

Photo- and Thermoinduced Sol-Gel Transitions in Blends of Azobenzene Copolymers and Pluronic Surfactants

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Abstract Novel self-assembling copolymers of 4-Methacryloyloxyazobenzene and NN-dimethylacrylamide (MOAB-DMA) exhibiting a pronounced photoviscosity effects in water are described. An optimum polymer architecture corresponding to maximum contents of the azobenzene moieties that allowed for the aqueous solubility of the MOAB-DMA copolymer at ambient temperature was observed at a molar fraction of the MOAB moieties in the copolymer of 0.2. When blended with Pluronic F127 copolymers, the MOAB-DMA solutions become both irradiation- and temperature-sensitive and capable of sol-gel transitions depending on the MOAB-DMA content. Effect of the MOAB-DMA copolymer addition to concentrated Pluronic F127 solutions was studied by controlled stress rheology. The presence of the amphiphilic MOAB-DMA copolymers in the micellar Pluronic solutions enabled irradiation-dependent shifts in gelation temperature, while the viscoelastic gel modulus was not significantly affected by the MOAB-DMA copolymers, indicating that cubic lattice of the Pluronic responsible for the gel formation was not compromised. The UV- and T-dependent gelling media might prove to become viable electrophoretic separation matrices.

Index Terms azobenzene, Pluronic F127, photoviscosity effect, poly(*trans*-methacryloyloxyazobenzene-co-N,N-dimethylacrylamide).

I. INTRODUCTION

Stimuli-responsive polymers exhibiting sol-gel transition behavior in response to external stimuli such as temperature, pH, and light have been extensively researched as responsive materials for separation and biological applications.[1] Among them, azobenzene-containing polymers have attracted considerable interest because of their unique propensity to undergo conformational transitions due to the azobenzene isomerization.[2-5] The azobenzene undergoes the photoinduced *trans/cis* isomerization under UV irradiation, while the reverse *cis/trans* isomerization can be induced thermally or photochemically, using visible light ($\lambda > 400$ nm). Such a conformational change may give rise to concomitant changes in physical and chemical properties of azobenzene-containing polymers. A photoinduced phase separation of polymer solutions is a typical example of such changes.[6] However, very few studies of the photoregulated sol-gel transition behavior have been reported in the literature.[7] Those include polymers that possess lower critical solution temperature (LCST) in aqueous solutions. Herein, we addressed a question whether a cubic lattice formed by close-packed micelles of the thermosensitive Pluronic® F127 polymer can be modified by specifically designed, amphiphilic azobenzene-containing polymers to result in polymer blends with irradiation-tunable sol-gel transition properties. Since the azobenzene group is extremely hydrophobic, it must be conjugated with a hydrophilic moiety in order for the resulting copolymer not to phase-separate from its aqueous solution. We chose N,N-dimethylacrylamide (DMA) as such a water-soluble moiety. In this work, physical polymer blends were chosen that would retain the stiffness of the Pluronic gels, while enabling the gelation temperatures to generally remain in the useful range and be finely tuned by the UV irradiation. Pluronic F127 was chosen due to the most dramatic gelation effects that it exhibits among other Pluronic surfactants.

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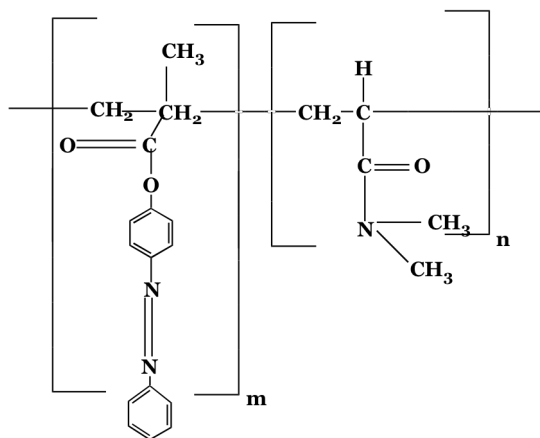
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II. EXPERIMENTAL SECTION

A. Materials.

Pluronic F127 (average composition, EO₉₉PO₆₇EO₉₉), triblock copolymers of ethylene oxide (EO) and propylene oxide (PO) were obtained from BASF (Mount Olive, NJ). *trans*-Methacryloyloxyazobenzene-dimethylacrylamide (MOAB-DMA) was synthesized by free-radical copolymerization of methacryloyloxyazobenzene with N,N-dimethylacrylamide using AIBN as an initiator in THF at 70°C.[8] The azobenzene monomer was synthesized by condensation of 4-hydroxyazobenzene and methacryloyl chloride in tetrahydrofuran (THF), with triethylamine (TEA) acting as a promoter. Two fractions of the MOAB-DMA copolymer were synthesized, with weight-average molecular weight at 4 and 24 kDa and polydispersities being in the 1.1-1.3 range.



