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POLYISOIMIDE FOR IN-SITU RIGID-ROD MOLECULAR COMPOSITE APPLICATIONS

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A new material concept using in-situ rod formation from a coil-like poly(tetramethyl isoimide) was explored for rigid-rod molecular composite applications. Its feasibility relies mainly on an adequate degree of isomerization leading to a rod-like polyimide of sufficient length for reinforcing the composite. Isomerization induced thermally was demonstrated in solutions and in the solid state with visible-light and infrared spectroscopies. X-ray scattering revealed that the polyisoimide was amorphouse while the polyimide was highly crystalline. However, gel permeation chromatography showed a low degree of isomerization and possible polymer degradation. This was further supported by the absence of birefringence and anisotropy in light scattering from the converted polyimide. Computations on related dimers indicated that a high degree of isomerization was unlikely due to polyisoimide conformational restriction. Attempts to fabricate molecular composites utilizing this concept did not result in rigid-rod reinforcement from the polyimide.

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FOREWORD

This is an interim report on thermal isomerization of coil-like polyisoimide to polyimide, a rod-like polymer, for exploratory rigid-rod molecular composite applications. The research was conducted between December 1986 to September 1987 by personnel from the University of Dayton Research Institute (UDRI) and from the Polymer Branch, Air Force Wright Aeronautical Laboratories, Materials Laboratory. The synthesis effort was provided by J. A. Webster. Gel permeation chromatography was conducted by C. L. Benner. Isomerization, morphology, numerical modeling and composite processing were investigated by C. S. Wang, S. J. Bai, and T. E. Helminiak. This study was sponsored by the USAF/AFWAL Materials Laboratory under Contract F33615-87-C-5241 to UDRI. The Project Engineer monitoring the UDRI contract was I. J. Goldfarb.

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INTRODUCTION

Recent development of rigid-rod molecular composites using molecularly dispersed heterocyclic aromatic rod-like polymers as the reinforcing unit for matrix polymers exhibited significant enhancement in thermal stability, chemical resistance and mechanical properties of the matrix polymers.(1,2) In spite of these desirable characteristics, difficulties in processing have so far inhibited practical utilization of the rigid-rod molecular composites.

The rod-like polymers do not show any glass transition or melting behavior prior to thermal degradation; therefore conventional melt-processing is not feasible for molecularly dispersing the rod-like molecules in a host matrix. Currently, the dispersion is achieved by co-dissolving the rod-like polymers and the matrix polymers in a few strong protic acids capable of dissolving the rod-like polymers. This severely restricts the selection of matrix materials because most of them are not chemically stable in the acids. Moreover, the rod-like molecules are inherently incompatible with coil-like molecules and can assume a nematic liquid-crystalline state above a critical concentration. Aggregation of the rod-like polymers occurs above the critical concentration, and the resulting phase separation gives a drastic decrease in the reinforcement efficiency of the rod-like molecules and consequently the composite mechanical properties decrease. In order to circumvent these two difficulties, a new material concept using an in-situ rigid-rod polymer as the reinforcing unit for molecular composite applications has been proposed(3) and evaluated.

The candidate material for this new approach is a poly(tetramethyl isoimide) which will undergo an isomerization from a coil-like polyisoimide to a rod-like polyimide upon heating, as sketched in Figure 1. The polyisoimide is soluble in aprotic solvents, which widens the selection of host matrices. The polyisoimide is a coil-like polymer which avoids the aggregation of the rod-like polymer in the composite solution. However, the success of this approach depends primarily on adequate isomerization for rod-like imide segments to sufficient length giving, thereby, high reinforcement in the composite.

In this investigation, the isomerization of the polyisoimide was studied in anhydrous N,N-dimethylacetamide (DMAc) solutions and in the solid state. The results were analyzed by gel permeation chromatography (GPC) for molecular size determination and by infrared spectroscopy for degree of chemical conversion. Optical microscopy and small-angle light scattering were used to observe the depolarization behavior due to the formation of the rod-like polyimide. X-ray scattering was applied for morphological measurements. Molecular modeling was employed to simulate the oligomeric structures of the isoimide and the imide. Two molecular composite systems were explored for the fabrication of in-situ rigid-rod molecular composites. For compatibility considerations, two molecules of structure similar to the polyisoimide were chosen as the matrix. One matrix was an isoimide

