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Anomalous dilute solution properties of segmented polydimethylsiloxane–polyurea copolymers in isopropyl alcohol

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Abstract

Preliminary characterization of amphiphilic segmented copolymers of polydimethylsiloxane and urea ‘hard blocks’ was conducted by measuring isopropyl alcohol (primarily) dilute solution viscosities via capillary viscometry. The traditional data analysis techniques, which provide for extrapolation of intrinsic viscosities from these experiments, revealed that increasing concentrations of polymer produced lower reduced viscosities rather than the expected higher values. A very approximate data fit reveals negative Huggins and Kraemer constants from these analyses, which are highly unusual. In a solvent such as DMF, a similar polymer having poly(tetramethylene oxide) and urea blocks and measured with identical conditions exhibited the expected behavior, showing increasing reduced viscosities over concentrations in the same range. However, the non-linearity of the data is suggestive of much more complex hydrodynamic, or supramolecular, interactions that are not clarified by the initial research.

Keywords: Viscosity; Silicone–urea; Supramolecular

1. Introduction

Silicone–urea segmented copolymers contain extremely flexible and non-polar polydimethylsiloxane (PDMS) oligomers which alternate along the chain with urea linked polar sequences (PU) exhibiting strong specific attractions. These polymers display very interesting chemical, physical and mechanical properties in the solid state where desirable features like high modulus and extensibility are possible. For example, the extreme dichotomy of structure within each chain is well known to lead to microphase separation in the bulk which generates a ‘self-reinforcing’ stress–strain response. Synthesis of these polymers utilizing traditional diisocyanate chemistry schemes has been somewhat limited by a lack of solubility of the polymer, which rapidly falls as molecular weight increases. Now, however, using an isopropyl alcohol (IPA) solvent route, this restriction has been removed which provides access to a wide variety of such materials, and to the solution properties [1]. Recently, such amphiphilic block polymers in aqueous and other polar solutions have gained a great deal of attention because of their self-assembling tendencies that suggest biomedical and drug delivery applications. In this present paper a preliminary set of observations on some interesting facets of the segmented PDMS-PUs in dilute IPA and other solutions is explored only from the perspective of their viscosities measured in the traditional fashion, where such supramolecular assemblies are not expected for most random coil homopolymers.

Since the beginnings of rigorous polymer characterization over 75 years ago, the measurement of dilute solution viscosities has provided a platform from which to probe many fundamental properties. The well-known example is, of course, use of the intrinsic viscosity to measure average molecular weights via the Mark–Houwink–Kuhn–Sakurada (MHKS) relationship [2]. Among the many applications of dilute solution experiments on polymers appearing in the literature are those to determine average chain dimensions [3], aggregation [4], solvent power of mixed solvents [5], conformational transitions [6], the excluded volume and

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hydrodynamic effects (e.g. Fox and Flory) [7], polymer–solvent interactions [8] and various types of polyelectrolyte behavior [9].

In this current report, an unusual concentration dependence of the dilute solution viscosities of the silicone–urea copolymers is documented. When dissolved in isopropyl alcohol, which can hydrogen-bond with only the PU sequence (and itself), a competition apparently takes place in the solvation mechanism that leads to anomalous behavior. As mentioned, the synthesized segmented copolymers have subunits that are dramatically different in inter- and intra-molecular energies. As isopropyl alcohol is added to dilute the polymer in order to measure viscosities, a three component system is thermodynamically established. Traditionally, a truncated power series in the polymer concentration is required to adequately analyze such viscometric data—either the Huggins [10] or Kraemer [11] formulations, among a number of choices [3], being employed in actual practice. Suitable expansions of these two equations can be shown to be equivalent; and, each may be derived from the original Einstein 1906 relationship for the viscosity of unsolvated spheres by using suitable approximations. The molar mass of the polymeric solute appears on modifying the Einstein formulation leading to expressions containing the limiting viscosity number, herein referred to as the intrinsic viscosity, $[\eta]$, such as in the MHKS formula mentioned above.

2. Background

2.1. Concentration dependence of dilute polymer solutions

The analysis of dilute solution viscometry data may proceed via the Huggins' form of the concentration dependence:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \qquad (1)$$

where c is the concentration in g/dL, η_{sp} is the specific viscosity which is equal to the viscosity increase produced by the solute relative to the original value, and k_H is the Huggins' constant, a form of second virial coefficient for macromolecular solutions. Extrapolation of the left-hand side of Eq. (1), i.e. the reduced viscosity, to zero concentration in the 'Huggins' plot' provides the intrinsic viscosity which, in turn, is used to obtain the k_H. Alternatively, the Kraemer expression also yields the intrinsic viscosity:

$$\frac{\ln(\eta_{rel})}{c} = [\eta] + k_K[\eta]^2 c \qquad (2)$$

where the relative viscosity, η_{rel}, is simply obtained as the ratio of the solution viscosity to the pure solvent viscosity measured under identical conditions, and k_K is Kraemer's constant.