Scheme 1: Structure of the MOAB-DMA polymer

B. Preparation of F127 and MOAB-DMA aqueous blends

The low-molecular weight (4 kDa) MOAB-DMA was found to be sparingly soluble in water. Hence, in order to obtain molecularly dispersed blends, both MOAB-DMA and Pluronic polymers were dispersed in THF at different ratios, as THF appeared to be a good solvent for both polymers. The THF was then vacuum-evaporated from the solutions and the resulting solid blends were redispersed in DI water resulting in transparent solutions.

C. Procedures

Photoirradiation was carried out with a 200 W mercury ARC lamp (Oriel, Model 6283) mounted on an arc lamp housing (Model 66902) and powered by an arc lamp power supply (Model 68910). The UV illumination was carried out in dark in deoxygenated conditions using 325 nm bandpass filter (Model 59800, used to obtain monochromatic UV

light). The setup was equipped with a heat-absorbing filter (Schott KG 4 Heat Absorbing, Oriel) to remove the heat generated by the UV and IR light. The intensity of irradiation was measured using an Accu-Cal™ 30 Radiometer (Dymax, Torrington, CT) to be 0.1 mW/cm² (325nm). The samples were irradiated for 24 hours to ascertain that there was complete conversion from *trans* to *cis* form. Rheological measurements were performed using a controlled stress Rheolyst Series AR1000 Rheometer (TA Instruments, New Castle, DE) with a cone and plate geometry system (cone: diameter, 2 cm; angle, 2°, truncation, 57 μm). Temperature control (internal resolution 0.016 °C) was provided by two Peltier plates. Dynamic experiments were carried in a controlled stress mode (temperature ramp ca. 2.5 deg/min). Dynamic light scattering experiments were performed with a Brookhaven Instruments BI-200SM equipped with a goniometer alignment software, a BI-9000 Correlator and a Spectra Physics He-Ne Model 127 laser operating at a scattering angle $\theta=90^\circ$ and a wavelength of incident light of 633 nm at a power of 50 mW. A 10 mL quartz scattering cell was thermostatted using refractive index matching silicone oil, and temperature was controlled to within 0.02°C.

III. RESULTS AND DISCUSSION

D. Effect of MOAB-DMA on gelation of Pluronic F127 solutions

When the MOAB-DMA copolymer solution was allowed to equilibrate in the dark, about 80-85% of the azobenzene moieties were present in their *trans*-conformation. The *trans*-form isomers are in their planar, apolar form that is extremely hydrophobic and promotes formation of aggregates that can be consequently incorporated into the Pluronic micelles upon blending. Those hydrophobic aggregates can reach sizes up to 30 nm and larger, while the Pluronic F127 micelles do not exceed 6 nm diameter.[9] However, some parts of the azobenzene segment aggregates can certainly be solubilized into the Pluronic micelle cores. Such a solubilization would lead to a stabilization of the micelle and thus lower the critical micellization temperature (cmt), analogously to the well-documented effect of solubilization of other non-polar solutes.[10]. The cmt is inherently related to the temperature where the sol-gel transition in the Pluronic solutions occurs, because the gel comprises a close-packed micellar lattice.[11, 12]

These considerations explain the observed effect of the MOAB-DMA addition to the Pluronic solutions (Fig.1). The temperatures at which the storage moduli increased indicating massive formation of micelles that crowded the system thus dramatically enhancing its elasticity, corresponded to the gelation temperatures (further referred to as T_{gel}). The instant of gelation was measured as the temperature where $G' = G''$. The T_{gel} systematically declined with the concentration of the added MOAB-DMA, resulting in over 15 °C decrease within the concentration

range studied (Fig.2). Notably, the UV irradiation of the blends resulted in measurable and systematic shifts in the T_{gel} , which was observed to be lower in the solutions where the majority of the azobenzene groups were in their *cis*-, more polar, conformation.