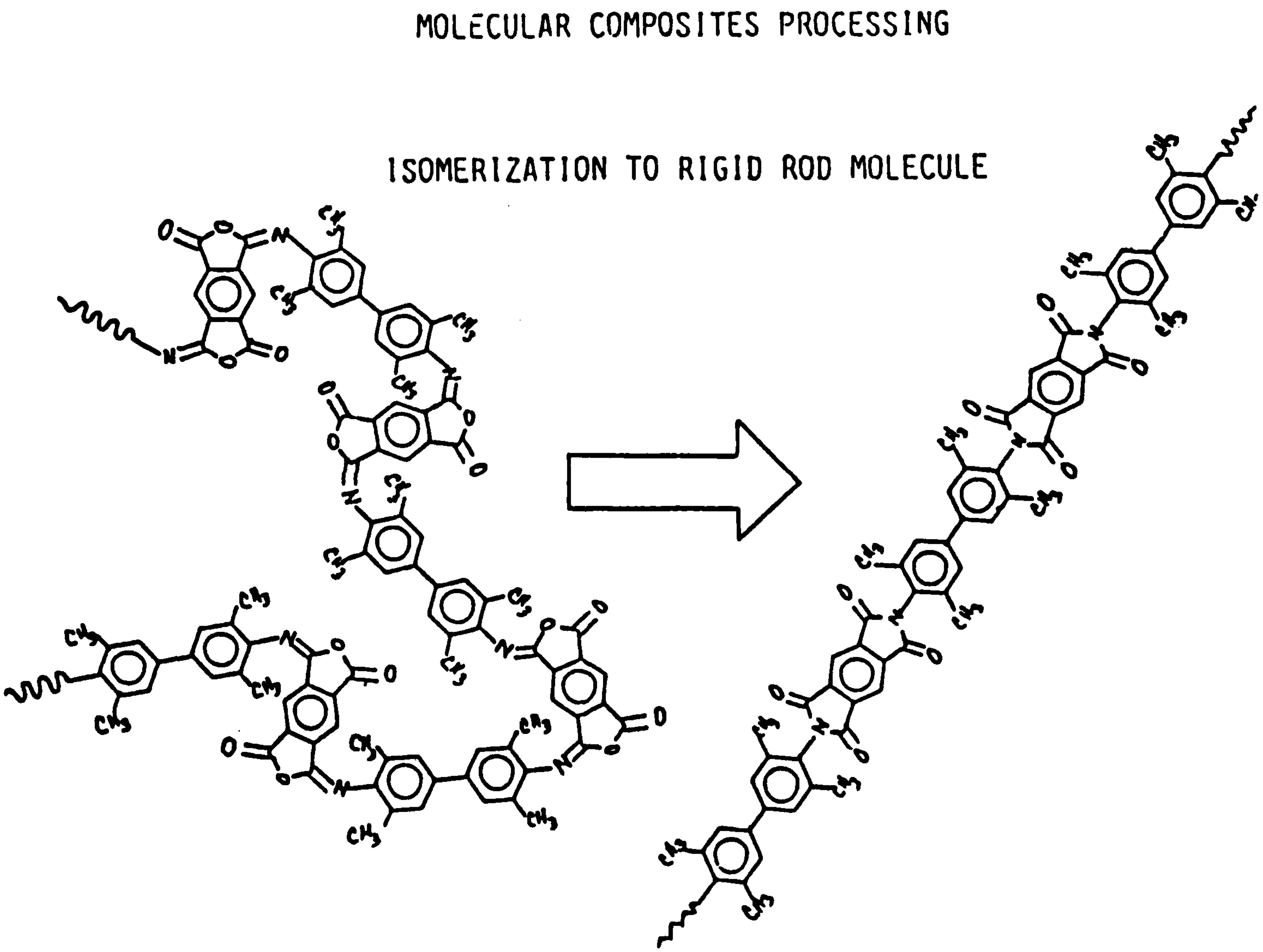


Figure 1. Concept of isomerization of a coil-like polyisoimide into a rod-like polyimide.

resin, HR600P, and the other matrix was a polyimide of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole (mPBI).

THERMAL ISOMERIZATION

The isomerization of the polyisoimide in DMAc was carried out at various temperatures at concentrations up to about two weight percent. The advantage of a relatively dilute solution for isomerization is that each polyisoimide molecule is isolated and can be isomerized without being inhibited by neighboring molecules. Figure 2 shows a set-up for the studies below the boiling point of DMAc (166°C). At higher temperatures, the isomerization was conducted with the solution sealed in glass tubes. These experiments showed that, with heating, the solution changed color from orange to dark brown, and then yellow. The color change is believed to indicate the isomerization of the isoimide to the imide. Further heating caused the isomerized polymer to precipitate from the solution. Table 1 presents the thermally induced isomerization as a function of time and temperature. Results of isomerization were characterized by GPC and infrared spectroscopy.

GEL PERMEATION CHROMATOGRAPHY

The isomerization of the coil-like polyisoimide to the rod-like polyimide was studied in DMAc. For the same molecular weight, the isomerized polyimide is expected to have a larger hydrodynamic volume than the polyisoimide, which may be detected

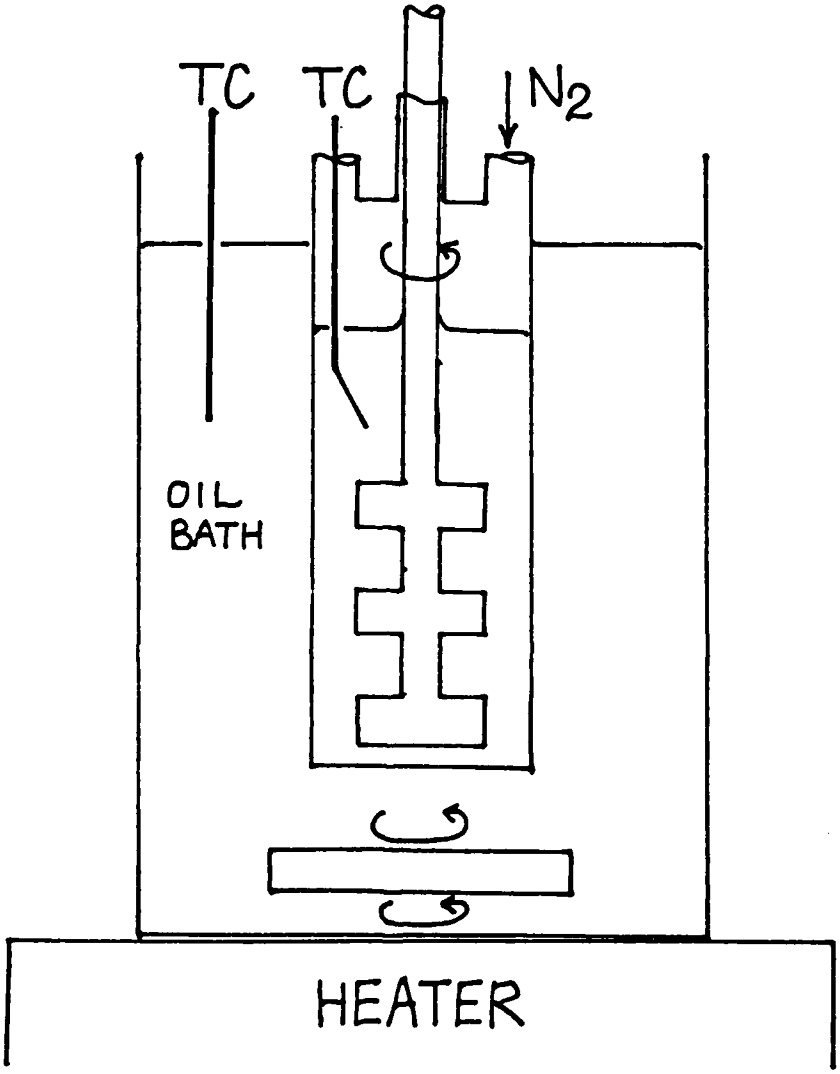


Figure 2. Sketch of apparatus for heat induced isomerization of polyisoimide in solution.