Both the Kraemer and the Huggins expressions are used in double extrapolations of dilute solution data in which the LHS of Eqs. (1) and (2) appear as functions of concentration. Approximately equal intercepts at $c=0$ are typically observed and are averaged to give the intrinsic viscosity. From such data, the determined k_H values are positive (with extraordinarily few exceptions in the literature), indicating that the Huggins' plot of η_{sp}/c vs. c has a positive slope. The k_K is also obtained as the slope of the appropriate graph and is theoretically 0.5 dimensionless units lower than k_H, and may have negative values [12]. Caution is appropriate here since some authors insert a negative sign on the RHS of Eq. (2) which was not in the original paper [10].

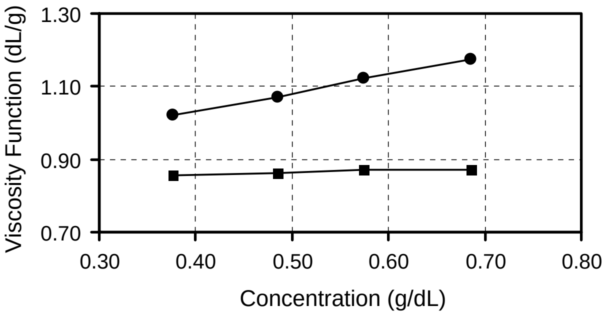

Fig. 1. Dilute solution viscosities of sample PEU-1 in DMF. Huggins (●) and Kraemer (■) analyses. The viscosity function is either the left hand side of Eq. (1) or Eq. (2), respectively.

2.2. Example of traditional results

For illustration, a typical Huggins/Kraemer dual analysis appears in Fig. 1 for a model polyurethane (designated PEU-1, Table 1) we synthesized as described below. Based on a poly(tetramethylene oxide) soft segment of 2000 g/mol, and containing 40% by weight of hard segments obtained from a cycloaliphatic diisocyanate (HMDI) and 1,4-butanediol, this sample was dissolved in dimethylformamide for the viscosity measurements. Linear regressions of the data on PEU-1 yield intrinsic viscosities of 0.8012 and 0.8455 dL/g for the Huggins and Kraemer treatments, respectively, with excellent linearity in each case. From the slopes, using Eqs. (1) and (2), values of 0.8509 and 0.03617 were calculated for k_H and k_K, respectively.

The Huggins' coefficient is thought to depend on molecular weight, branching, and possibly viscometer shear rates, although universal models for each case are not available. In the present publication these factors are not investigated. The focus is on unusual solvent–polymer interactions that emerge from the concentration dependent viscosities of the dilute solutions. Therefore, the shear rates have been kept low, branching is not a factor, and molecular weights are similar throughout the series of materials detailed below. The molecular picture for interpretation of k_H and k_K is not simple.

Table 1
Compositional characteristics of copolymers

Sample code	Oligomer type	Oligomer M_n (g/mol)	Chain extender	Hard segment content (wt%)
PSU-1	PDMS	2500	DY	17.0
PSU-2	PDMS	2500	ED	18.0
PSU-3	PDMS	7000	DY	10.2
PSU-4	PDMS	7000	DY	19.6
PSU-5	PDMS	2500	ED	23.0
PEU-1	PTMO	2000	BD	40.0

Factors that enter into the determination of the k_H and k_K values in this research are: (1) chain stiffness of the segments, (2) intramolecular interaction energies between the blocks, (3) intermolecular thermodynamic interactions among the segments (varying with concentration), (4) intermolecular hydrodynamic interactions of each block with the solvent (as in the Kirkwood and Riseman model) and with each other (including chain expansion and excluded volume effects). For example, H-bonding of urea hard segments with the solvent, and H-bonding of the solvent with itself are expected to be important.

3. Experimental

3.1. Materials

Bis(4-isocyanatocyclohexyl)methane (HMDI) with a purity better than 99.5% was obtained from Bayer, Germany. Aminopropyl terminated polydimethylsiloxane (PDMS) oligomers with number average molecular weights ranging from 900 to 7000 g/mol were obtained from Th. Goldschmidt AG, Essen, Germany, or from Wacker-Chemie GmbH, Munich, Germany. Poly(tetramethylene oxide)glycol with $M_n=$ 2000 g/mol (PTMO-2000) was obtained from DuPont. Reagent grade *n*-dibutylamine (DBA), tetrahydrofuran (THF), dimethylformamide (DMF), isopropyl alcohol (IPA), 1,4-butanediol (BD) and ethylene diamine (ED) were acquired from Merck. 2-Methyl-1,5-diaminopentane (DY) was supplied by DuPont. Dibutyltin dilaurate (DBTDL) was obtained from Witco. All reactants and solvents were used as received.

