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Observation of a Porous Gel Structure in Poly(*p*-phenylenebenzobisthiazole)/97% H_2SO_4

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ABSTRACT: The gelation of poly(*p*-phenylenebenzobisthiazole) (PBT) in 97% H_2SO_4 has been visualized "live" by using epiillumination video microscopy. When hot isotropic solutions are cooled, a distinctly porous structure is seen to emerge out of a uniform, homogeneous solution. The gel melting temperature increases with polymer concentration and molecular weight. It is also established that 97% H_2SO_4 is a good solvent for the polymer at 100 °C and that only minor degradation occurs at this temperature.

Introduction

Rodlike polymers can exhibit structure in solution, the most striking example being liquid crystalline order. A detailed knowledge of phase behavior and structure of rodlike polymers in good solvents led to the production of ultrahigh-modulus fibers.[1,2] However, during the usual dry-jet, wet-spinning process, the fiber passes through a nonsolvent coagulation bath—i.e., the solvent power is suddenly and drastically reduced.[3] In a variety of rodlike polymer/solvent systems, it is becoming clear that the morphological result of a sudden decrease in solvent power is gelation.[4–6] Not only does gelation play a role in fiber spinning, it may be a useful phenomenon in its own right, e.g., where porous materials or interpenetrating network composites are sought. Gelation appears to be the result of an attempt by the system to phase separate, complicated by initial aggregation, entanglement, convection, and specific interactions between solvent, polymer, and nonsolvent. The kinetic process of gelation, that is, the transition from good to poor solvent, is very important. Samples prepared by adding a poor solvent directly to the rodlike polymer merely fail to dissolve; no gel results. Although gelation during fiber spinning occurs primarily due to solvent composition change, a reduction in solvent power sufficient to initiate gelation can also be accomplished by rapid thermal quenching. In this paper, we report on the thermally induced gelation of solutions of poly(*p*-phenylenebenzobisthiazole) (PBT) in 97% sulfuric acid. After first exploring the stability of PBT/H_2SO_4 solutions at 100 °C, we present phase boundaries for gelation. Finally, epiillumination fluorescence microscopy is used to visualize directly the melting of the gels and also the reverse process: emergence of gel structure from isotropic, homogeneous one-phase solutions.

Materials and Methods

Two preparations of PBT were synthesized by Dr. J. F. Wolfe at SRI International by polycondensation of terephthalic acid with 2,5-dimercapto-1,4-phenylenediamine in poly(phosphoric acid). The two samples, PBT-7.3 and PBT-18, had intrinsic viscosities of 7.3 and 18 dL/g in methanesulfonic acid (MSA) at 30 °C, respectively, by prior measurement.[7]

Reagent grade 97% H_2SO_4 (Fisher) was used without further purification. For phase boundaries and gelation studies, solutions prepared by weight were sealed in glass machine vials with Teflon-faced liners. The solutions were homogenized at about 100 °C on a thermostatically controlled stirring hot plate by the action of a magnetic flea. Solutions for viscosity were prepared by weighing PBT directly into volumetric flasks. The solutions were transferred to viscometers immersed in an oil bath at 100 ± 0.07 °C by using prewarmed pipets. For studying the stability of viscosity with time, a Cannon–Fenske type viscometer fitted with stopcocks to shut out the atmosphere except during measurement was used. For intrinsic viscosities, a suspended-level (Ubbelohde) type viscometer was used. Solvent flow time was 620 s. Dilutions were accomplished in the viscometer by addition of known volumes of prewarmed solvent. A nitrogen blanket was provided to prevent moisture contamination. All transfers of solution or solvent were performed as quickly as possible to reduce moisture contamination.

Melting transitions were determined by suspending the samples in an oil bath situated on a Whatman programmable stirring hot plate. The oil was stirred by a magnetic bar. As a thermistor controlled the oil bath through a temperature ramp of 2 °C/min, temperature was read to 0.1 °C with a platinum resistance thermometer. The disappearance of structure during melting was also observed microscopically with a Mettler FP-80 thermal microscopy unit. Several methods of mounting the gels in the thermal microscopy unit were attempted, as discussed in "Results". Melting observations were made on an Olympus BH-2 microscope using both transmitted light and epiillumination fluorescence (excitation band: 380–490 nm; observation band: >510 nm).

