Stimuli Responsive Graft Polysiloxanes

ANCA DANIELA RUSU[1,2], CONSTANTA IBANESCU[1,3]*, ELENA RESMERITA[1], BOGDANA SIMIONESCU[1,4], MARICEL DANU[3], VLAD HURDUC[1], SORIN ALEXANDRU IBANESCU[3]
[1] "Gheorghe Asachi" Technical University of Iasi, 73 Prof. dr. docent Dimitrie Mangeron Str., 700050 Iasi, Romania
[2] CEA, LIST Saclay, Laboratoire Capteurs et Architectures Electroniques, 91191 Gif-sur-Yvette, Cedex, France
[3]"Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Vodă Alley, 700487 Iasi, Romania
[4]"Costin D. Nenitescu" Organic Chemistry Center, 202B Splaiul Independentei, 71141 Bucharest, Romania

Stimuli sensitive amphiphilic polymers based on partially substituted graft polysiloxanes were obtained and characterized. The polymers were synthesized in a two-step reaction, starting from a polysiloxane with chlorobenzile groups in the side chain. In the first step, the polysiloxane was modified with dinitro- or azo-aromatic group and, in the second step, the unreacted chlorobenzile groups were grafted with thermo-sensitive poly (N, N-dimethylacrylamide (PDMA) side chains in a Single Electron Transfer-Living Radical Polymerization (SET-LRP) reaction. The polymer structures and their properties were investigated by ^{1}H-NMR spectroscopy, DSC, fluorescence and UV-VIS spectroscopy and rheology. Because of the amphiphilic character, these polymers are self-assembling in aqueous solution in a core-shell micelles, the critical concentration of the aggregation value being in the 10^{-1} range. The thermo-sensitive character, the lower *critical solution temperature (LCST) and the conformational changes of the side-chains are evidenced by rheological temperature sweep tests.*

Keywords: stimuli responsive polymers, rheology, azo-polysiloxane, dimethylacrylamide

Stimuli-sensitive polymers, also known as "smart polymers", have attracted much attention of the researchers during the last years. This type of polymers can recognize a stimulus as a signal, due to a sensitive component contained in the chemical structure. The response of the material to the variable conditions of the environment determines a reorganization of polymers chains architecture, translated in novel properties of the polymeric system [1, 2]. Different external stimuli can be used to induce responsive reactions in polymeric systems, the purpose is having control on modulating properties [2-5]. Temperature [6-10] and light [11-15] are two of the most widely used stimuli in environmentally responsive polymer systems.

Soluble in specific solvents, more often water, thermo-sensitive polymers are characterized by a phase separation when heated above the lower critical solution temperature, LCST [16, 17]. Another property of interests is the thermo-thickening behaviour, caused by the formation of hydrophobic microdomains and defined as association temperature [10]. Polymers bearing amide groups form the largest group of temperature responsive polymers [18]. Poly (N, N-dimethylacrylamide) (PDMA) is well known to have an excellent solubility in a large range of solvents [19] and it is usually copolymerized with another thermo-responsive macromolecules in order to obtain a new material with a desired LCST [20-23]. Moreover, there are some literature data according to which PDMA has an LCST in aqueous solution above 100 °C [24] or even higher, at 216 °C [25].

Azobenzene molecules have been intensively studied during the last years because of their photo-responsive behaviour, based on the UV *trans–cis* isomerization capacity [12, 26]. The specific response of such materials correlated with different polymeric architectures can be associated with various phenomena such as phase transition, surface relief grating or film contraction [13, 15].

To graft different types of acrylic monomers on a hydrophobic main chain in order to obtain polymers sensitive to external stimuli characterized by the self-assembly ability, Single Electron Transfer-Living Radical Polymerization (SET- LRP) [27] represents an election method [28]. This paper presents the synthesis and characterization of novel stimuli sensitive polymers, obtained by grafting polysiloxane (PSI) carrying partial substituted clorobenzyl groups in the side chain, with N, N-dimethylacrylamide (DMA). The purpose of grafting thermo- and photosensitive segments on a hydrophobic main chain is the obtaining of double responsive systems with tunable properties.

Double responsiveness of the synthesized polymers was induced by grafting the azo-polysiloxanic main chain with polyacrylamidic backbones. Upon UV-irradiation, the azobenzene groups in the polymeric materials turn from the more hydrophobic *trans*-form to the more hydrophilic *cis*-configuration. As a result, an increase of the LCST of the dual-responsive polymers depending on the isomerization degree [1] is obtained.