3.2. Polymer synthesis

A two-step procedure, the 'prepolymer method', was used for the preparation of the silicone–urea copolymers. The first step was the formation of isocyanate-terminated prepolymer, followed by the chain extension with diamines to form high molecular weight segmented copolymers. Reactions were carried out at room temperature, in a three-neck, round bottom flask, fitted with a nitrogen inlet, stirrer and an addition funnel. A calculated amount of HMDI was introduced into the reactor. The amine terminated PDMS oligomers were weighed in a flask, dissolved in IPA to make about 25% solution by weight and introduced into the addition funnel. Separately, diamine chain extender solutions were also prepared in IPA (25% by weight). Prepolymer was obtained at room temperature by adding the PDMS solution to the HMDI solution in the reactor over 3–5 min. This was followed by the dropwise addition of the chain extender solution through the addition funnel, again at room temperature. The reaction mixture was perfectly homogeneous throughout and no precipitation was observed. The novel choice of IPA as the solvent system in order to allow high molecular weights to develop by maintaining complete solution is a major contributor to the successful synthesis of the polymers. Room temperature reaction of the IPA with the isocyanate was insignificant over the employed reaction times [1]. Completion of the reactions was determined by following the disappearance of the strong isocyanate peak at 2270 cm^{-1} with FTIR spectroscopy. Total reaction times were usually 30 min or less. The products obtained were coagulated in isopropanol/water (50/50 by volume) mixture, filtered and dried to constant weight in a vacuum oven at 50 °C.

A polyether–urethane copolymer, PEU-1, was prepared in a three-neck, round bottom reaction flask fitted with an overhead stirrer, thermometer and dry nitrogen inlet. The flask is charged with a calculated amount of HMDI and PTMO-2000, heated to 80 °C and stirred. The reaction commenced on addition of 150 ppm of DBTDL catalyst in 1 mL of toluene. Progress of the reaction was monitored by FTIR spectroscopy. Prepolymer formation was completed in 2 h. Prepolymer was dissolved in DMF and a stoichiometric amount of BD in DMF was added to the reaction mixture. Maintaining 80 °C, complete disappearance of isocyanate peak in the FTIR spectrum was taken as the stopping point. The obtained product was coagulated in methanol, filtered and dried in a vacuum oven at 50 °C.

3.3. Polymer characterization

FTIR spectra were recorded on a Nicolet Impact 400D spectrophotometer with a resolution of 2 cm^{-1}. Intrinsic viscosities were determined using Ubbelohde viscometers, at 25 ± 0.1 °C. The solvent used for silicone–urea copolymers was IPA. The intrinsic viscosity of the PEU-1 polyether-urethane polymer was determined in DMF.

For dilute solution viscosity measurements, both freshly prepared solutions and solutions which had been aged for 30 min or 1 h were investigated. All these solutions are completely transparent to the eye; furthermore, rapid dissolution of the solute was easily obtained. Samples were tested after thorough mixing of the diluting solvent volumes, which were employed to generate the different concentrations required for analysis. Many of the solutions were tested again after 1 h of 'rest' in order to examine for polymer absorption, aggregation, etc. Such time-dependent effects were found to be negligible. The standard deviation in our flow time measurements was less than 0.5%.

4. Results

Table 1 lists the polymers that were investigated along with their soft-segment type and its average molecular weight. Also shown in Table 1 are the chain extenders for each polymer and the overall weight percent of hard segment in the final specimen, a measure of the amount of H-bond capable urea in each chain. The PEU-1 sample presented in the last row is the only example having a polyether soft segment rather than that based on siloxane, and is the only oligomer extended with urethane as opposed to urea functionalities.

Specimen PEU-1 provides a 'typical' example whose viscometric data appear in Fig. 1. These PEU-1 solutions are seen to show the expected concentration dependence of viscosities, with positive Huggins and Kraemer constants.

The analysis is initially focused on larger trends, which are apparent in the solution viscosity data; in this regard, linear

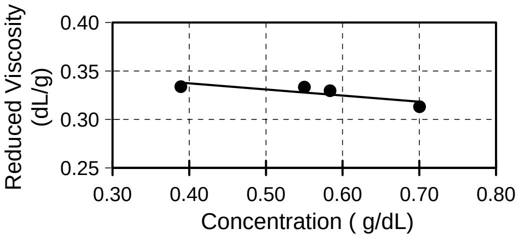

Fig. 2. Linear regression of viscosity data for PSU-2 in IPA/THF (2/3 by volume). This graph illustrates an ‘apparent’ Huggins’ constant determination. An overall negative slope trend is indicated from this data.