The Mettler FP-80 thermal microscopy unit is equipped with upper and lower heating elements that surround the sample during observation. In this configuration, the indicated temperature is very accurate, as tested by melting points of known standards. Unfortunately, the unit is not well-suited to use with most objectives with magnifications higher than 10×. However, by removing the upper heating element (and substituting a 10-Ω, 10-W load resistor in the electrical circuit), convenient temperature variation at higher magnifications (up to 40× objective) can be obtained. There is, however, a loss of accuracy in temperature above about 100 °C in this configuration, as well as the danger of potential thermal damage to the microscope objectives. Additionally, at high magnification, substantial photobleaching was seen in the epiillumination fluorescence configuration. In order to overcome this problem, incident intensity was reduced with neutral-density filters, and a silicon-intensified video camera (Dage/MTI Series 66) was used to detect the image, which was scarcely visible to the eye. Electronic contrast enhancement measures, such as gain and bias offset, were not needed. All video microscopy was performed on a Leitz Ortholux II microscope (excitation band: 340–380 nm; observation band: >400 nm). For presentation, the recorded video image was recalled to a monitor screen and photographed on 35-mm film.

Absorption spectra were measured from 190 to 600 nm on a Hewlett-Packard Model 8451A diode-array spectrophotometer. One-centimeter quartz cells were held in a brass block, whose temperature was controlled by a circulating fluid. Temperature was measured to ±0.1 °C by a small (2 mm × 8 mm × 1 mm) platinum resistance thermometer located in the brass block.

Results

An immediate concern was the stability of PBT at elevated temperatures in hot 97% H_2SO_4. Figure 1 shows

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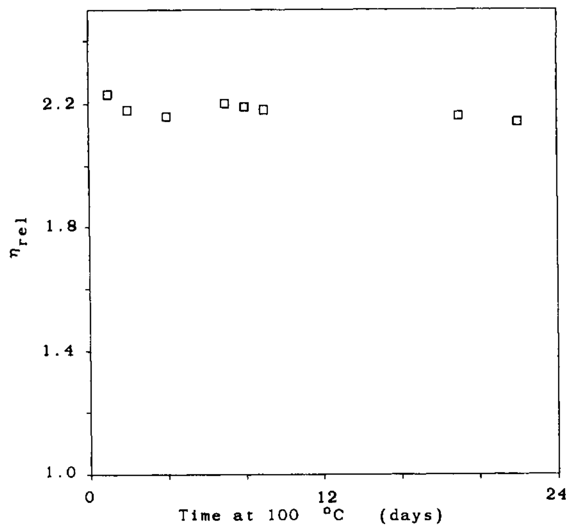

Figure 1. Relative viscosities of PBT-7.3 in 97% H_2SO_4 as a function of time. c = 0.198 g/dL. T = 100 °C.

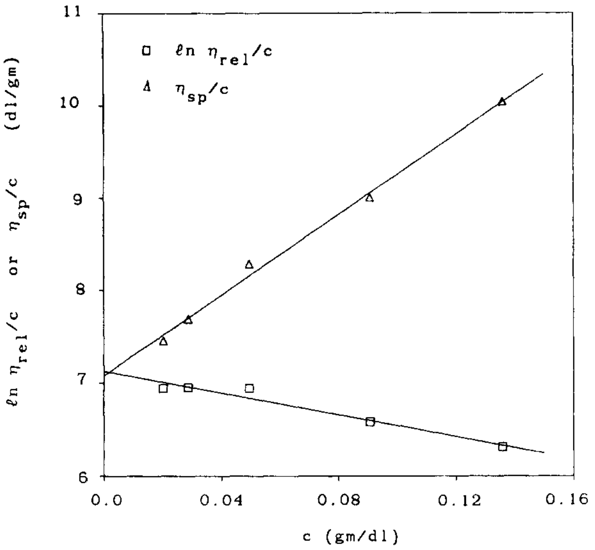

Figure 2. Double plot of viscosity data to obtain intrinsic viscosity, $[\eta]$: squares, $c^{-1} \ln (\eta_{rel})$; triangles, η_{sp}/c; solid lines, unweighted least-squares fits. PBT-7.3 in 97% H_2SO_4 at 100 °C. $[\eta]_{H_2SO_4}$ = 7.1 dL/g (compare to value in MSA: 7.3 dL/g).

that PBT degrades only slightly over a period of 3 weeks at 100 °C. As the samples prepared for all studies were dissolved in considerably less time, degradation should not be a significant factor in our results.

