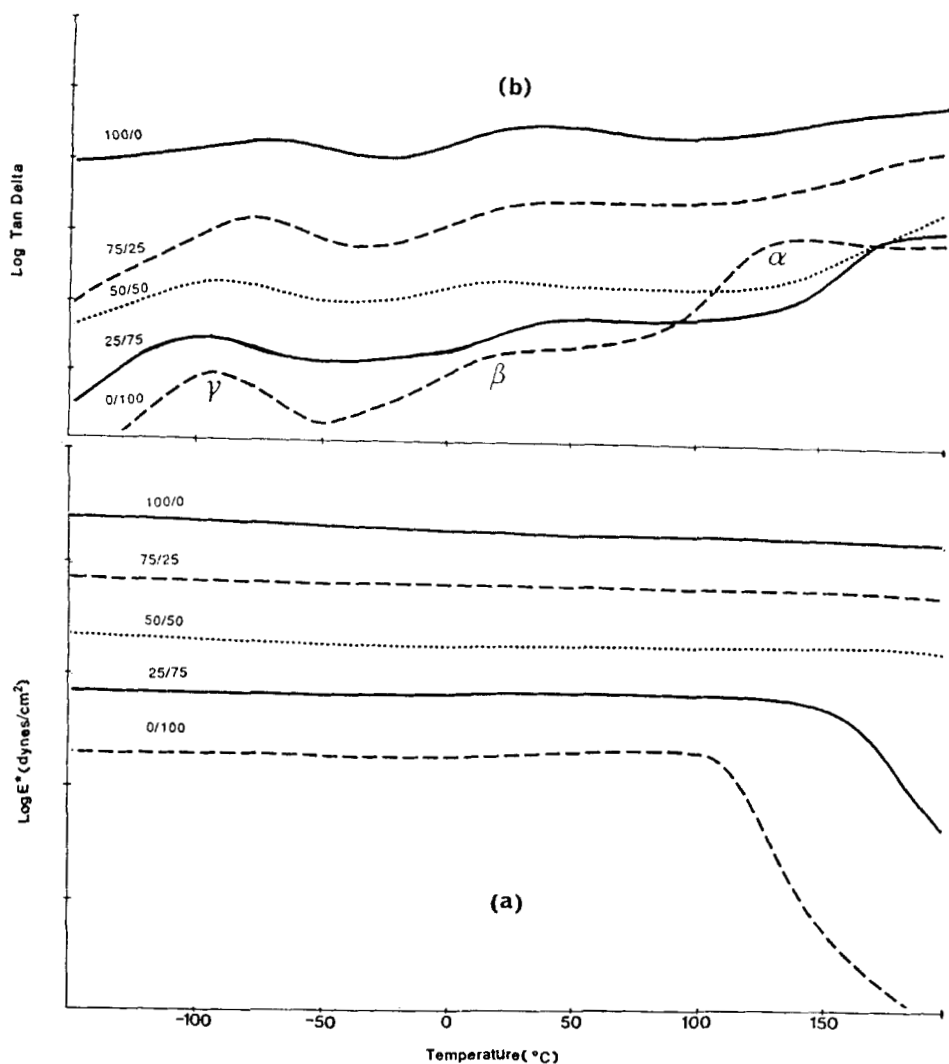


FIG. 2. (a) Storage modulus (E' , log scale) versus temperature ($^{\circ}\text{C}$) for composites of Polymer II and poly-*N*-vinylpyrrolidone. (b) $\tan \delta$ versus temperature ($^{\circ}\text{C}$) for composites of Polymer II and poly-*N*-vinylpyrrolidone.

β -relaxations are either very weak or nonexistent in Polymer I, and they are weak and broad in Polymer II (Fig. 2b). Unfortunately, the temperature of the α -relaxation of both polymers exceeds the working range of the DMA instrument as it is currently configured and could not be measured. It should be noted that for the blends of Polymer II, the positions of the γ - and β -relaxations have increased slightly, diminished in intensity, and broadened somewhat relative to PNVP. Polymer I blended with P4VP shows more dramatic results as the concentration of the rodlike polymer increases.