regression lines were fitted to the Huggins’ and Kraemer’s data in order to estimate the constants associated with each model. As will be seen below, this is a rough approximation since there is considerable deviation from linearity in much of the data within certain concentration ranges. Such variation is undoubtedly important in interpreting the molecular scale changes that occur as each polymer is diluted. Fig. 2, made for sample PSU-2 dissolved in a mixed IPA/THF solvent, shows one of the poorest data correlations to the predicted Huggins’ linear relationship. However, the overall negative slope of the reduced viscosity with increasing concentration is clear, even in this selected ‘worse-case’ of the data. Scanning through Figs. 3–9 reveals that neither Huggins’ nor Kraemer’s approaches was adequate to describe the complex non-linear trends which appear in the viscosity–concentration data. In this present paper the principal emphasis is on presenting these overall general trends of the data. Detailed explanations of the obviously complex molecular-level events that govern the exact shapes of each of the analytical plots of the results are expected to require additional experiments such as dynamic light scattering to clarify.

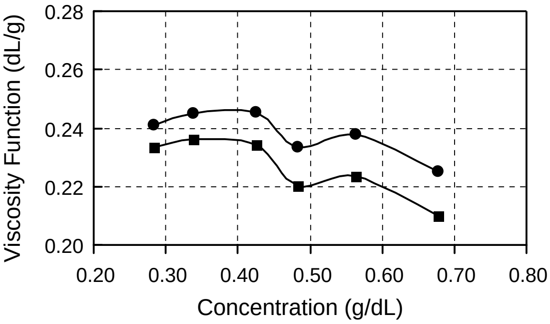

Fig. 5. Dilute solution viscosities of sample PSU-5 in isopropyl alcohol. Huggins’ (●) and Kraemer (■) analyses are shown with the viscosity function being either the left hand side of Eq. (1) or Eq. (2), respectively.

Table 2 contains all of the average intrinsic viscosities derived from the discussed linear regressions of the viscosity experimental results. The values are reasonable for high molecular weight polyurea segmented block copolymers—cast films of these samples show high tensile strengths and

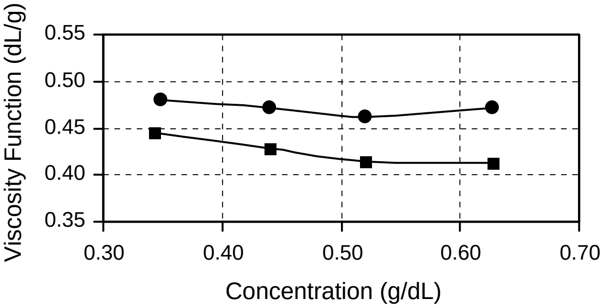

Fig. 3. Dilute solution viscosities of sample PSU-4 dissolved in IPA. Huggins’ (●) and Kraemer (■) analyses are shown with the Viscosity Function being either the left hand side of Eq. (1) or Eq. (2), respectively.

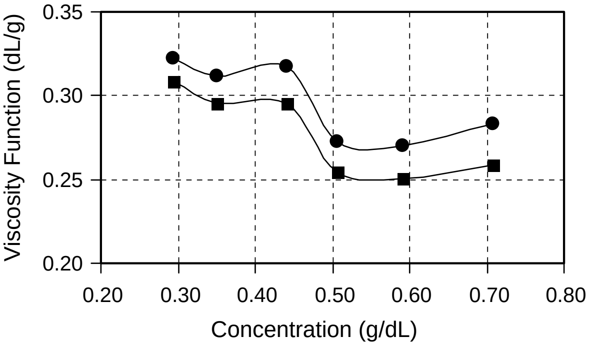

Fig. 6. Dilute solution viscosities of sample PSU-5 in ethanol. Huggins’ (●) and Kraemer (■) analyses are shown with the viscosity function being either the left hand side of Eq. (1) or Eq. (2), respectively.

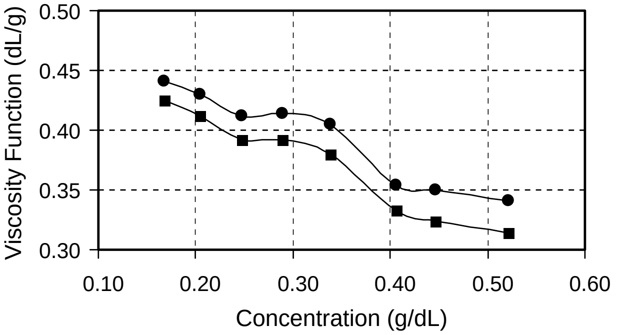

Fig. 4. Dilute solution viscosities of sample PSU-3 in IPA. Huggins’ (●) and Kraemer (■) analyses are shown with the Viscosity Function being either the left hand side of Eq. (1) or Eq. (2), respectively.

