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Polymer 40 (1999) 4099–4103

polymer

Elastic constants in dilute poly(styrene)/nematic liquid crystal solutions – effects of concentration and molecular weight

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Received 1 June 1998; accepted 18 August 1998

Abstract

We utilized the light scattering from the anisotropy of turbidity (LSAT) method and evaluated, for the first time, the three elastic constants of dilute solutions of polystyrene (PS) in 4-pentyl-4′-cyanobiphenyl (5CB) nematic solvent. Within the solubility range of this system (less than 5%), the elastic constants of *splay* (K_1), *twist* (K_2), and *bend* (K_3) of PS/5CB solution were determined as a function of concentration and molecular weight of PS solute. The experimental results showed a systematic diversion of the elastic constants and, in particular, a large increase in K_1 with increasing concentration and molecular weight of PS. The results are in agreement with the predicted theoretical models and other experimental data. Determination of K_i in polymer/nematic solutions with LSAT is a promising experimental approach to study the macromolecular chain structure of flexible, semi-flexible and rigid-rod polymers in anisotropic regimes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Elastic constants; Concentration; Molecular weight

1. Introduction

Recent progress in the research and development of liquid crystalline polymers has generated many interests for the utilization of experimental techniques to probe and study the structure-property relations, mechanical and dynamical properties of the macromolecular systems in the mesomorphic states. In addition to many useful possibilities, the mesomorphic media could also allow for the measurements of the new material properties including the macroscopic properties, such as the three bulk elastic constants.

The apparent influence of the physico-chemical parameters on the elastic moduli of nematic polymers were predicted theoretically [1,2] and were observed in a few experiments [3–9]. Although the available knowledge of viscoelasticity in nematic polymers is not yet conclusive, it was found that the elastic moduli are more sensitive to the physico-chemical parameters than their monomeric analogs. In particular, the existing experimental studies in both thermotropic and lyotropic polymer liquid crystalline systems indicate that, the splay modulus K_1 is the largest of the three elastic constants. This is in qualitative agreement with the available theoretical model, which suggests that certain degree of chain flexibility exists in rigid-rod polymer structures that could be monitored by the trend of molecular weight dependence of either K_1or K_1/K_3 ratio [1,2]. Although, as a result of intractability, high viscosity and insolubility of most polymer liquid crystal structures, the experimental verification of theoretical models is difficult, the study of polymer-nematic solutions in dilute regimes was yet another approach to probe the physical, mechanical and dynamical properties of polymer chain structure in anisotropic medium. In contrast to the compatibility of mesomorphic polymers, the flexible polymers do not readily dissolve in nematic solvents. It was reported that, in these systems, the mesomorphic order is rapidly destroyed near the polymer chain, inducing a large biphasic spread in the nematic-to-isotropic transition temperature [10–14].

The continuum nematic moduli of elasticities, i.e., the three elastic constants of the anisotropy of molecular interactions, are known to be sensitive to the physico-chemical environment of the system. Apart from the well-developed field-induced methods, the light scattering techniques have a number of other advantages. These include the experimental simplicity, avoiding the surface treatment, a simultaneous evaluation of all the three elastic moduli, and, last but not the least, their potential utilization in the measurement of the elastic moduli of both thermotropic and lyotropic polymer systems.

In principle, the elastic constants of nematic polymers can be studied either in their melts or in their solutions. However, because of problems such as polymer degradation, low surface anchoring and other technical difficulties, measurements of the elastic constants in nematic polymers

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PII: S0032-3861(98)00645-4

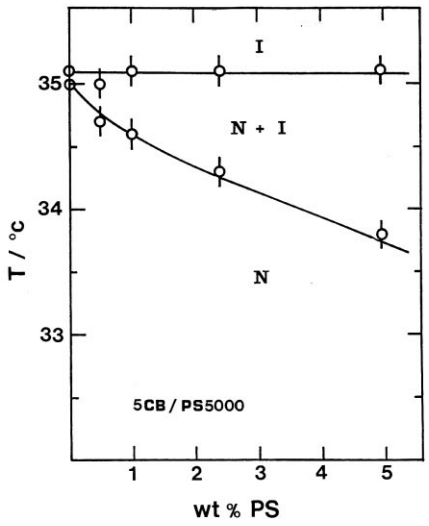

Fig. 1. Nematic-isotropic transition temperatures of PS/5CB solutions as a function of PS concentration.

with the conventional field-induced technique has not been successful. Instead, the light scattering of anisotropy of turbidity (LSAT) could show a promising alternative approach for determination of elastic moduli and for establishing corresponding empirical laws in nematic polymer systems. More specifically, such empirical relations could provide quantitative information about the chain structure and conformations, as well as the molecular weights of intractible polymer systems in the nematic phase.

