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Molecular Composites Comprising Rodlike and Flexible Polymers. 1

R. A. Gaudiana* and T. Adams

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

R. S. Stein

Polymer Research Institute, University of Massachusetts, Amherst, Massachusetts 01002

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Attempts to make molecular composites from rodlike and flexible polymers dissolved in a mutual solvent are predicted to result in phase separation due to unfavorable entropy of mixing. This prediction was first made by Onsager[1] and later by Flory[2] and has been verified many times.[3]

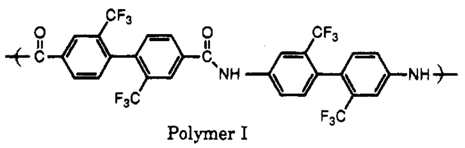
Poly(*p*-phenyleneterephthalamide) (P*p*TA), poly(*p*-phenylenebenzothiazole) (PBT), and polyglutamates (PG) are typical, extensively studied rodlike polymers which spontaneously form biphasic solutions above a certain concentration and form phase-separated binary mixtures with flexible polymers. Several strategies have been investigated which attempt to overcome entropy-driven demixing by enhancing the enthalpy of intermolecular interactions between the rodlike and flexible chain polymers. Some recent examples which report limited success are PBT with poly[2-(acrylamido)-2-methylpropanesulfonic acid][4] and a variety of polyglutamates with poly(vinyl phenol).[5] Morphological, solution (solvent:methanesulfonic acid and other strong acids), and mechanical properties of PBT in a polybenzimidazole matrix (ABPBI) have been extensively studied for the last several years.[6] With these combinations particle sizes may be as low as 50–100 Å. Other strategies include an approach which is similar to semiinterpenetrating networks[7] and grafting side chains on the backbone of a semirodlike polymer to enhance its miscibility with the homopolymer of the graft.[8]

Several years ago we discovered that the incorporation of noncoplanar biphenyl monomers into polyamides, poly(ester amides), and polyesters significantly improved the solubility of the resulting rodlike polymers. Many of the polyamides for example are soluble in common solvents such as THF, acetone, or dimethylacetamide without the use of a solubilizing agent such as LiCl, and several of the polyesters are soluble in chloroform. A surprising feature of these solutions is the absence of a lyotropic phase even at concentrations which far exceed their critical values.[9] On the basis of these findings, we had correctly anticipated that homogeneous solutions consisting of, for example, THF, a biphenylene-containing, rodlike polyester, and a flexible polymer (a polysulfone), could be easily obtained;[10] polyamides and poly(ester amides) with a variety of flexible chain polymers such as several types of nylon, acrylonitrile, styrene–acrylonitrile, etc., and the appropriate solvents also made homogeneous solutions. Unfortunately, when the solvent was removed, either slowly or quickly, phase separation occurred in every case.

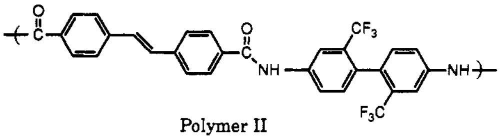
On the basis of the reported success of the "kinetic" or in-situ approach for forming molecular composites in the case of cellulose acetate and vinyl monomers,[7] we recently decided to attempt to make molecular composites using wholly-aromatic polyamides which are significantly more rodlike. The solubility of the polymer in the monomer is the key to the success of this strategy, and it is also the most limiting requirement in light of the insoluble nature of most rodlike polymers. The propagation rate of the vinyl monomer is so high that within minutes a significant increase in solution viscosity is readily apparent. The rate of increase in viscosity, particularly at the local level, far exceeds the diffusion rate of the rodlike polymer, thereby preventing phase separation.

Using this concept, the rodlike polymer was dissolved in a monofunctional, polymerizable monomer (multifunctional monomers could have been used but were found unnecessary) which serves as the solvent. Methylbenzoin ether (1–4 wt % based on monomer) was added as the photoinitiator; the reaction was carried out in a water-jacketed reactor (Pyrex filter) using a medium-pressure Hanovia lamp in a nitrogen atmosphere. We subsequently found that at least one example in each of the three previously mentioned classes of polymers could be dissolved in a vinyl monomer with a photoinitiator. Photopolymerization of the resulting homogeneous solutions yielded optically clear, nonscattering films and pieces, the shape of which depends on the shape of the polymerization vessel.