Furthermore, potential biomedical applications of the smart polymeric nanocarriers were taken into consideration. Stimuli responsive amphiphilic polymers are of substantial importance for various applications requiring the combination of hydrophilic and hydrophobic properties which these materials exhibit.

Experimental part

Materials

The monomer DMA (Sigma–Aldrich, Steinheim, Germany) was once passed through a basic-alumina column to remove the polymerization inhibitor. 2, 2'-bipyridyl (Fluka) was purified by recristallization, dried under vacuum and stored under argon atmosphere. All other

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* *email: ibanescu@ch.tuiasi.ro*

Table 1
CHARACTERISTICS OF THE SYNTHESIZED POLYMERS

Sample code	Sample	Substituent	Substitution degree	Polymerization degree on the side chain	M_n	T_g, °C	LCST °C
S1	Nitro-PSI-g-PDMA	2, 4-dinitophenol	15 %	13	48000	-14	47
S2	Azo-PSI-g-PDMA	Azobenzene	20 %	33	103000	-9	45

M_n – molecular weight
T_g – glass transition temperature
LCST – the lower critical solution temperature

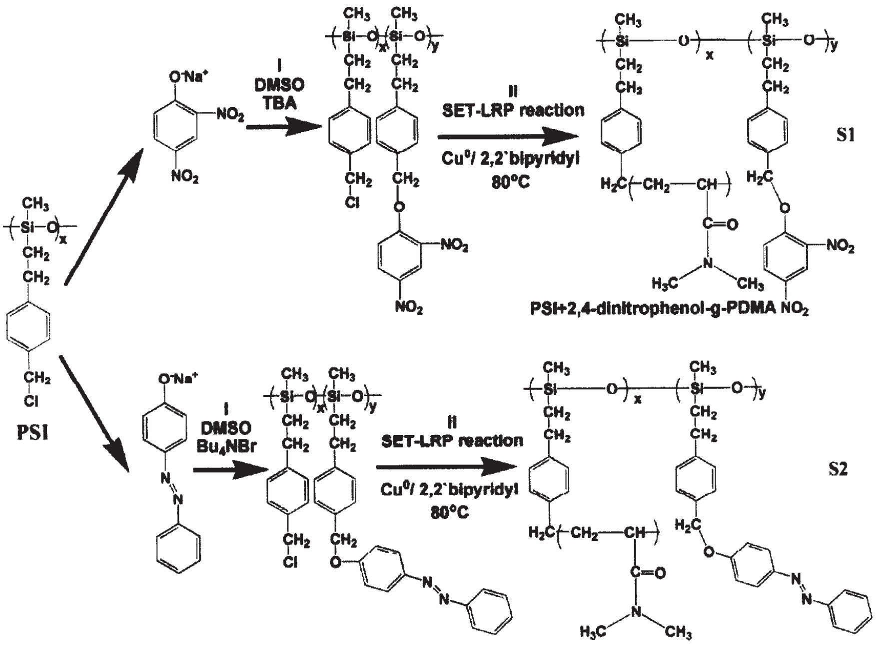

Fig. 1. General reaction scheme for stimuli responsive polymers synthesis

solvents (chloroform, dimethylsulfoxide (DMSO), diethyl ether) and chemicals from Sigma–Aldrich, Steinheim, Germany, were used as received. The synthesis and purification of the PSI macroinitiator was performed according to reference [29].

Polymer synthesis

For all samples the first reaction step is the nucleophilic substitution of the chlorobenzil groups with sodium salt of 4-(phenylazo) phenol or 2, 4-dinitophenol (the substitution reactions were performed according to reference [13]). In the second step, the unreacted clorobenzil groups were grafted with PDMA side chains. More details concerning the SET-LRP reaction can be found in a previous paper [30].

Characterization

The synthesized polymers were characterized by ^{1}H-NMR, UV-Vis and fluorescence spectroscopy, DSC and rheology. ^{1}H-NMR spectra were recorded on a Bruker 400 MHz spectrometer, using cloroforme as NMR solvent. Glass transitions temperature (T_g) was investigated by a Mettler Toledo DSC 1 operating version 9.1 with a heating/cooling rate of 10 K/min and the DCS curves were plotted by a STAR software. For the DSC analysis, the samples were encapsulated in aluminum pans having pierced lids to allow the evaporation of the volatiles components.