To explain this counterintuitive result, we conducted a series of dynamic light scattering measurements of the aggregate size in the MOAB-DMA solutions without Pluronic. The relaxation time distributions at three representative MOAB-DMA concentrations in water are shown in Fig. 3. The relaxation time distributions were found to be bimodal with fast and slow-mode relaxation peaks corresponding to smaller and larger aggregates, respectively. With the increase in the polymer concentration, the contribution of the fast mode fraction corresponding to the smaller aggregates increased several-fold compared to the slow mode peak. These observations explain the overall decrease of the z-average hydrodynamic radius of the MOAB-DMA chains with concentration

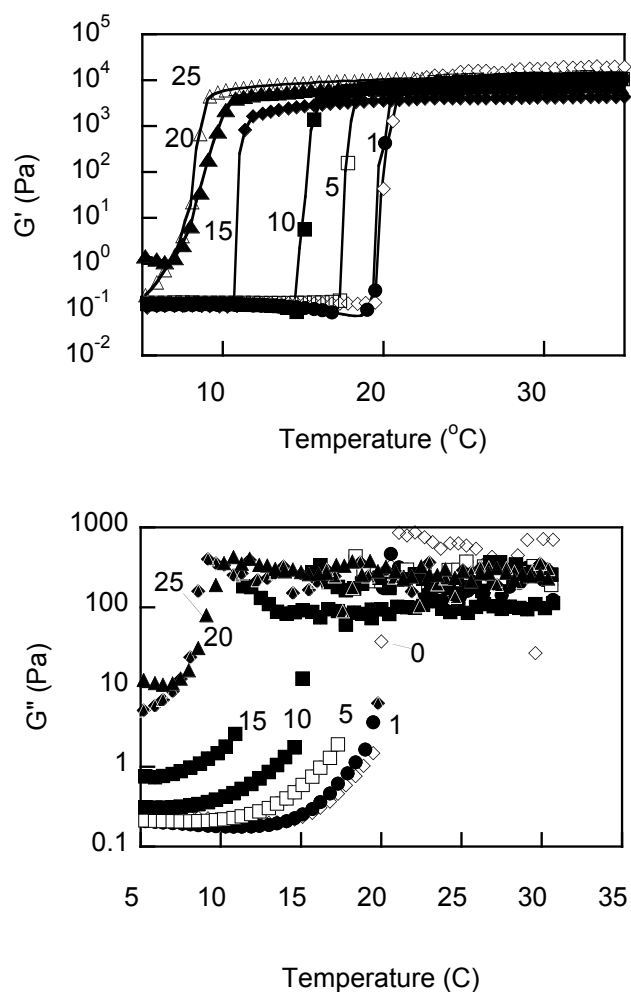
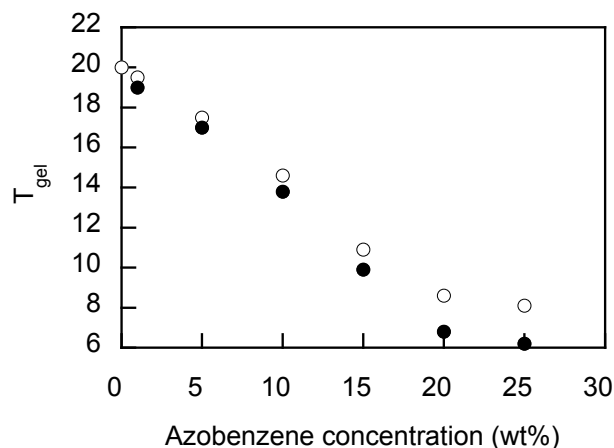


Figure 1: Storage (G') and loss (G'') moduli of aqueous solutions of Pluronic F127 (30 wt%) with varying content of MOAB-DMA copolymer as functions of temperature. Numbers stand for wt% of the MOAB-DMA. Angular frequency 6.28 rad/s, stress 0.6 Pa, pH 7.0.

Figure 2: Effect of the azobenzene moiety concentration in 30%



Pluronic F127 solution with the MOAB-DMA copolymer added on the gelation temperature (T_{gel}). The T_{gel} is defined as a T where $G' = G''$ in the temperature ramps (Fig.1). Open and filled points correspond to the *trans*- and *cis*- forms of the azobenzene groups in the MOAB-DMA attained before and after UV irradiation of the solutions, respectively. The irradiation was conducted for 24 h as described in the Experimental section.