TABLE 1

TEMPERATURE AND TIME DEPENDENCE OF THE ISOMERIZATION OF POLYISOIMIDE IN DMAc

Bath Temperature (°C)	100	175
Time for Color Change	overnight	40 mins
Time for Precipitation	4 days	4 hrs

by GPC. Anhydrous DMAc was used to elute the solutions from a 10^5 Å microstyragel column at a flow rate of 1 ml/min. A single wavelength ultraviolet detector set at 280 nm was used to monitor the effluent.

A solution of the polyisoimide in DMAc at 0.5 weight percent was heated in an oil bath at 175°C for 40 minutes and then cooled gradually to room temperature. The heated solution showed no observable precipitation at this time but after three days at room temperature some precipitation was observed. GPC measurements were conducted for the solution at these three stages. The results are given in Figure 3. The chromatogram for the heated solution shows a broadened tail and a small new peak at longer elution times suggesting the converted polymer has a smaller hydrodynamic volume. The prolonged solution maintains the similar chromatogram with an additional small peak at 3.80 min. elution time. This indicates, indeed, a larger hydrodynamic volume was formed, which could possibly be isomerized or gelled polyisoimide.

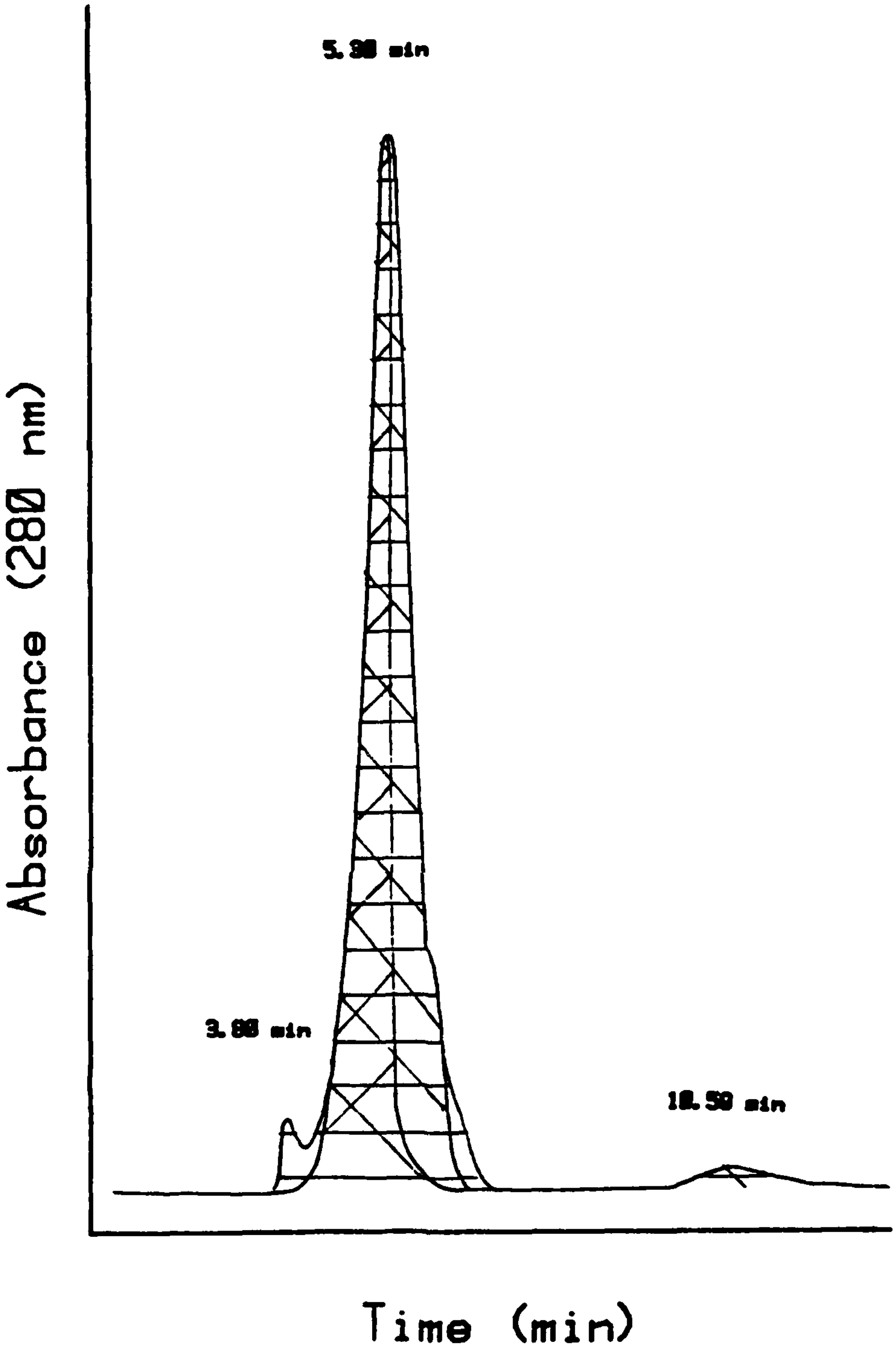


Figure 3. Gel permeation chromatographs of polyisoimide solution; ▨ original, ▧ heated at 175°C for 4 hrs, and ▤ heated and left at room temperature for three days.

In another case, the polyisoimide appears to have degraded at elevated temperatures in the solution rather than to have isomerized into a rod-like polyimide as proposed. This is evidenced in Figure 4 by the longer elution times for the most of the polymer present in the heated solution. Additional GPC results of the isomerization at different heating rates and concentrations further confirm that the converted molecules have a hydrodynamic volume no larger than that of the polyisoimide. Thus, GPC on heated polyisoimide solutions does not show a high degree of isomerization occurred leading to a rod-like molecule.

INFRARED SPECTROSCOPY

The starting polyisoimide and the converted polyimide, either as solution precipitates or as cast films, were examined by a fourier-transform infrared spectrometer, Beckman FT-1100. Infrared absorption spectra were taken over a wavenumber range of 600-4000 cm^{-1}. The absorption bands for the isoimide ring can be identified distinctly at 900-950 (C=N), 1680-1730 (C=O), and 1789-1841 (lactone ring with exocyclic double bond) cm^{-1}. Similarly, the imide ring can be identified at 1350-1390 (imide ring), 1707-1730 (sym. C=O), and 1776-1794 (asym. C=O) cm^{-1}. These are clearly shown in Figure 5 where the absorption of the isoimide ring decreases significantly while the absorption of the imide ring increases after the polyisoimide had been heated to 250°C. This has been consistently observed for the polyisoimide heated in DMAc or as films. The evidence strongly suggests that the isomerization does occur upon heating the polyisoimide.