In view of the previous applications of the LSAT method to evaluate the elastic constants of the lyotropic polypeptide solutions [15] and the recent experimental modification of this technique [16], in this work, we investigated the effect of chain structure of a flexible polymer solute on the elastic constants of a nematic solvent. In this report, we selected dilute solutions (<5w/w%) of polystyrene (PS) in the nematic 4-pentyl-4′-cyanobiphenyl (5CB) solvent as a model system and determined the three elastic moduli, K_1, K_2 and K_3 in these solutions as a function of the molecular weight and concentration of PS. Attempts were made to find phenomenological relations between the flexible chain structure of PS and the elastic responses of the nematic solvent.

2. Experimental

2.1. Materials

The PS samples with molecular weights of $M_w = 485$, 1050, 3100, 5000, 8500 and 10300 were obtained from Waters Inc. and were used as such. The reported polydispersity of PS samples were $M_w/M_n = 1.1$.

The 5CB nematogen material with $T_m = 22.0$°C and $T_{NI} = 34.4$ was obtained from Merck UK Ltd. with purities of 99.9% and were used without further purification. The transition temperatures of the nematogenic mixtures were determined with a Zeiss Universal polarizing microscope equipped with a Linkam THM600 hot-stage and a TMS90 Automatic Temperature Programmer.

Due to the limited solubility of PS in 5CB, the solutions at 1–5w/w% concentration range were prepared in sealed microvials and mixed at 40°C temperature bath for over two weeks, in order to ensure a complete mixing. All experimental studies of turbidity measurements and elastic constant evaluations were carried out at a temperature range of 21°C–24°C, depending on the concentration and molecular weight of the solution.

2.2. LSAT method

With light scattering approach, the measurements of total scattering intensities at the three selected geometries of a uniaxial nematic phase provide the values of the anisotropy of turbidity, from which all three elastic constants can be simultaneously evaluated. The PS/5CB solutions were placed in a Wilmad or a Helma precision optical cell with *square* cross-section having an inside thickness (optical path) of $l = 0.3$ cm. The cell was placed in a home-built temperature control unit designed to fit between adjustable poles of an Oxford Instrument N38 electromagnet. The magnetic field intensity of up to $B = 0.6$ T was used to induce a uniaxial orientation of the nematic director.

The turbidities of the aligned nematic phase were determined by accurate measurements of the *total scattering cross section*; σ_j, at the three selected geometries, where the light intensities were measured as a function of the angle of detection and the values at the plateau level were chosen to measure the corresponding σ_1, σ_2 and σ_3 turbidity values. The precise turbidity measurements were carried out by systematic elimination of the sources of experimental errors arising from undesired surface and bulk contributions of the nematic director and geometry of the cell.

Evaluation of the elastic constants requires not only the precise values of the turbidities, but also those of the refractive indices n_o and n_e, as well as the temperature of the nematic phase. The values of n_o and n_e of the nematic solutions at relevant temperatures were measured with an Abbe refractometer by using the same on-line laser beam. The final evaluation of the elastic constants were carried out by a comparison between the experimental and theoretical values (i.e., the turbidities, refractive indices and temperature of the uniaxial nematic phase) by a computer search routine, which uses the necessary iterations to converge and to find the best elastic constants with a tolerance of less than 0.1%. The largest uncertainties in the experimental values basically arise from the turbidity measurements and are within 5%. This provides an estimated error of the same order of magnitude in the extracted elastic constant values. The theoretical and experimental details of this method are mentioned elsewhere [17–21].

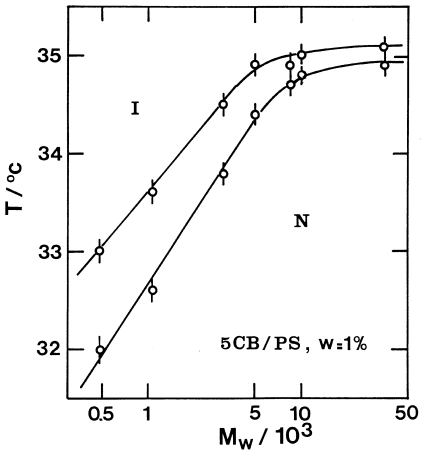

Fig. 2. Nematic-isotropic transition temperatures of PS/5CB solutions as a function of PS molecular weight.

3. Results and discussions

3.1. Solubility

The solubility of PS in 5CB is rather low and, because of the incompatibility of their molecular structures, it is difficult to obtain a homogeneous and stable solution above a concentration range of about 5wt.%. The effect of this incompatibility can be observed through the spread of nematic-to-isotropic transition (T_{ni}) temperature. In these solutions, determination of T_{ni} (or clearing point) is not straightforward, because of the existence of a biphasic region at which both nematic and isotropic phases coexist.