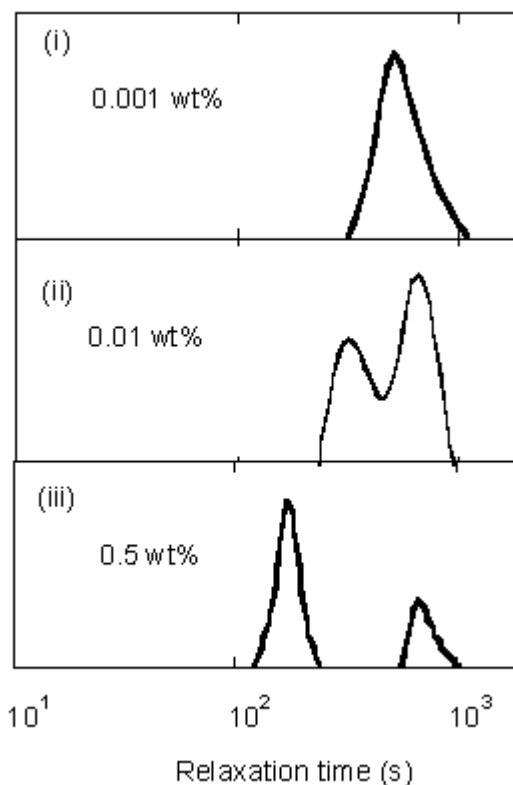


Figure 3: Representative distributions of relaxation times obtained in dynamic light scattering (DLS) experiments in aqueous solutions of MOAB-DMA at $T=25^{\circ}\text{C}$ and $\text{pH}=7$. Polymer concentrations in wt% are shown on charts.

observed in the same measurements (Fig.4). The hydrodynamic radius obtained from the diffusion

coefficient declined 2-fold at concentrations above 0.008 wt% indicating the appearance of a significant population of smaller aggregates at these polymer concentrations. Hence, it appeared that the isomerization to the skewed, polar, cis form inhibits hydrophobic interactions among azobenzene groups and causes the azo units to dissociate from the aggregates resulting in a population of smaller aggregates. These unimeric or oligomeric, small azobenzene aggregates (Fig.3) are more available for incorporation in the existing Pluronic F127 micelles when the MOAB-DMA is added to the Pluronic solution. A higher fraction of the azobenzene group incorporation results in a more profound shifts in the cmt as reflected in the lower T_{gel} (Fig.2).

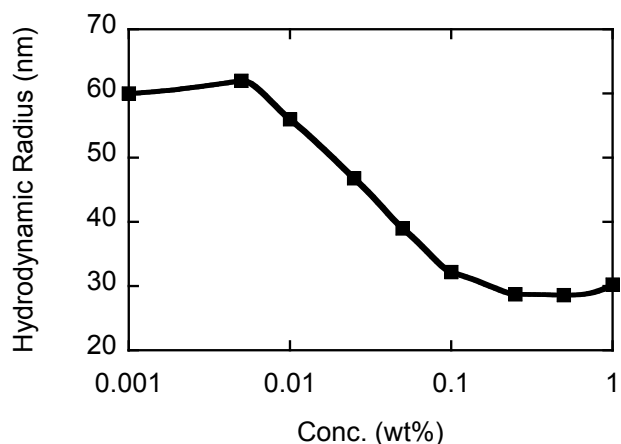


Figure 4. Concentration dependence of hydrodynamic radius of the dynamic light scattering (DLS) experiments in aqueous solutions of MOAB-DMA at $T=25^{\circ}\text{C}$ and $\text{pH}=7$ obtained from DLS at $q=90^{\circ}$.

IV. CONCLUSIONS

An effect of the photosensitive MOAB-DMA copolymer addition to the thermogelling solutions of Pluronic F127 was demonstrated. The MOAB-DMA lowers the gelation temperatures (T_{gel}) more effectively upon transition to the cis-isomer of its azobenzene groups. This effect can be explained by more efficient incorporation of the dissociated cis-azobenzene moieties to the Pluronic micelles. Such phenomena can be applied to the design of both spatially and temporally resolved separations using intelligent polymer matrices.

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