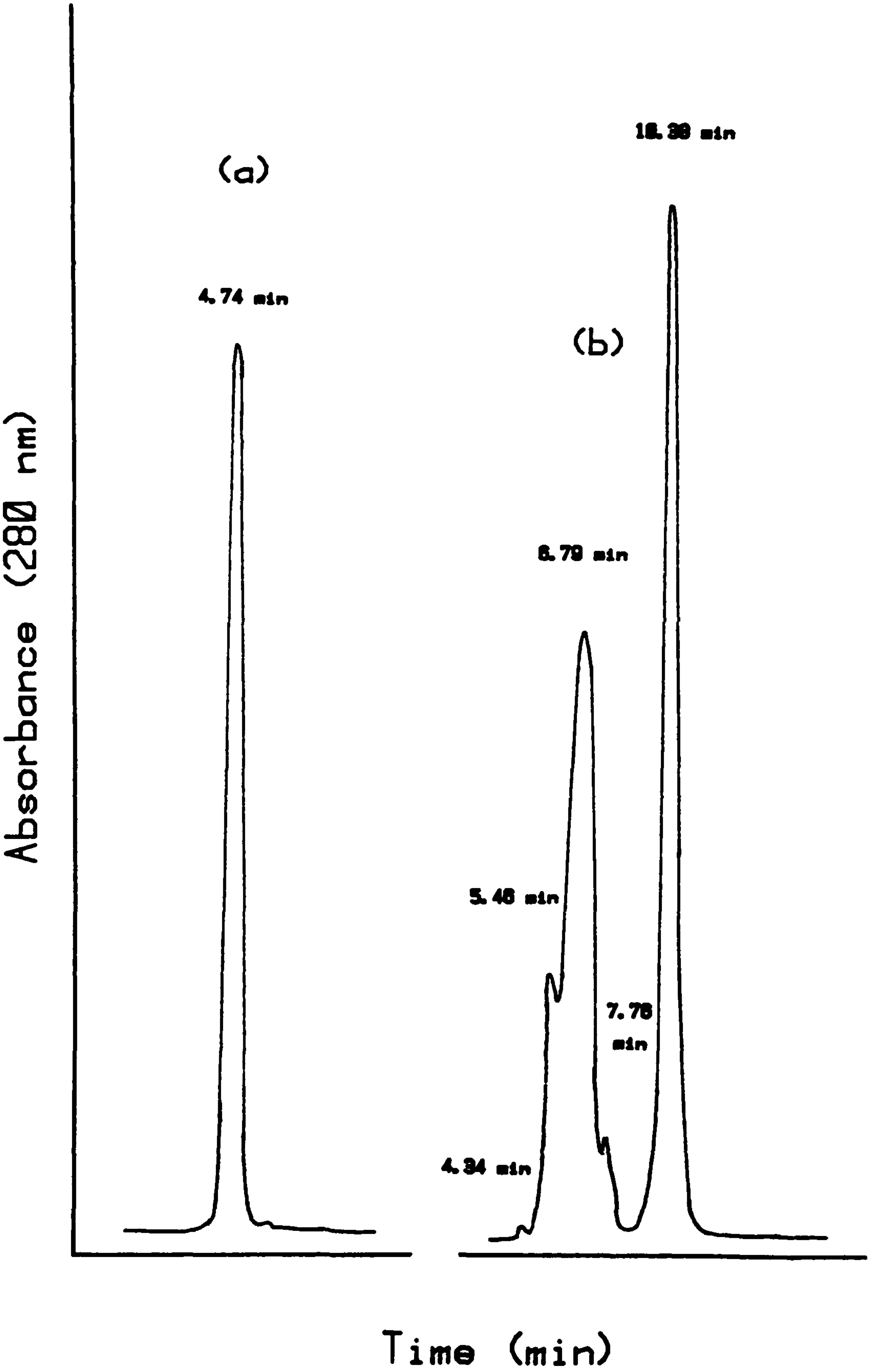


Figure 4. Gel permeation chromatographs of a) original and b) heated polyisoimide solution.