The thermosensitivity of the polymers was investigated using an Anton Paar, Physica MCR 501 modular rheometer with a Peltier system for the temperature control. For the tests, plane-plane geometry was used. The upper plate from stainless steel has 50 mm in diameter, the distance between the plates was set at 0.5 mm. During all rheological experiments, a solvent trap was used to minimize the solvent evaporation. Fluorescence spectra were recorded on a Shimadzu 5301PC spectrophotometer, at room temperature. To evaluate the aggregation capacity of the polymers, the classical method using pyrene fluorescence spectroscopy was used [12, 31]. The intensity ratio (I1/I3) of the first (I1) over the third (I3) vibration band of the emission spectrum of pyrene, at 373 and 384 nm, respectively, was used to detect the formation of micelles. In aqueous solution the I1/I3 ratio value, corresponding to the free pyrene in water, is situated around 1.70–1.75. For dilute solutions (less than 10^{-1} g/L), the ratio I1/I3 is around 1.7, no aggregation process being evidenced. The polymer photochromic behaviour was investigated in $CHCl_3$ solution and solid state using a UV lamp source (100 W) equipped with a 365 nm filter. UV-Vis spectroscopy was performed with a Shimadzu UV-Vis spectrophotometer.

All solutions were prepared by disolving the polymers in a minimun volume of THF, followed by the adition af a water volume (drop by drop) depending on the sample concentration, under strong stiring. After the solution preparation, THF vas evaporated.

Results and discussions

The synthesis of stimuli responsive polymers was performed using as macroinitiator a polysiloxane (PSI) with a molecular weight of M_n = 4800-5000, having chlorobenzyl groups in the side chain. A two step reaction was involved. In the first step, polysiloxane with chlorobenzyl groups in the side chain was modified with 2, 4-dinitophenol (DNP) (S1) or azobenzene groups (S2), as shown in table 1. In the second step, the unreacted chlorobenzyl groups were

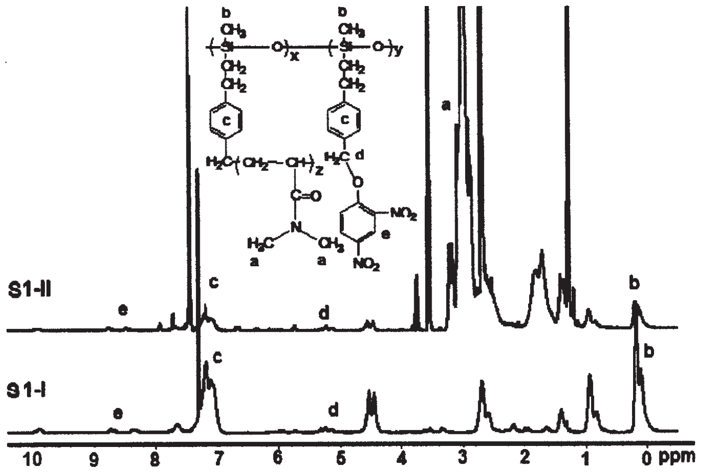

Fig. 2. ^{1}H-NMR spectrum of nitro-PSI-g-PDMA (S1)

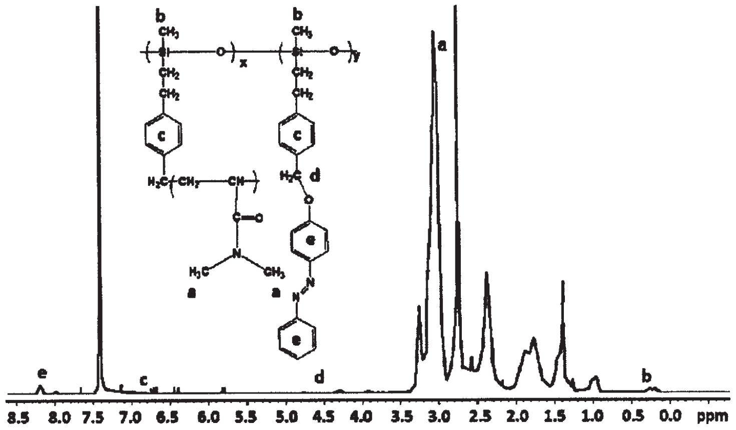

Fig. 3. ^{1}H-NMR spectrum of azo-PSI-g-PDMA (S2)