Peak broadening is an indication of a larger range of relaxation times for the transitions from which it may be concluded that on a local level the rodlike and

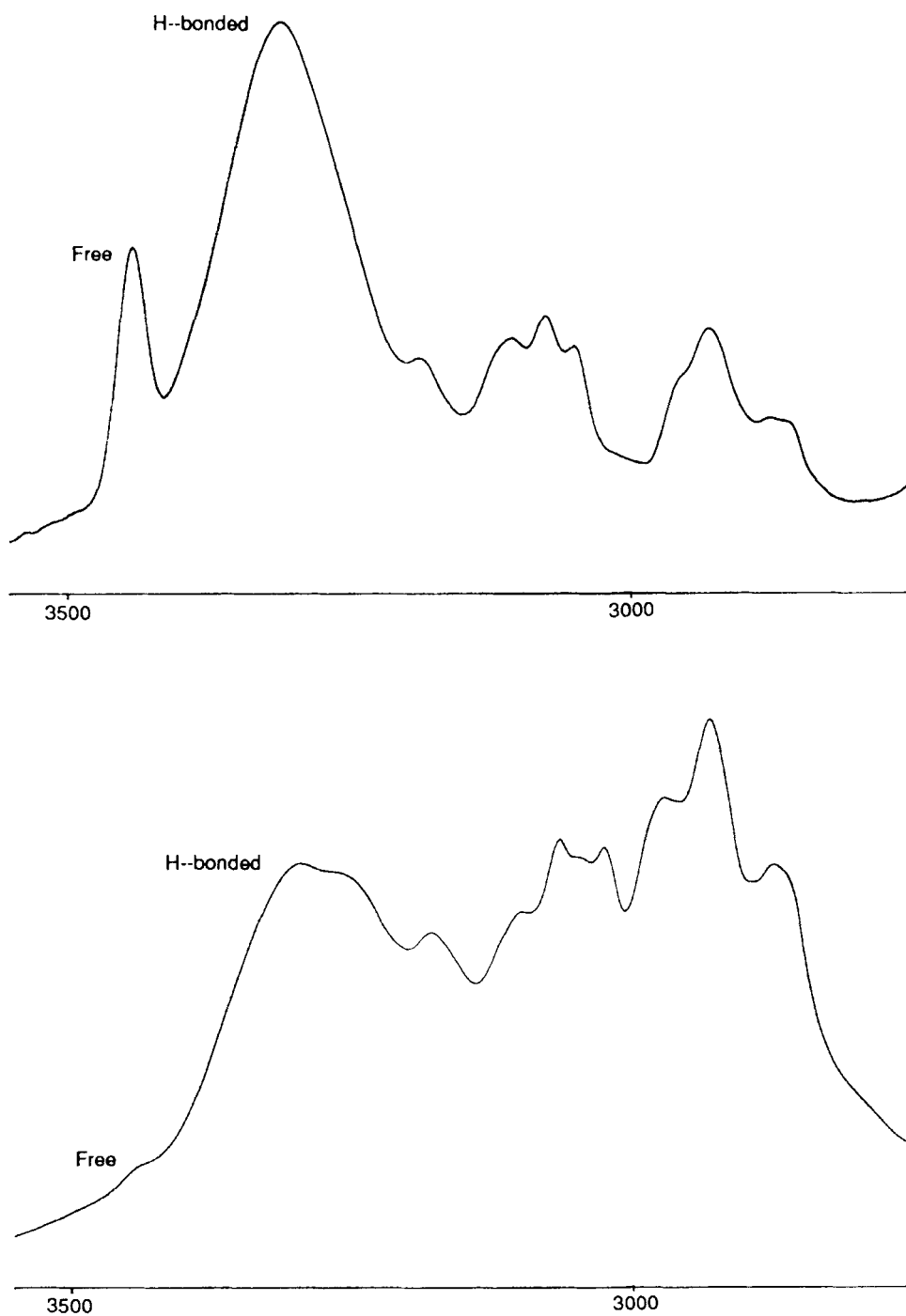


FIG. 3. N—H stretching vibrations of Polymer I (top curve) and a composite of 70 wt% Polymer I and poly-4-vinylpyridine (bottom curve).