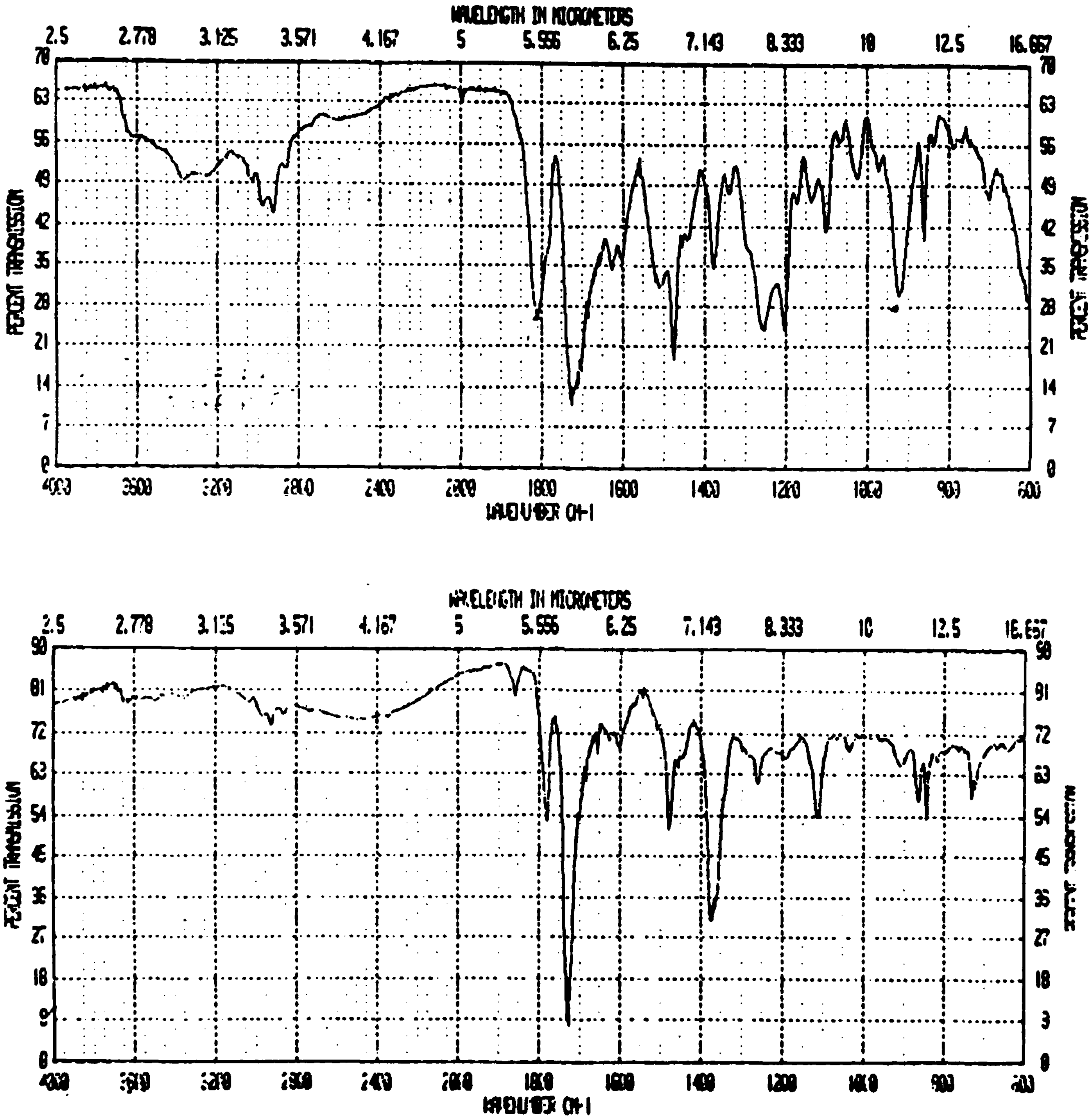


Figure 5. Infrared absorption spectra of polyisoimide (top) and heated polyisoimide.

OPTICAL MICROSCOPY

The isomerization of polyisoimide in solutions and films was examined using a Leitz ORTHOLUX microscope. Polarized light was used to determine the existence of birefringence in the heated polyisoimide. If the degree of isomerization is high, the rod-like polyimide of considerable length can be formed which should depolarize the light strongly. Detailed examination of the specimens under polarized light did not observe birefringence in the isomerized polymer. In addition, in-situ microscopic examination of the polyisoimide heated in a Mettler hot-stage did not show any birefringence up to 200°C. However, in one case, the glass sample tube developed a hairline crack releasing DMAc during heating, and the resultant films showed birefringence indicating that the polyisoimide had indeed converted to the rod-like polymer with a size near the wavelength of the visible light. Repeated attempts to reproduce this isomerization condition were not successful.

SMALL-ANGLE LIGHT SCATTERING

Another complementary technique utilizing the depolarization of polarized light by a rod-like particle is small-angle light scattering. The light scattering used a polarized He:Ne laser source with a wavelength of 632 nm. An analyzer was set to detect any Hv scattering due to the isomerization of a coil-like polyisoimide into the rod-like polyimide. Except for the precipitated film showing birefringence obtained from the cracked tube, all other specimens failed to show any Hv scattering. This suggests that the prescribed isomerization did not generate significant amount of rod-like polyimide of meaningful length.

X-RAY SCATTERING

X-ray scattering measurements on the polyisoimide and the polyimide specimens were carried out using a flat-film camera with pin-hole collimation. Cu Kα radiation from a Rigaku RU-300 rotating anode generator was the X-ray source. Each specimen was compacted and attached onto the exit of the collimator. Variations in the sample-to-film distance allowed us to cover both wide-angle (WAXS) and small-angle (SAXS) X-ray scattering measurements.

In this study, the WAXS covered a reciprocal space of $40 > Q > 4\ \mathrm{nm}^{-1}$, where $Q = 4\pi \operatorname{Sin}(\theta/2)/\lambda$, λ is the wavelength and θ is the scattering angle. Equivalently, this allows studies of a real space distance, d, of $0.16 < d < 1.57$ nm, which is most relevant to the unit cell structure, lattice orientation, and molecular packing. The SAXS covered a reciprocal space of $13.44 > Q > 1.20\ \mathrm{nm}^{-1}$, or $0.47 < d < 5.24$ nm, which is related to the supermolecular structure of the specimen. X-ray scattering intensities were registered on OSRAY or Kodak AA films.