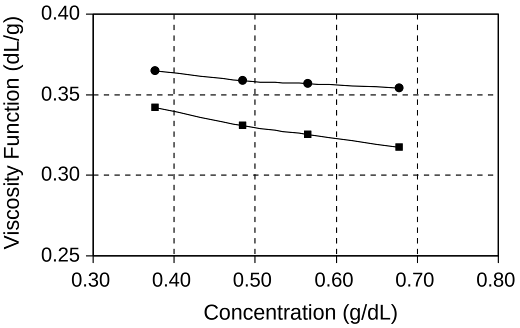

Fig. 7. Dilute solution viscosities of sample PSU-1 in isopropyl alcohol. Huggins’ (●) and Kraemer (■) analyses are shown with the viscosity function being either the left hand side of Eq. (1) or Eq. (2), respectively.

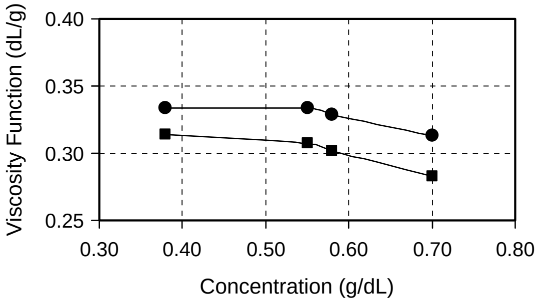

Fig. 8. Dilute solution viscosities of sample PSU-2. Huggins' (●) and Kraemer (■) analyses are shown with the viscosity function being either the left hand side of Eq. (1) or Eq. (2), respectively.

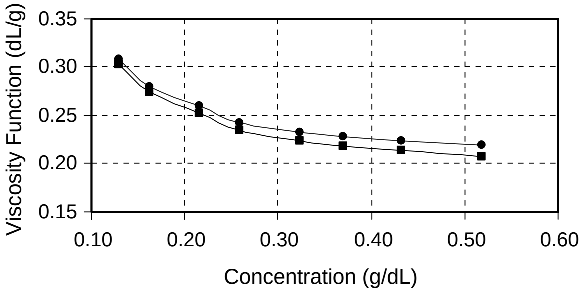

Fig. 9. Dilute solution viscosities of sample PSU-3 dissolved in IPA with 0.2% of dissolved LiCl. Huggins' (●) and Kraemer (■) analyses are shown with the viscosity function being either the left hand side of Eq. (1) or Eq. (2), respectively.

elongations at break. GPC results (not presented here) on very similar segmented systems made by identical procedures indicate number average molecular weights in the 50,000 Da range, consistent with the good mechanical response.

The calculated apparent Huggins' and Kraemer's constants for each polymer are also listed in Table 2. Specimens exhibiting more negative slopes were placed lower in this table. We note the negative values of k_H for all of the PDMS containing samples. As the PDMS block molecular weight increased, the k_H values became more negative. For example, PSU-3 with intermediate concentration of urea hard blocks and the highest PDMS block MW has the extraordinarily large negative value of $k_H = -1.2629$. Decreasing the hard block concentration by about a factor of 1/2, sample PSU-4, exhibits a k_H of -0.1676. All of the Kraemer's constants fall to the more negative side of the Huggins' constant values, as they should.

To aid in the interpretation of the unusual viscometry trends it was of interest to examine viscosities of mixed solvents without dissolved polymer. Thus, in Fig. 10 are shown capillary viscometer flow times of IPA which has been diluted with tetrahydrofuran (THF) at the indicated volume fractions. One notes that over a 77% reduction in the flow times (viscosity) of the IPA was found.

It is noted from Figs. 5 and 6 that both IPA and ethanol solvents yield similar viscometry results. A maximum in the Huggins and the Kraemer graphs was found between concentrations of 0.3 and 0.5 g/dL, while the overall approximated apparent constants of the data from the slopes were negative.

5. Discussion

The trend of the data, as approximated by the viscosity functions in Eqs. (1) and (2), indicates decreasing reduced viscosities with increasing solution concentration. In other words, with more polymer present, after normalization of the concentration by a linear correction, the viscosity increase produced by the polymer becomes less and less with each increase in polymer. Usual arguments focus on the hydrodynamic volume of the polymer to explain changes in dilute solution viscosity. One can estimate the critical overlap concentration, c^*, where the solution changes from 'dilute' to 'semidilute' by $[\eta]^{-1}$. Such an approximation yields a range of $c^* = 2.05$–2.87 g/dL which is at least four times larger than the maximum concentration used in the present experiments. A brief literature review will be presented in order to find similar results in other systems.