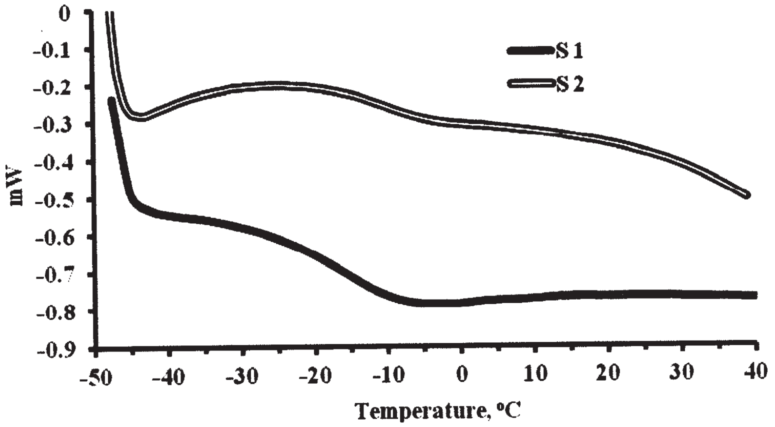

Fig. 4. DSC curves of nitro-PSI-g-PDMA (S1) and azo-PSI-g-PDMA (S2)

grafted with N, N-dimethylacrylamide monomer, in a typical SET-LRP reaction (fig.1).

The chemical structures of the modified polymers were confirmed by ^{1}H-NMR spectroscopy (fig. 2. and 3.). The substitution degree was evaluated based on the signals corresponding to the methylenic chlorobenzyl (4.5 ppm) before the reaction and $-C_6H_4$-CH_2-O-$C_6H_3N_2O_4$ (nitro-PSI-g-PDMA) or $-C_6H_4$-CH_2-O-C_6H_4 (azo-PSI-g-PDMA) from 5.0 ppm, after the substitution reaction. The signals for PDMA side-chains appear at 2.9 ppm.

The glass transition temperature, corresponding to the synthesized samples, have been evidenced by DSC analysis using a Mettler Toledo DSC-1 Star System apparatus, at a nitrogen flow rate of 150 mL/min and 3 to 5 mg samples weight. For all samples, two heating and one cooling cycles have been performed between -50 and 40°C. As mentioned in previous papers [30, 32], considering the first heating scan can be influenced by the sample's "history", only the curves corresponding to the second heating scan are presented in figure 4.

Tethering the PDMA groups on the polysiloxane chain leads to the increase of the glass transition temperature from –40°C (for the polysiloxane) to -9 °C in the case of azo-PSI-g-PDMA and to -14°C for nitro-PSI-g-PDMA. The Tg was calculated as the inflection point on the DSC curves.

Due to the presence of PDMA hydrophilic side chains and the hydrophobic modified polysiloxane main chain, the synthesized polymers have an amphiphilic character, translated into the formation of polymeric micelles in aqueous solutions. Some of these micelles undergo physical form transition in response to temperature changes [1].

To evaluate the aggregation capacity of the polymers, the classical method using pyrene fluorescence spectroscopy was used. The polarity of the micelles core was analyzed by monitoring the changes in the excitation and emission spectra of pyrene in polymer solutions [29].

To obtain micelles, stimuli-responsive polymers were dissolved in THF, then water was slowly added under continuous stirring, followed by the evaporation of THF. The critical aggregation concentrations (CCA) were estimated

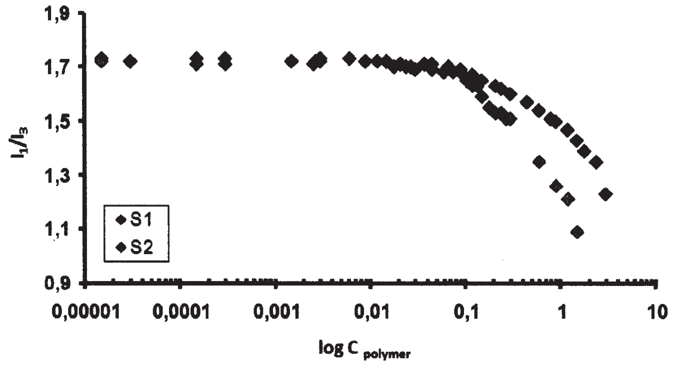

Fig 5. CCA of the amphiphilic polymers (S1 - nitro-PSI-g-PDMA and S2 - azo-PSI-g-PDMA)