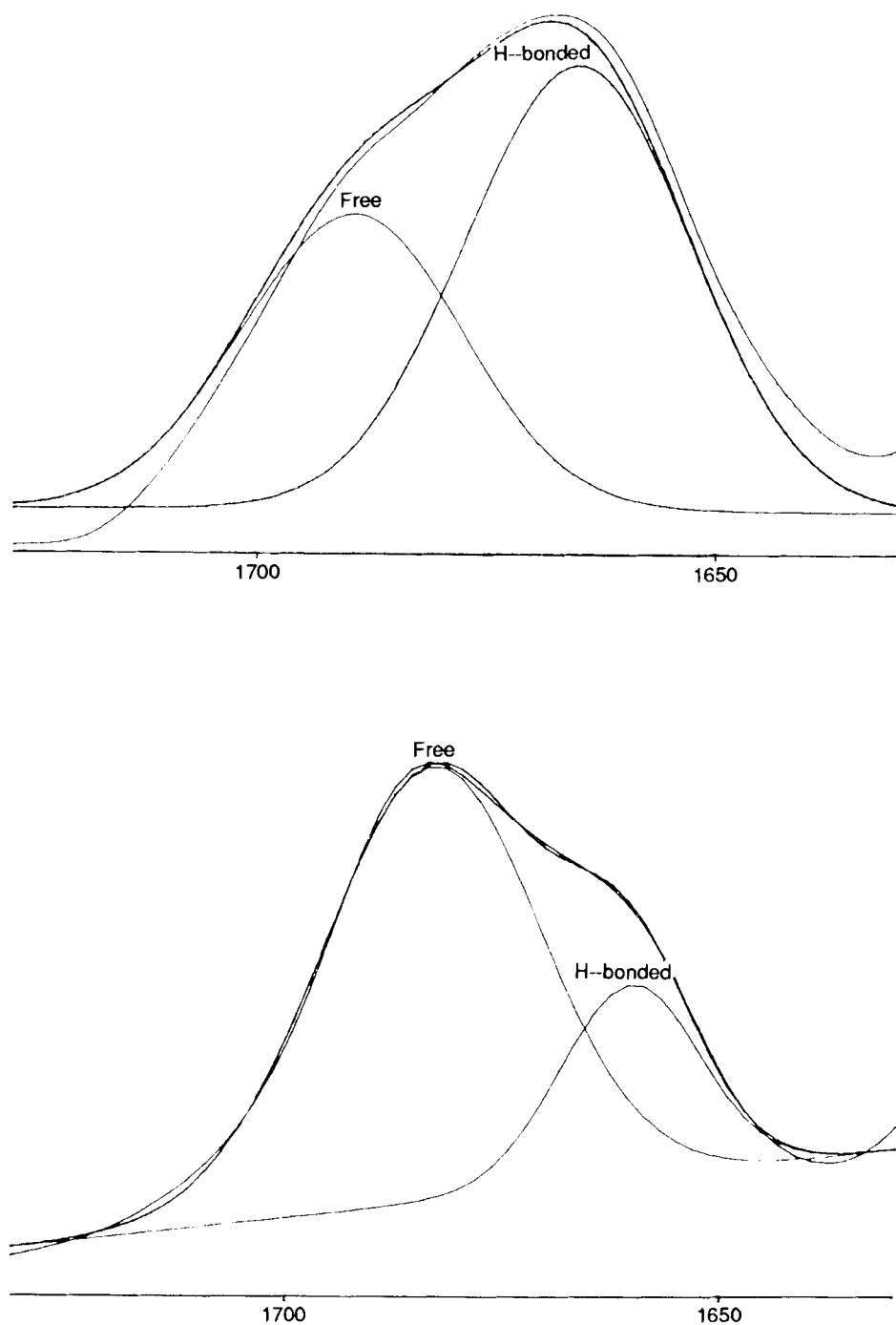


FIG. 4. Absorption and deconvoluted spectrum of the carbonyl stretching vibrations of Polymer I (top curve) and a composite of 70 wt% Polymer I and poly-4-vinylpyridine (bottom curve).

flexible polymers must be strongly interacting. This is additional evidence for the existence of molecular dispersion in these materials. Dielectric measurements which are currently underway will help quantify the extent of these interactions.