Theoretical and experimental results [3,6,7] report positive k_H values that lie well within the range of 0 to +1 where the smaller numbers are reported for better solvents. Somewhat larger Huggins' constants of 0.7 or higher are found for polymers in solvents approaching the theta point. According to Riseman and Ullman, k_H should be 0.6 for random coils and 0.733 for rods in solution [13]. In the case of better solvents,

Table 2
Dilute solution viscometry results

Sample	Solvent	$[\eta]$, dL/g[a]	k_H	R^{2b}	k_K
PEU-1	DMF[c]	0.8234	0.8509	0.9993	0.0362
PSU-5	IPA[d]	0.2567	−0.0435	0.6368	0.06318
PSU-5	Ethanol	0.3490	−0.1175	0.6019	−0.1400
PSU-4	IPA	0.4870	−0.1676	0.4056	−0.5086
PSU-1	IPA	0.3743	−0.2491	0.9461	−0.5875
PSU-2	IPA:THF[e]	0.3585	−0.4800	0.6851	−0.7649
PSU-3	IPA	0.4884	−1.2629	0.9398	−1.4554

[a] Average of Huggins and Kraemer values found from linear least squares regressions.
[b] Statistical parameter from linear regression fit of Huggins' data.
[c] Dimethylformamide.
[d] Isopropyl alcohol.
[e] 2:3 Ratio by volume.

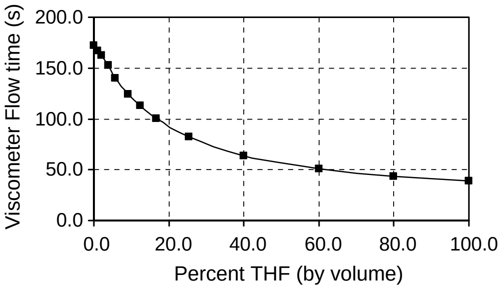

Fig. 10. Reduction of the viscometer flow times of IPA by THF at 298 K. The flow time of pure IPA in this viscometer was 172.4 s.

observed k_H values on the order of 0.25–0.35 are typical [3,7]. This means that excellent solvents will produce Kraemer's constants that are negative [7]. Inspection of the Polymer Handbook for values of Huggins' constants [14] indicates only three negative values in approximately 800 systems reported, with the majority of values falling between 0.2 and 1.0. The three negative k_H measurements are reported in one paper which concludes there are conformational changes in poly (methyl methacrylate)/ester solutions at a number of temperatures [15]. In the case of diblock copolymers, a solvent that is selectively better for one block has been noted to produce negative slopes in the Huggins evaluations; unfortunately, the data are not presented [16]. Various models [7] indicate that if negative values of the Huggins' constant were observed at certain concentrations they would represent exceptionally strong polymer solvent interactions. Such attractions would not be in the usual class of random coil-solvent intermolecular attractions, but might indicate conformational transitions.

Some possibilities for unusually strong polymer–solvent interactions that might lead to maxima in the Huggins' plots for uncharged macromolecules have been discussed [17,18]. Of course, at higher concentrations in these systems, only the negative slope region would be seen, and a negative k_H would be calculated. In Sudduth's generalized viscosity model [8] from which both Huggins' and Kraemer's equations are obtained at low concentrations, a solvent–polymer interaction parameter, σ, appears and has limits of $-[\eta] \leq \sigma \leq [\eta]$ with the more negative values indicating better solvents. For Sudduth's negative σ values, this theory predicts a maximum in the Huggins' plot of reduced viscosity vs. concentration as well as lines with negative slopes in the Kraemer plots. Sudduth examines the widely cited research of Paals and Hermans on polyelectrolyte sodium pectinate aqueous solutions [19] in which a maximum in the Huggins' plot appears, but is replaced by the more typical positive slope straight lines at higher ionic strengths. He shows that the Kraemer analysis would produce a more interpretable model of the concentration dependence. Second virial coefficients may also be obtained from the generalized model.

When one combines macromolecular segments of vastly dissimilar thermodynamic characteristics into a copolymer structure, unusual behavior is expected. With a solubility parameter of 15.6 $(\mathrm{J/cm^3})^{1/2}$ even with a modest degree of polymerization, segments of PDMS are quite incompatible with similar molecular weight polyurea segments which have a solubility parameter of 45.6 $(\mathrm{J/cm^3})^{1/2}$. An important question is what happens to these segmented polymers in dilute alcohol solutions when the H-bonding aggressiveness of the urea linkages with the solvent can contribute to the chain shape.

Average chain conformation, intermolecular assemblies and perturbed solvent flow, may all be reflected in the determination of the intrinsic viscosity in standard Ubbelohde capillary viscometers as was conducted. In this regard, in order to clarify the interpretation of the experiments, the solutions were maintained at 25 ± 0.01 °C in a water bath and typical capillary transient flow times of more than 100 s were observed leading to better than 0.1% reproducibility. Both freshly prepared solutions and some which had aged for 30 min or for 1 h were investigated. The solutions were completely transparent to the eye and polymer dissolution was easily obtained. Essentially identical results were obtained for viscometer flow times irrespective of solution age, stirring, etc. No obvious indications of micelles or supermolecular aggregates were found in simple experiments. Fig. 1 indicates that in DMF the sample PEU-1 viscosities behave exactly in the expected dilute solution fashion of a random coil polymer in a good solvent, exhibiting no 'aggregation' response. Of course, for PEU-1, with the PTMO segment, the DMF is less of a block-selective solvent than in the PDMS-containing copolymers. A mixed solvent of IPA:THF (2:3 by volume) used for viscometry on sample PSU-2 also produced the negative Huggins' constant as seen in Fig. 2.