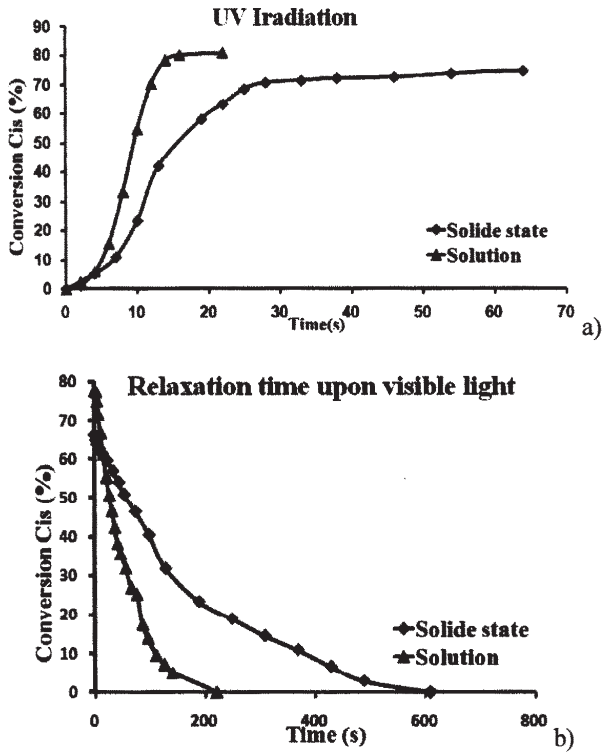

Fig. 6. Photo-chromic behaviour of the azo-polymer

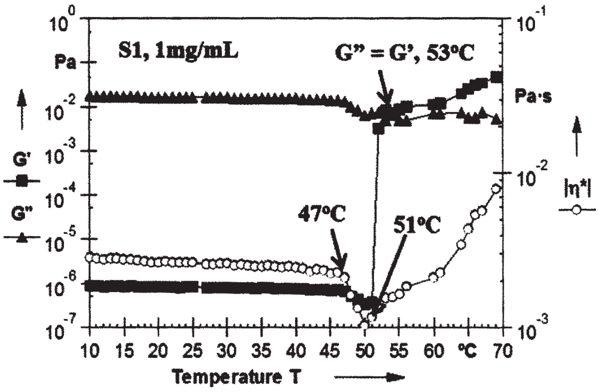

Fig. 7. Temperature sweep for 1 mg/mL water solution of nitro-PSI-g-PDMA (S1)

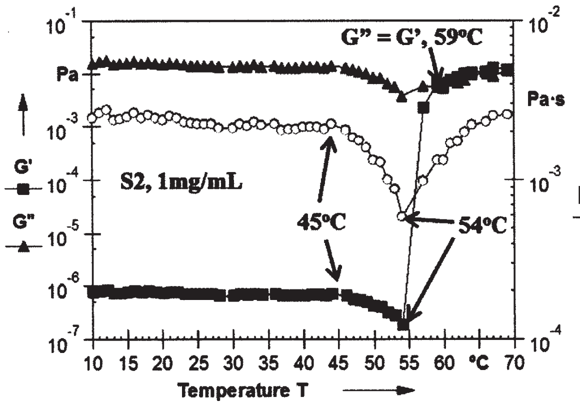

Fig. 8. Temperature sweep for 1 mg/mL water solution of azo-PSI-g-PDMA (S2)

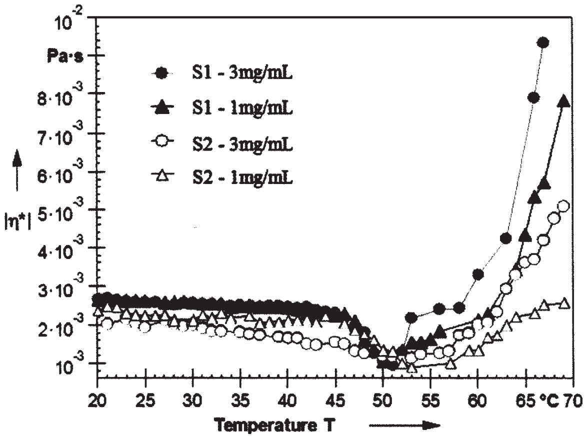

Fig. 9. Complex viscosity variation with temperature for nitro-PSI-g-PDMA (S1) and azo-PSI-g-PDMA (S2) at two different concentration

as the first inflexion point from the curves that represent the plot of the I1/I3 ratio as a function of polymer concentration. The CCA values are in the same range, of $1.7x10^{-1}$ g/L for the graft azo-polysiloxanes (azo-PSI-g-PDMA) and $1.2x10^{-1}$ g/L for the graft nitro-polysiloxanes (nitro-PSI-g-PDMA) (fig. 5). The strong hydrophobic character of the azobenzenic groups is reduced by the hydrophilic PDMA lateral chains and the result is an increase of CCA; for example, a azo-polysiloxane modified with ternary amine has a value of CCA in 10^{-3} range [6]. In water solution samples nitro-PSI-g-PDMA and azo-PSI-g-PDMA are self-assembling in micelles at a specific CCA, the hydrophobic substituted polysiloxane forming the core of the micelles and the thermo-sensitive hydrophilic PDMA arranging in a shell formation.