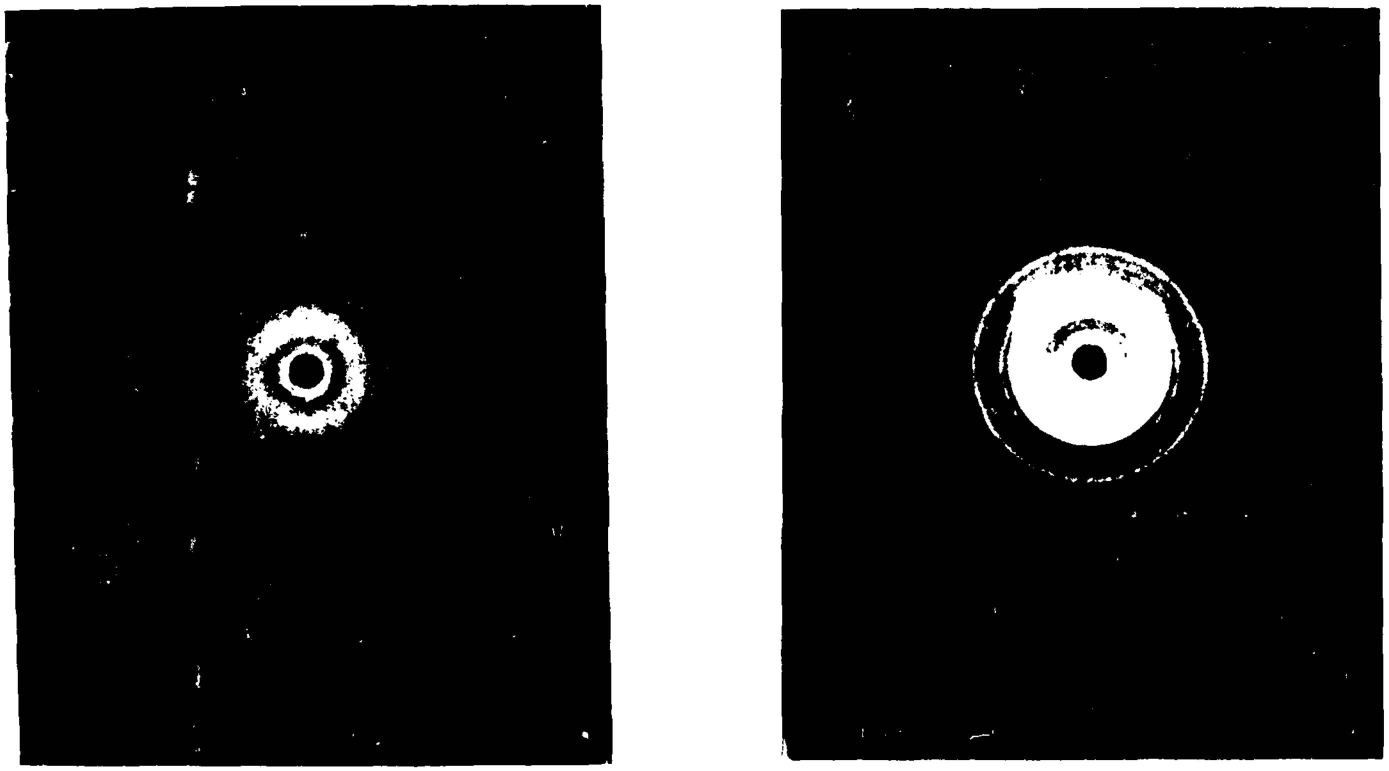
The WAXS showed isotropic scattering patterns for both specimens. There were two highly diffuse rings for the polyisoimide suggesting structural order of the polymer was poor, and seven sharp rings for the polyimide suggesting the polymer was highly ordered with the possible existence of a crystalline phase. The WAXS patterns are given in Figure 6 and the measured scattering angles and calculated repeat distances are listed in Table 2. The SAXS on the polyimide showed a faint reflection ring for 1.77 nm and scattering from voids. The scattering pattern is given in Figure 7.

MOLECULAR MODELING

Computer modeling of the monomers and the dimers of the isoimide and the imide was performed using SYBYL, a molecular modeling system developed by Tripos Associates, Inc. Using an energy minimization scheme, the molecules can be simulated numerically and the equilibrium isomeric states can be calculated under selected boundary conditions.

According to the calculations for the monomers, the isoimide and the imide have about the same repeat unit length, 1.78 and 1.73 nm, respectively, for the most favorable (lowest energy) conformations. Considering the molecular width of 0.7 nm, the aspect ratio of monomer length to diameter is 2.5. For a molecular composite fiber, an aspect ratio of 100 is considered necessary for the rod-like molecules to provide significant reinforcement.(1,2) This is equivalent to 40 consecutive imide repeating units, thus requiring an extremely high degree of isomerization.

Calculations on the isoimide dimer were also performed. The computations on the isoimide trans-dimer and cis-dimer gave similar results. For instance, using a torsion angle increment of 30°, the computation of the isoimide trans-dimer reveals that



(a) (b)

Figure 6. WAXS intensity patterns for a) original and b) heated polyisoimide.

TABLE 2

SCATTERING ANGLES AND REPEAT DISTANCES FROM WIDE-ANGLE X-RAY SCATTERING

Polymer	θ (°)	Repeat Distance (nm)
Polyisoimide	23.1	0.39
	14.3	0.62
Polyimide	28.1	0.32
	25.6	0.35
	23.7	0.38
	22.0	0.40
	18.2	0.49
	15.0	0.59
	10.5	0.84

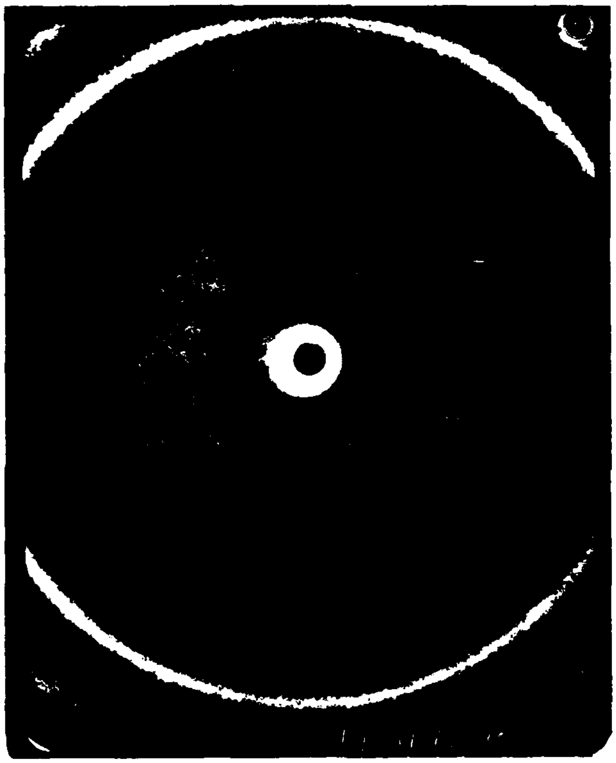
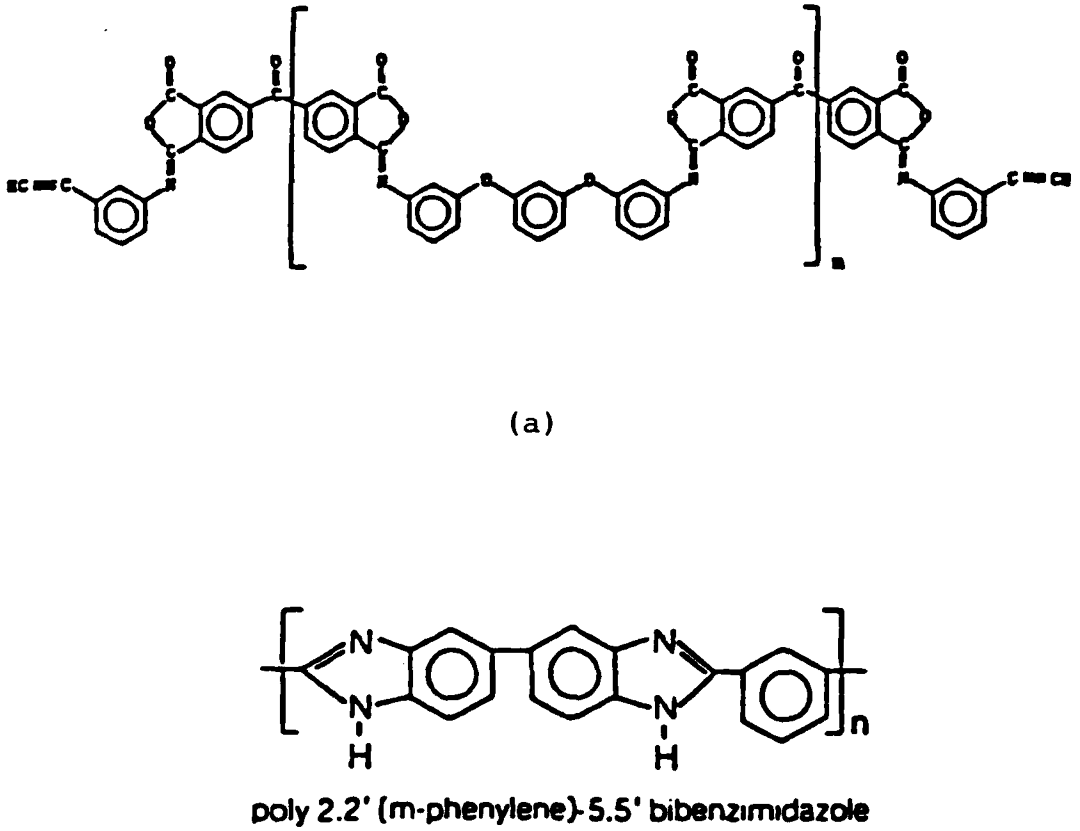