The complexity of the inter- and intra-molecular interactions responsible for the presented data on our siloxane/urea/IPA ternary combination makes a simple interpretation of the reduced viscosity and specific viscosity results improbable based on only the simple experiments completed. In the literature, some models are found for other systems that suggest reasonable possibilities for the currently observed data.

A few of the many studies on charged polymers may provide clues to explain the solution behavior of the silicone–urea copolymers. For uncharged polymers our observed experimental results are rare. In contrast, it is possible to rationalize such negative 'apparent' Huggins' constants, k_H, over certain concentration ranges of polyelectrolytes in aqueous solution. In the well-known 'polyelectrolyte effect' on viscosity, there is a (dilute) aqueous solution concentration, c_p, above which increasing the dissolved polymer exponentially lowers the reduced viscosity—much as observed in our samples. Theoretically, many have shown this to be related to changes in the ionic strength of the solution, which translate into variation in electrostatic repulsion and osmotic effects. This phenomenon is experimentally accessible because of large subsequent changes in the average conformational dimensions of the chains. Obviously, in the limited concentration region where this occurs one would obtain as an approximation a linear region where there would be a negative Huggins' constant.

The exact response of the polyelectrolyte conformation has been documented as related to solvent quality, solution temperature, polyelectrolyte concentration, and the presence of added salts [8,20]. One of the more interesting demonstrations of the polyelectrolyte effect that has relevance for our investigations is the influence of dissolved salts on the Huggins' analysis where at $c > c_p$ a suppression of the electrostatic chain expansion is observed due to counter ion association with the interior of the polymer coil. The papers include the classical and often cited work of Paals and Hermans [19] and many others where a maximum in the reduced viscosity appears on polymer dilution as modulated by ionic strengths [21]. Even the intrinsic viscosity shows this 'salt-effect' and is the subject of continuing discussion [22]. Thus, it is of interest to compare the viscosity treatments where the same polymer, PSU-3, has been dissolved in IPA (Fig. 3) and also in IPA containing 2.0% dissolved LiCl (Fig. 9). A dramatic difference is observed in the polymer concentration dependence in the two cases. From Fig. 9 where the LiCl is present, one notes the concave up shapes of the two analyses quite similar to those in the polyelectrolyte effect, with an overall negative slope (which decrease) maintained over all of the concentration range. Addition of salts such as $CaCl_2$ in micromolar amounts to amphiphilic block copolymers in dilute aqueous solutions are reported to initiate spontaneous assembly into a variety of supramolecular aggregates [23].

The currently investigated amphiphilic polyurea–siloxanes have the capability of exceptionally strong hydrogen bonding, both inter- and intramolecularly [24–26], which have been modeled with quantum mechanical calculations. There are also repulsive intra- and inter-molecular forces between the hard and soft blocks which work thermodynamically to produce phase separation in the solid films of these samples.

Viscometric experiments in mixed solvents are interesting for they may illustrate the dynamic competitions that take place to determine the polymer's conformation. One study of poly(vinyl chloride), PVC, in various proportions of xylene (non-solvent) and cyclohexanone (moderately good solvent) shows that the intrinsic viscosity shows a strong maximum at a 50% (vol) composition. At that point of high solvation, the Huggins' constant reaches a minimum value of ca. 0.05, one of the lowest noted [5]. The authors speculate that dilution of the cyclohexanone lowers its local concentration about the PVC coil as well as interrupting the intermolecular H-bonding between loosely complexed cyclohexanone molecules, which frees these for chain solvation. Cowie and McEwen [27] have formulated a model to explain such cosolvency along the lines of the preceding argument. The presently discussed siloxane urea segmented copolymers dissolved in IPA provide for a similar molecular competition to that found in the cosolvency observations. In a very simple experiment, the flow times of IPA in a capillary viscometer were determined as the system was diluted with THF as described above, and results appear in Fig. 10. The very large reduction of viscosity of the IPA caused by the addition of THF is apparent as is the non-linearity of the dilution effect. In a different Ubbelohde viscometer having a flow time of 162.74 s for IPA, the dissolution of 2% (wt) of LiCl increased this time to 278.7 s, all at 298 K. Each of these experiments illustrates in the viscometric complexity of these dissolved amphiphilic block polymers.