In Fig. 1, we show the T_{ni} transitions in a dilute regime of PS/5CB solutions as a function of PS concentration, having a molecular weight of $MW_{PS} = 5000$. The incompatibility of PS and 5CB within $C_{PS} = 0–5$w/w% range is observed by a progressive broadening in the T_{ni} biphasic region. Such a broadening effect reaches over 2°C at the upper limit of solubility range (i.e., $C_{PS} = 5\%$). The increase in C_{PS} also destabilizes the nematic phase, by decreasing T_i (lower curve). These phase transitions results are in agreement with those previously reported by Dubault et al. [10–13] for PS in other nematic solvents. It is worth noting that, as we evaluate the elastic moduli of PS/5CB solutions at about 12°C below their T_{ni}, whether T_i and T_n have the same [12] or different [13] thermodynamic origins, are irrelevant in the present study.

The effect of molecular weight of PS on the phase transition of the PS/5CB solutions (Fig. 2), are determined in solutions with $C_{PS} = 1\%$. The results indicate that, at $MW_{PS} = 485$, the T_{ni} of 5CB is decreased by about 2°C and exhibit a biphasic spread of about 1°C. By increasing the MW_{PS} up to 5000, the T_{ni} is increased linearly, reaching the transition temperature of pure 5CB, but having a coexistense phase within about 0.5°C range. Above the $MW_{PS} = 5000$, the T_{ni} of solutions become almost identical to that of 5CB solvent.

Evidently, in order to eliminate the effect of biphasic spread on the turbidites, refractive indices and elastic moduli imposed by the concentration and molecular weight of PS, all measurements were carried out far below the corresponding transition temperatures of the solutions, namely at a temperature of; $\Delta T = T_i - T = 12.5$°C below the initiation of the biphasic temperature.

Table 1
Effect of PS concentration on the elastic constants of PS/5CB solutions

C_{PS} (wt%)($MW_{PS} = 5000$)	K_i (10^{-7} dyne)				
	K_1	K_2	K_3	$<K>$	K_1/K_3
0	7.2	3.9	9.5	6.9	0.76
0.5	12.6	3.4	6.0	7.3	2.1
1	18.9	3.5	4.6	8.9	4.1
2	20.0	3.2	4.3	9.2	4.7
5	21.5	3.0	4.1	9.5	5.2

3.2. Elastic constants

In Tables 1 and 2, we present the evaluated elastic moduli of PS/5CB solutions as a function of the concentration and molecular weight of PS, repectively. The elastic moduli of 5CB solvent are also indicated in Table 1 ($C_{PS} = 0\%$) for comparison. In addition to the individual values of the three moduli, K_1, K_2 and K_3, in both Tables 1and 2, the *average elastic constant*; $<K> = (K_1 + K_2 + K_3)/3$, as well as the K_1/K_3 ratio are also tabulated. It is worth noting that, as the LSAT method is based on measurements of bulk turbidity values in a magnetically-oriented uniaxial nematic host, the flexible structure of the solute PS backbone should assume an extended chain conformation. This effect on the elastic constants of nematic solvent could be directly correlated to both the concentration and chain length (or molecular weight) of the PS solute. From the data obtained from Tables 1 and 2, we provide the following interesting observations:

3.2.1. Concentration effect:

From Table 1 and Fig. 3, we show the effect of concentration of PS on the elastic moduli of 5CB solvent. The results reveal the following phenomena:

K_1 *increases*, whereas K_2 and K_3 *decrease* with the concentration of PS. One also notices that, variations of the three K_i with concentration are *not* linear, where they reach the saturation values at a PS concentration range of about 2%. The large divergence of K_1 at lower concentration range is in agreement with the theoretical predictions [1,2], and is a direct evidence of the PS chain flexibility effect. Also, the convergence of all three moduli at higher concentration range indicates that, the PS chain structure in the uniaxial nematic solvent reaches the extended conformation state at a certain concentration value, above which the

Table 2
Effect of PS molecular weight on the elastic constants of PS/5CB solutions

MW_{PS} ($C_{PS} = 1\%$)	K_i (10^{-7} dyne)				
	K_1	K_2	K_3	$<K>$	K_1/K_3
485	7.5	3.6	6.7	5.9	1.1
1050	10.2	3.6	5.7	6.5	1.8
3100	14.8	3.5	4.6	7.6	3.2
5000	18.9	3.5	4.6	8.9	4.1
8500	28.5	3.7	2.6	11.6	11.0
10300	35.5	3.1	2.7	13.8	13.2

elastic constants are not affected by polymer chain structure and, hence, are not changed anymore.