Figure 7. SAXS intensity pattern for heated polyisoimide.

the dimer has 108 stable isomeric states of binding energy from 136 to 149 Kcal/mol. Except for two states of binding energies of 140 and 144 Kcal/mol, all the other states assume an extended chain conformation. If this result is also valid for the polymer and a minimum aspect ratio of 100 for the polyimide is required for molecular composite applications, then 80 percent of the polyisoimide molecules would have one non-extended isomeric state and, hence, are <u>not energetically favored</u> to be a fully extended chain. This would impose additional restrictions in forming a rod-like polyimide by isomerizing the polyisoimide.

MOLECULAR COMPOSITES

Although the isomerization of the polyisoimide was not demonstrated conclusively in forming a rod-like molecule with significant length, two molecular composite systems utilizing this isomerization chemistry for in-situ rigid-rod reinforcement were explored. The first system involved a matrix of HR600P, which is a thermoset resin with isoimide structure, for film casting. The second system involved a matrix of a polyimide polymer, mPBI, for fiber spinning. The molecular structures of these two matrices are shown in Figure 8. The basic consideration for the selection of these two host polymers is their compatibility with the polyisoimide and the polyimide.



(a)

(b)

Figure 8. Chemical structures of a) HR600P resin and b) mPBI polyimide.

Polyisoimide/HR600P Composite Films

The polyisoimide has an isomerization temperature of about 220°C, while HR600P resin has an initial glass transition temperature of 150°C and a curing temperature of about 200°C. Therefore, the compatibility consideration is critical for the two materials to inhibit the phase separation during the isomerization of the polyisoimide and the curing of HR600P resin. Solutions of the polyisoimide and HR600P of various proportions were prepared in DMAc at a concentration of about two weight percent. The solutions were cast into films by evacuating the solvent. The films were orange in color and optically transparent. After heating at elevated temperatures, the films became dark and showed 30 percent weight loss which was mainly due to the evaporation of residual DMAc. Figure 9 shows the dynamic mechanical properties of a cast polyisoimide/HR600P film measured with a Rheovibron. The film showed a decrease in dynamic modulus between 120°C and 170°C, which could be due to the softening of HR600P.

The polyisoimide/HR600P films at various compositions were placed in a Lindbergh furnace for curing HR600P and isomerizing polyisoimide under nitrogen atmosphere at 300°C for two hours. Unfortunately, with one exception, the films cracked during heating. Table 3 lists the tensile properties of the polyisoimide/HR600P films. The film remaining intact after heating failed to show any significant improvement in tensile properties after the isomerization of polyisoimide, the curing of HR600P and the evaporation of residual DMAc.