Spectral analyses (FTIR) of films Polymer I and P4VP indicate that a strong enthalpic interaction exists between the two polymers in the form of hydrogen bonding between the hydrogen atom of the N—H group of the amide and the nitrogen atom of the pyridine ring (Figs. 3 and 4). For example, in Fig. 3, top curve, the free N—H band of the amide group of Polymer I may be clearly seen in the 3400–3500 cm^{-1} range along with the hydrogen-bonded vibrations. In the carbonyl region of Polymer I (Fig. 4, top curve), where accurate quantitation of the percent hydrogen bonding is possible, 36% of the carbonyl groups are free, and therefore 64% must be bonded to amide hydrogens. In the spectrum of a sample containing 30 wt% of P4VP (Fig. 3, bottom curve), the free N—H vibration is nearly absent. The free carbonyl band (Fig. 4, bottom curve), however, has increased significantly, and deconvolution indicates that 85% of the amide carbonyls are not hydrogen bonded. These results strongly suggest that the basicity of the nitrogen atom of the pyridine ring coupled with its high molar concentration, e.g., 30 wt% = 74 mol% P4VP, competes successfully with the carbonyl oxygen atom of the amide group for the hydrogen atom. Hence, the amide hydrogens are predominantly bonded to the flexible matrix polymer, thereby freeing the carbonyls.

FTIR spectra of Polymer II shows the same effect in the N—H stretching region, but the results cannot be quantified due to the fact that the carbonyl vibration of PNVP, the only flexible chain polymer found thus far for Polymer II, overlaps with the carbonyls of the rodlike polymer.

Examination of the films of composites made by either technique by means of polarized optical microscopy shows that the network is predominantly isotropic with regions of very diffuse, low retardation. Initial light-scattering experiments using a HeNe laser at 633 nm indicate that there are no scattering domains greater than approximately 100 nm. Films of Polymer I (50 wt%) in P4VP which were stored at 120°C for 20 days remained optically unchanged. Examination of the surface of these films are featureless when examined by near field scanning optical microscopy and scanning electron microscopy; these techniques should allow the visualization of textures and domains in the 300–400 and 200–300 Å ranges, respectively. These experiments will be repeated on cryomicrotomed and freeze-fractured samples.

We have also begun examining multicomponent blends of a rodlike and two flexible polymers, and although very few experiments have been attempted up to this point, we have made a blend consisting of 20 wt% Polymer I and a 1:1 mix of P4VP and polystyrene. If this approach can be exploited further, then a wide range of thermomechanical properties should be attainable.

CONCLUSIONS

In this paper we described two techniques for generating nonscattering films comprising rodlike and thermoplastic, flexible chain polymers. The first is similar to the semi-interpenetrating network approach in which a rodlike polymer is dissolved in a monomer of a flexible chain polymer along with a photoinitiator. Upon

irradiation the rate of viscosity buildup exceeds the rate of diffusion of the rods which prevents phase separation. In the second approach, a rodlike polymer and a flexible chain polymer are dissolved in a mutual solvent which, after evaporation of the latter, yields nonscattering films equivalent to those obtained via the former technique.

Light scattering, optical and electron microscopy, and thermal analyses do not show any evidence of phase separation. Heat treatment of the films over extended periods also does not cause phase separation. Dynamic mechanical analysis demonstrates a significant reinforcing ability of even 25 wt% rodlike polymer in the flexible matrix.

FTIR spectroscopy of one of these combinations suggests that a strong enthalpic interaction in the form of hydrogen bonding between the polyamide and the matrix polymer may be a significant contributor to this stability.

In conclusion, we have presented evidence that strongly suggests that for the first time wholly-aromatic, rodlike polyamides have been combined with thermoplastic, flexible chain polymers to form thermodynamically stable, molecularly dispersed composites.

ACKNOWLEDGMENT

The authors would like to thank Dr. Mohan Srinivasarao for obtaining scanning electron micrographs, for arranging for near field scanning optical microscope analysis at AT&T Bell Labs, and also for many very help suggestions.

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Received October 15, 1991

Revision received November 25, 1991