Methanesulfonic acid and chlorosulfonic acid are the best solvents for PBT at near-ambient temperatures.[8] In order to compare the molecular state of PBT in 97% H_2SO_4 at 100 °C to these solvents, we may consider Figure 2. The intrinsic viscosity in 97% H_2SO_4 (7.1 ± 0.1 dL/g) is virtually identical with that in MSA at 30 °C (7.3 dL/g). There is no evidence for aggregation. The intrinsic viscosity of PBT-18 in 97% H_2SO_4 is somewhat lower (15.5 ± 0.5 dL/g) than in MSA (18 dL/g). It is important to emphasize that the solvation power of 97% H_2SO_4 is strongly temperature dependent (see below). However, Figure 2 suggests that at 100 °C, 97% H_2SO_4 may be a suitable solvent for characterization and/or processing of PBT. It should be noted that, even at 100 °C, 97% H_2SO_4 is much less dangerous than chlorosulfonic acid at room temperature (e.g., there are no toxic vapors and direct contact with the skin, though moderately painful, will not result in hospitalization or permanent disfiguration if dealt with quickly).

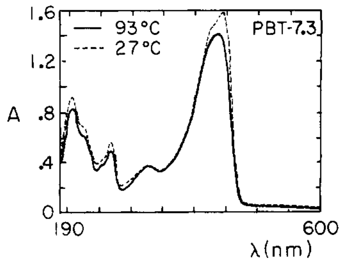

Figure 3. UV–visible absorption spectra for PBT-7.3 in 97% H_2SO_4 ($c = 4.6 \times 10^{-6}$ g/mL): (—) T = 93 °C; (---) T = 27 °C.

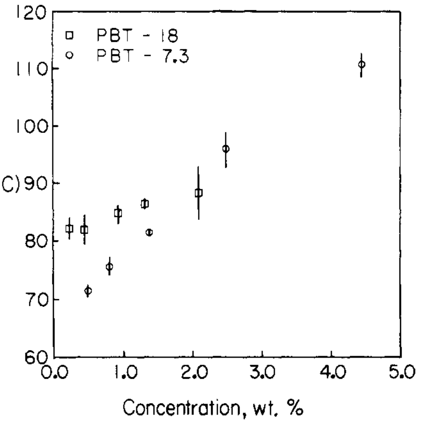

Figure 4. Phase boundaries determined by visual transitions of ca. 0.5-mL samples. 2 °C/min. See text.

The color of PBT and its solutions depends on solvent and temperature. Dry PBT has the color of rust. Hot solutions in 97% H_2SO_4 are yellow-green, tending toward "brackish" at high concentrations, but are never opaque at the thicknesses and concentrations studied here. The gel state is an opaque, vivid yellowish-green, even at 0 °C, but on exposure to water or atmospheric moisture the color reverts to rust. Figure 3 shows the UV–visible absorption spectrum for PBT-7.3 at several temperatures. There is some enhancement of the absorbance peaks at lower temperatures, but the general features are independent of temperature and strikingly similar to the spectrum in MSA at ambient temperature.[9] The peak near 440 nm is assigned to the main heterocycle absorption, shifted considerably toward the red, indicating substantial conjugation, due to the polymeric nature and protonation. No change in the position of this peak with temperature was observed.

Phase boundaries as determined by visual observation of ca. 0.5-mL samples are shown in Figure 4. The transition was identified by the change of appearance from opaque yellow-green to transluscent greenish-brackish. For most points shown on this diagram, PBT solutions below the transition met the true criterion of gels: they were substantially dilute solutions which exhibited no steady-state flow.[10] Some of the dilute solutions appeared to be microgel slurries, in which green particulate matter was suspended in solvent, without actually forming a structurally robust three-dimensional network.

There is, of course, no guarantee that the transitions measured as just described correspond to the disruption of the gel structure. Before turning to this question, we note that harsh handling of PBT gels can affect the phase boundaries. For example, if a bit of gel is scooped out with a spatula and placed on a glass microslide, solvent will be squeezed out from the gel. The polymer-rich region will melt at a much higher temperature than the undisturbed gel. Thus, an undisturbed bulk sample of the gel (ca. 0.5