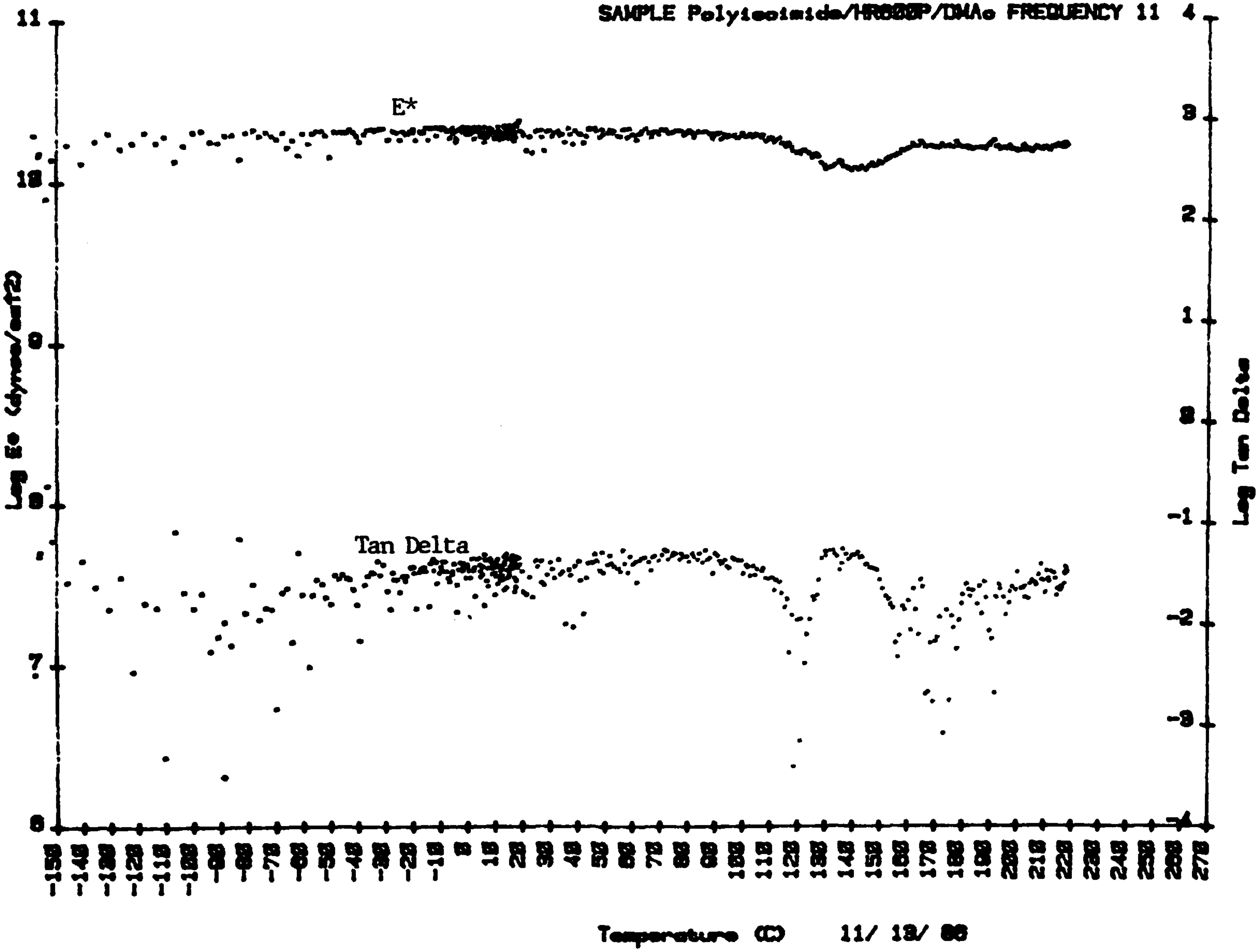


Figure 9. Dynamic mechanical properties of a molecular composite of 50/50 composition polyisoimide/HR600P.

TABLE 3

TENSILE PROPERTIES OF POLYISOIMIDE/HR600P COMPOSITE FILMS BEFORE AND AFTER ISOMERIZATION

Isoimide/HR600P/DMAc (wt/wt/wt)	Strength (Ksi)	Modulus (Ksi)	ϵ_b (%)
24/47/29	8.5	520	1.9
46/27/27	11.2	520	5.4
35/35/30	5.0	310	3.5
50/50/0*	4.5	430	1.0

*Film of 35/35/30 composition heated at 300°C for 2 hours.

Polyisoimide/mPBI Composite Fibers

Since the polyisoimide failed to show a rigid-rod reinforcement to HR600P films after heating, this second approach is to align the polyisoimide molecules in the composite prior to the isomerization to facilitate the forming of the rod-like polyimide. The alignment of the polyisoimide molecules was provided by spinning fibers from solutions.

Two polyisoimide solutions were prepared in DMAc to fabricate neat polyisoimide fibers by dry-jet, wet spinning. The initial concentrations were at two weight percent of the polyisoimide, then the concentrations were increased by evacuating the solvent. One solution formed gel at about six weight percent of the polymer and could not be spun into a fiber. The other solution showed a lesser degree of gelation at a concentration of 4.1 weight percent. This was observed during the fiber spinning when lumpy gels were extruded from the spinneret. Furthermore, this solution was not viscous enough to form a continuous fiber.

High quality mPBI fibers are commercially produced by spinning from DMAc solutions. To utilize this spinning advantage, a polyisoimide/mPBI composite solution was prepared for fiber processing. The polyisoimide and mPBI were separately dissolved in DMAc at 1 and 25 weight percent, respectively. In the latter case, two weight percent of LiCl was added to enhance the solubility. Proportional amounts of these two solutions were then mixed to obtain a 50/50 polyisoimide/mPBI composite solution of two weight percent. On the fourth day of mixing, a certain degree of gelation took place. This gelation is most likely through the amic acid groups in the polyisoimide. The mechanism of gelation may be due to the hydrolysis of the polyisoimide into the amic acid groups from residual water present in LiCl or DMAc. This hypothesis is supported by infrared spectra of the polyisoimide precipitated from the DMAc solution containing LiCl, which shows no isoimide absorptions.

CONCLUSIONS

A novel approach to fabricate in-situ rigid-rod molecular composites using the polyisoimide chemistry has been evaluated. The rigid-rod precursor is soluble in aprotic solvents and has a coil-like conformation. This approach depends on the thermal isomerization of a coil-like polyisoimide into a rod-like polyimide. This isomerization was studied extensively using various techniques. Two molecular composite systems were processed based on compatibility considerations. Results are summarized as follows:

(1) Although the polyisoimide is soluble in aprotic solvents such as DMAc, its solubility is still low for solution processing. The high boiling point of DMAc also poses problems for residual solvent removal. In addition, the polyisoimide is unstable in an environment containing water. Trace amounts of water could cause gelation in the solutions, that creates further difficulties in processing the polymer.

(2) Extensive infrared spectroscopic studies indicate that isomerization of the polyisoimide does occur either in DMAc solution or in the solid state upon heating. With one exception, all the results from GPC, optical microscopy small-angle light and X-ray scattering demonstrate that the isomerization does not generate significant amount of rod-like polyimide with meaningful length for rigid-rod molecular composite applications.

(3) Molecular modeling for the isomeric states of the isoimide dimers suggests that the polyisoimide molecule is not likely to be a fully extended chain. This chain conformation restricts the complete conversion of the polyisoimide to the rod-like polyimide even in a solution. The transformation of

the polyisoimide into the polyimide is more unlikely in a solid state composite. Thus, the application of the polyisoimide for in-situ rigid-rod molecular composite is deemed infeasible.

(4) The attempts to fabricate rigid-rod molecular composites of fibers and films by applying this in-situ rod formation concept were not successful, either in demonstrating a viable processing scheme or in actual gain in the tensile properties from the reinforcement of the in-situ rod.

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