In a recent publication, polystyrene-*block*-poly(*N*-ethyl-4-vinylpyridinium bromide) in dilute aqueous solutions, where the blocks have obviously very strong 'mismatches' of intermolecular energies, are observed to exhibit critical micelle concentration (cmc) behavior as low as 10^{-7} M. Our concentrations are in the range of 10^{-4} M in the present work, where the amphiphilic difference is not so large [28].

Other investigators have recently looked at dilute solution properties of poly(methacrylic acid) and PDMS block copolymers of various block molecular weights [29]. These ABA systems have hydrophobic/hydrophilic pairings as do our materials. In making comparisons a constant acid content of 0.11 M was maintained in dilute aqueous polymer solutions. Fluorescence probe spectroscopy was used to determine conformational and aggregation changes as solution pH was adjusted with conc. NaOH. As the pH was adjusted with NaOH and exceeded 5.0 a conformational change from compact to expanded coil was inferred from changes in the spectra. Presence of NaCl in the solutions influenced the outcomes. The investigators concluded that in these dilute aqueous solutions of triblocks that differ so significantly in intermolecular interactions, the concentration of the polymer played a major role in globular domain formation. In spite of working with concentrations that were lower than C^* (the critical chain overlap concentration), interchain aggregation leading to hydrophilic assembly formation seems to explain the results best [29].

At higher concentrations of triblock (ABC) copolymers of strongly amphiphilic nature, supramolecular assemblies are reported in THF/water solutions. Although kinetically controlled, the assemblies exhibit a micellar rod-to-sphere transition through a continuum of morphological intermediates as the solution is mediated by a water soluble positively charged carbodiimide [30].

Scattering techniques and fluorescence spectroscopy were used to characterize diblock copolymers of 2-(dimethyl amino)ethyl methacrylate and 2-(diethyl amino) ethyl methacrylate which produce supramolecular assemblies from unimers on raising the pH from 2 to 3 to above a critical value. In the more acidic solutions, protonation of the amine groups produces polyelectrolyte-like solution behavior, as observed in our experiments where the changing concentration of the copolymers may serve to trigger conformational changes on the sub-micellar level [31].

In amphiphilic block copolymers of poly(2-ethyl-2-oxazoline) and poly(ε-caprolactone), aqueous cmc values in the range of 4×10^{-3} g/L were found to be lowered as the hydrophobic block increased in molecular weight. Larger micelles were also observed at longer block lengths [32]. In the present research, no obvious trends between the hydrophobic block molecular weight and the changes in slope that appear in Figs. 2–9 are apparent. A complex set of factors must regulate the concentration dependence of the reduced viscosities.

Similarly, water soluble amphiphilic poly(2-hydroethyl vinyl ether)-*block*-poly(2,2,2-trifluoroethoxyethyl vinyl ether) was revealed to form core-shell spherical micelles at a cmc of 1% (wt), around 1×10^{-4} M, with a corresponding large decrease in surface tension. Block molecular weight was found to influence the results [33].

If one regards the amphiphilic silicone–urea copolymer as its own cosolvent then a strong H-bonding transient network can be assumed with the IPA solvent and segments of the polymer which will shift as the energetics of the ternary interactions varies. In other words, as copolymer concentration is increased the urea block concentration increasingly disrupts the IPA associations, releasing those molecules for chain solvation and expansion. The effect of the dissolved LiCl is postulated to act in a similar manner, producing the behavior seen in Fig. 9. Effectively, the 'solvent' is changing in quality as the concentration of polymer is increased in these solutions. These speculations on the simple experiments of this report may be clarified by instrumental approaches of a more sophisticated nature, with scattering and fluorescence research being the obvious choices.

6. Conclusion

In this preliminary investigation it was found that dilute isopropyl alcohol solutions of high molecular weight segmented copolymers based on silicone soft segments and urea hard segments have unexpected viscometric properties. In contrast to the usual positive slope relationship between reduced viscosity and increasing concentration of the polymer, non-constant negative slopes were observed in approximated Huggins' and Kraemers' type analyses. However, the non-linearity of the data is suggestive of much more complex hydrodynamic, or supramolecular, interactions that are not clarified by the initial research. In a solvent such as DMF, a similar polymer having poly(tetramethylene oxide) and urea blocks exhibited a positive Huggins' constant behavior with increasing concentrations in the same range, with good linearity of the data. The observations of anomalies held over a variety of chemical compositions having different intrinsic viscosities, hard segment contents, and molecular weights of the PDMS blocks. In these amphiphilic materials it is possible that there are supramolecular assemblies, which depend in a complex way on the changing solvent power of the solution that accompanies dilution changes. Also conformational changes with the varying energy landscape of the different concentrations may cause expansion or contractions of the chains. Experiments of the dynamic light scattering, fluorescence probe and other types are required to aid in the interpretation of these experiments.

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