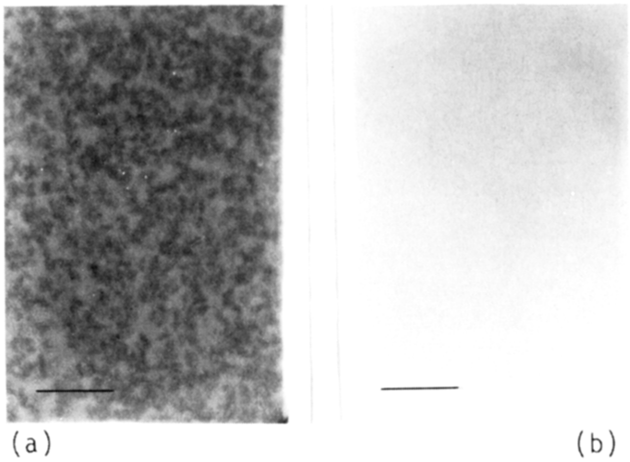

Figure 5. Epiillumination fluorescence photomicrographs showing melting of PBT gel, $c = 0.91$ wt %. Bright regions represent polymer. (a) Porous bicontinuous structure before melting; (b) structureless solution after melting. Initial objective: 40×, 0.65 NA. Bar marker = 50 μm (±10%).

mL) may melt at 90–100 °C, while a speck removed from the bulk will not melt until ca. 150 °C. (Note: this observation is true even at low magnifications when using both top and bottom heating elements of the Mettler hot stage and has nothing to do with the inaccuracies encountered with one heating element removed.) Attempts to follow the melting of the microscopic PBT gel structure were hampered by this problem. If a small drop of melted solution was drawn into rectangular capillary tubing or placed on a microscope slide and quickly covered and allowed to gel, it was possible to observe disappearance of sponge-like structures during melting using a 10× objective in the epifluorescence configuration. The melting process, however, was not easy to photograph at this low magnification, and this was an extremely tedious method for measuring gel melting points. Figure 5 shows the melting process at higher initial magnification, photographed with the upper heater of the thermal microscopy unit removed. As already discussed, temperature control is less than ideal in this configuration. Suffice it to say, melting points identified by disappearance of the sponge-like structures are similar to those identified by the appearance transition of bulk samples. The visual appearance transition does also seem to correspond to fluidity.

A video sequence showing *formation* of the porous PBT gel structure on cooling is shown in Figure 6. The process is notable for the fact that initially large inhomogeneities (Figure 6b,c) lead ultimately to a finer porous structure (Figure 6d). Visible nuclei are absent throughout the rather fast process.

Discussion

The behavior of rodlike polymers dissolved in good solvents is dictated by geometric asymmetry itself. Thus, chemically nonspecific theories, such as the original Flory treatment of rigid rod phase behavior,[11] may be successfully applied to a remarkable variety of rodlike macroparticles. One would not speak in terms of "universal" behavior, but there are clearly discernible similarities. The picture in poor solvents is less certain. Similar to many other rod-containing solutions, including less complex nonionic ones,[4,5,12,13] PBT solutions clearly gel when the solvation power is rapidly reduced. The mechanism of gelation, however, is not precisely known. The consistency of the UV–visible spectrum over a wide range of temperature in dilute solution argues against a dramatic change in protonation of the chain with temperature. The striking green color of the gels remains—even at temperatures as low as 0 °C—until water is introduced. Thus, the possibility that gelation in PBT/H_2SO_4 traces to phase stability considerations of geometrically asymmetric molecules in general, and not to specific ionic effects, must be admitted. This is not to suggest, however, that the resultant final morphology is unaffected by the polyion character of the PBT.

Miller and co-workers hypothesized[12,13] that gelation of nonionic poly(γ-benzyl α,L-glutamate) (PBLG) in poor solvents was the result of phase separation by a spinodal decomposition.[14] Initially, the evidence for this was circumstantial: (1) a distinctly bicontinuous structure—often the end result of spinodal decomposition—had been observed by freeze fracture electron microscopy and (2) the phase boundary is relatively flat, suggesting a narrow metastability gap. Kinetic structural investigations by light scattering did not show a classical spinodal mechanism in dilute PBLG gels.[15,16] However, certain "spinodal-like" features were evident, including the development of concentration inhomogeneities primarily via expansion of concentration gradient and not physical size. Dramatic variations in the scattering power (or turbidity) with gel temperature were also observed. A hypothesis explaining these results in terms of polymer mobility during the highly entangled state through which an isotropic solution must pass en route to equilibrium phase separation has been put forth.[17] Still, there is insufficient evidence concerning rodlike polymer mobility, the kinetics