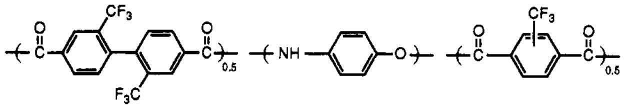
The molecular structures of the four polymers studied thus far are shown below. Polymers I, III, and IV were chosen because they represent the most soluble members of each of their classes. Polymer II was selected for two reasons: (1) it is the best characterized of all of the polymers in the class; (2) it has a very high refractive index and birefringence. These properties are important from the standpoint of certain optical devices which are described elsewhere.[11]



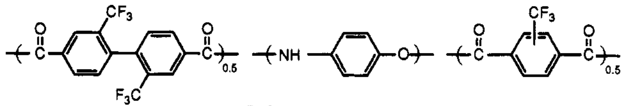
Polymer I



Polymer II



Polymer III



Polymer IV

Table I lists some initial results regarding the nature of the vinyl monomers and the upper limit of the concentration range for each of the rodlike polymers. Polyamide I can be dissolved in three vinyl monomers, e.g., 4-vinylpyridine (4VP), *N*-vinylpyrrolidinone (NVP), and methyl vinyl ketone, to fairly high concentrations. However, if the concentration exceeded approximately 10%, THF had to be added to the highly viscous mixtures in order to affect dissolution. Most of the solvent was removed during photopolymerization of the resulting non-

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Table I
Examples of Rodlike Polymers and Vinyl Monomers Which Form Molecular Composites via Photopolymerization

polymer	vinyl monomer[a]	composition[b]
polyamide I	4VP	1–99
	NVP	21
	MVK	23
polymer II	insoluble	
polymer III	4VP	9.0
	NVP	7.9
polymer IV	4VP	9.3
	NVP	8.4

[a] 4VP = 4-vinylpyridine; NVP = *N*-vinylpyrrolidinone; MVK = methyl vinyl ketone. [b] w/w % rodlike polymer.

Table II
Examples of Blends of Rodlike and Vinyl Polymers Which Form Molecular Composites after Solvent Evaporation

rodlike polymer	vinyl polymer[a]	solvent[b]	composition[c]
polyamide I	P4VP	pyridine	1–99
	PNVP	pyridine	≤36
	PNVP	NMP	≤32
	PStyr/P4VP (1:1)	THF	~20
polymer II	PNVP	TMU	1–99
polymer III	PNVP	pyridine	≤35
polymer IV	*d*		

[a] P4VP = poly(4-vinylpyridine); PNVP = poly(*N*-vinylpyrrolidinone); PMVK = poly(methyl vinyl ketone); PStyr = polystyrene. [b] NVP = *N*-vinylpyrrolidinone; TMU = tetramethylurea. [c] w/w % rodlike polymer. [d] All solvent–flexible polymer combinations gave scattering films.

scattering, glassy mixtures; the remaining traces were removed by heating after the reaction was complete. For polyamide I in 4- vinylpyridine, the entire concentration range could be attained by this technique, and nonscattering films and shaped pieces resulted from polymerization. In the polarizing optical microscope, several examples of these films consist of diffuse, low retardation zones which are intermixed with completely nonbirefringent areas, but there are no disclination lines or distinct boundaries separating these areas. Many other examples are completely isotropic. Light scattering indicates that there are no particles down to a dimension of approximately 1000 Å. In many examples a glass transition (via DSC analysis) could not be detected, and dynamic mechanical analysis shows a very pronounced reinforcing effect.[12]

Unfortunately, a monomeric solvent could not be found for polyamide II, but poly(ester amide) III and polyester IV could be dissolved in 4VP and NVP up to 8–9%. As in the example of polymer I, optically clear, nonscattering films were obtained upon irradiation; examination of the films in the polarizing microscope gave identical results. At the time of this writing, no other monomeric vinyl solvent has been found for any of these polymers.

During the course of this investigation it was deemed necessary for comparison purposes to make films of these rodlike polymers with already formed flexible chain polymers corresponding to the vinyl monomers using an appropriate solvent; a variety of combinations formed homogeneous solutions. Completely unexpectedly, certain very specific combinations of rodlike and flexible chain polymers and solvent generated optically clear, nonscattering films from these solutions after solvent evaporation. The results are summarized in Table II. In analogy to the results obtained by means of the in-situ technique, polyamide I forms molecularly dispersed composites over the entire compositional range with P4VP but only when pyridine is used as solvent. Similarly, PNVP can be blended with polymer I using either pyridine or NVP, but the highest concentration obtainable is 36 and 32%, respectively. It should also be noted that a 1:1 mixture of polystyrene and P4VP with as much as 20 wt % polymer I also forms nonscattering films; the ability to blend in another flexible polymer suggests that a variety of bulk properties may be attainable depending on the specific combinations selected. In analogy to polymer I, polyamide II also generates a molecular composite over the entire compositional range with P4VP but only if TMU is used as the solvent. We have not yet found any other polymer–solvent combination for polymer II.

Another completely unexplained result is the fact that polymer III can be blended with PNVP exclusively using pyridine as the solvent. P4VP with pyridine gives scattering films at about 20%. In support of our previous findings,[10] we have not found a polymer–solvent combination for polyester IV.

The fact that these composites can be heated for several days at or slightly above the glass transition of the flexible polymer attests to their thermodynamic stability. When fibers are drawn from the softened film, they develop birefringence but retain their optical clarity.

In conclusion, our results strongly suggest that certain, very limited examples of noncoplanar, biphenylene-containing polyamides, poly(ester amides), and polyesters generate molecular composites using the kinetic or in-situ approach, and, quite unexpectedly, many can also be made by means of solvent-assisted blending. A full report on these findings is being prepared.

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