The photosensitive character of azo-PSI-g-PDMA was studied both in solution (using $CHCl_3$ as solvent) and solid state. Upon irradiation of the sample with a UV lamp at 365 nm, the azobezene groups change the conformation from *trans* (thermodynamically stable isomer) to *cis* isomer (metastable). Based on this isomerization process, kinetic curves of *trans-cis* isomerization and the *cis-trans* relaxation phenomena were calculated. As shown in figure 6, the rate of *trans-cis* isomerization process in solution is higher than in solid state; 20 s were needed for the liquid sample to reach a 80 % conversion, while for the sample in solid state a 75 % conversion was reached in 70 s. The difference between the two processes is due to the decrease of the free volume of the material in solid state. The same different behaviour was registered during the *cis-trans* relaxation processes under visible light, where for the solid state 600 s were necessary.

The thermo-associative character of the synthesized graft polymers was determined using rheological measurements. Two types of rheological measurements were carried out: amplitude sweep and temperature sweep tests (oscillation). The amplitude sweep is generally used to determine the linear-viscoelastic range (LVR). Here, the oscillation frequency was kept constant $\omega = 10$ rad/s) while the oscillation amplitude (γ) was varied (between 0.01 and 100 %). All experiments were carried out at 25 °C. The limit of LVR was found to be at a maximum deformation $\gamma = 5$ % for nitro-PSI-g-PDMA and $\gamma = 1.5$ % for azo-PSI-g-PDMA.

A temperature sweep was carried out to evidence the phase transitions induced by temperature and thermo-associative phenomena. In the temperature tests, a constant frequency (f = 1 Hz) and strain amplitude (within the limits of the linear viscoelastic region for each sample) were set, the temperature being varied between 10 and 70 °C (with a heating rate of 1 °C/min).

The solution concentration was 1mg/mL or 3mg/mL in water. After preparation, the polymer solutions were left for 24 h to rest. For the investigated samples, a sharp variation of the viscoelastic parameters (elastic modulus, loss modulus and complex viscosity) was observed.

Figure 7 presents the temperature test for a 1mg/mL aqueous solution of nitro-PSI-g-PDMA in terms of storage modulus (G’), loss modulus (G”) and complex viscosity $|\eta^*|$. For low temperatures a specific liquid-like viscoelastic behaviour is characteristic, G” being higher than G’. Because of the balance of hydrophobic association and temperature-induced chain movement, the viscosity decreases smoothly between 10 and 45°C. In this temperature domain, the polymer micelles are hydrated and soluble in water. Between 45 and 50°C, a sharp decrease of the complex viscosity is noticed together with the decrease in both moduli, as a consequence of the dehydration of PDMA chains and the intermolecular collapse of the polymer aggregates. At 50 °C, the minimum on the G” and $|\eta^*|$ curves is reached while G’ sharply increases, due to intramolecular aggregation phenomenon, suppressing G” at 53 °C. At the intersection of viscoelastic moduli, liquid-solid transition takes place and a physical network is formed. A similar behaviour is observed for the azo-PSI-g-PDMA, 1mg/mL water solution, as illustrated in figure 8. Similar rheological behaviour was evidenced for unsubstituted thermo-sensitive side chains graft polysiloxanes [30, 32].

The increase of the solution concentration from 1mg/mL to 3 mg/mL (fig. 9) has no noticeable influence on the LCST value or rheological behavior. Only a decrease of 2 - 3 °C in the intramolecular aggregation temperature for the concentrated solutions was observed due to the reduction in distance between the polymer aggregates [23].

Conclusions

A series of stimuli sensitive polymers were obtained by a two-step reaction. Rheological tests revealed phase transitions phenomena around 45 °C by the modification of the viscoelastic parameters. The thermo-sensitive nature of polymers may be attributed to the acrylamide groups, while the azo-benzene groups are responsible for the sensitivity to light. The amphiphilic nature of polymers leads to the formation of micellar aggregates in aqueous solution. Because of their properties, these polymers can be used as related versatile intelligent systems as sensors [34] or smart catalyst [35].

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