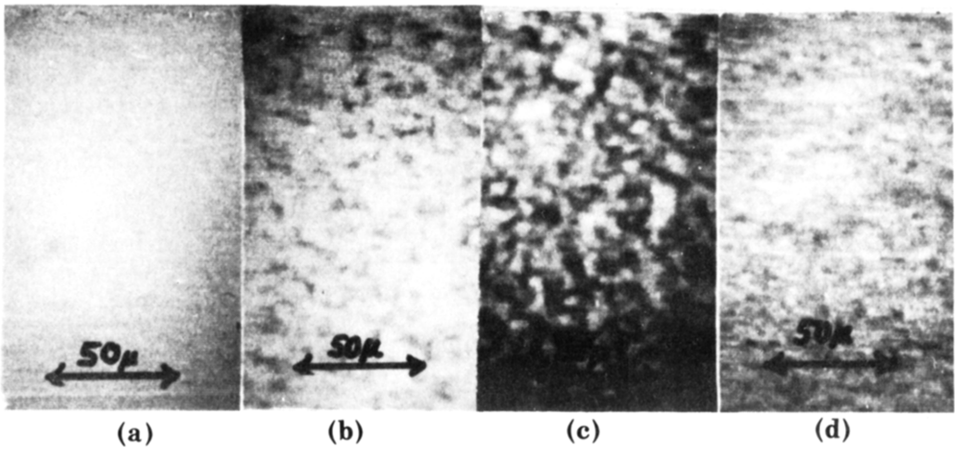

Figure 6. Video micrographic sequence, showing creation of gel from homogeneous solution (0.81 wt % PBT-7.3). All panels are the exact same region. Bright regions represent polymer. (a) Homogeneous solution: $t = 0$ s; $T = 100$ °C. (b) $t = 79$ s; $T = 74$ °C; −20 °C/min. (c) $t = 104$ s; $T = 65$ °C; −20 °C/min. (d) Fully formed gel: $t = 185$ s; $T = 47$ °C (holding).

of gelation from homogeneous and liquid crystalline solutions, and the local concentration of polymers during gelation to rule conclusively on the hypothesis.

The PBT/97% H_2SO_4 gels herein described could be considered at a state of development similar to PBLG gels a decade ago: there is circumstantial evidence for microphase separation by a nonequilibrium, nucleation-free mechanism from the decidedly porous, bicontinuous structures observed. Optical visualization of the gels also precludes any misgivings about the vagaries of preparing a mechanically weak gel structure for electron microscopy. (It may be added that, in some cases, fluorescently labeled PBLG gels do have porous, bicontinuous structures not too different from the PBT ones shown here.) Moreover, video epiillumination microscopy permits "real-time" visualization of the gelation process, with the very interesting result that initially large inhomogeneities give way to a smaller porous structure. This result, clearly visible in Figure 6, is difficult to explain, particularly in the absence of quantitative information on the local concentration of the emergent, PBT-rich phase. However, it may be noted that the processes studied so far are not isothermal. Isothermal gelation studies are in progress but are made difficult by their rapidity: often the gel is formed before the microscope can be focused.

Conclusion

PBT solutions in 97% sulfuric acid have been investigated, with the objective of understanding behavior in poor solvents. It has been established that 97% sulfuric acid is a good solvent at elevated temperatures, becoming a poor one as temperature is lowered, whereupon the solutions rapidly gel. Because gelation is induced without changing the solvent composition, this system is very convenient for further study. The gelation process itself and the final structure, which is porous, can be observed by optical microscopy. Although certain parallels can be drawn to chemically dissimilar nonionic rodlike polymers, suggesting the importance of general phase stability criteria for geometrically asymmetric particles, a conclusive gelation mechanism is not yet achieved for any rodlike polymer. Thus, it remains unclear what degree of commonality exists for rodlike polymers in poor solvents. From the macroscopic viewpoint, it would be interesting to compare the rheology of gels such as PBT/97% H_2SO_4 to that of their nonionic counterparts such as PBLG/toluene. Microscopically, future efforts in PBT and other rodlike polymer gels should be directed at a detailed picture of the local polymer concentration in the polymer-enriched phase as it emerges from both homogeneous and liquid crystalline solutions. Such studies could be carried out by quantitative microscopy and light scattering. Finally, it would be interesting to see whether the gels can be exploited for the production of porous materials and/or composites.

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Registry No. PBT (SRU), 69794-31-6; PBT (copolymer), 75454-67-0; H_2SO_4, 7664-93-9.

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