The elastic moduli show a consistent inequality $K_1 \gg K_3 > K_2$ within the entire range of the studied concentrations. K_1 is the most sensitive moduli and exhibits the largest variation. At the largest studied concentration (i.e., $C_{PS} = 5\%$), K_2 and K_3 are reduced by about 25% and 50%, respectively, whereas K_1 is increased by a factor of three with respect to the elastic constants of 5CB. The rapid increase of K_1 clearly indicates the effect of chain flexibility of PS on the elastic moduli of the 5CB host. The K_1/K_3 ratio in the PS/5CB solutions, as shown in Table 1, demonstrate a six-to-sevenfold increase. This again is a result of opposite variation trends in K_1 and K_3 moduli, as a result of increasing contribution of the PS chain flexibility. Similar results were also supported by the experimental data reported on thermotropic polymer melts, where K_1 was shown to have large

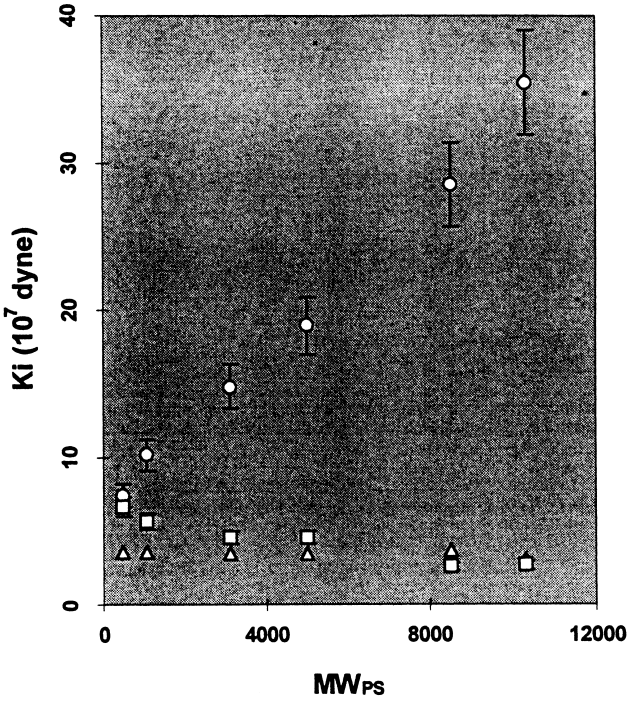

Fig. 4. Elastic constants K_1 (circles), K_2 (triangles) and K_3 (squares) of PS/5CB as a function of PS molecular weight.

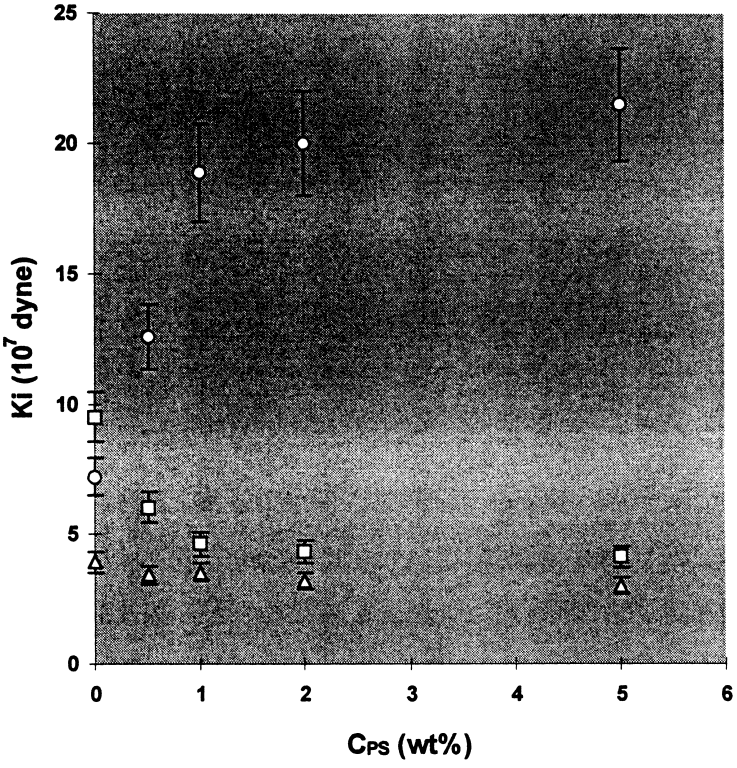

Fig. 3. Elastic constants K_1 (circles), K_2 (triangles) and K_3 (squares) of PS/5CB as a function of PS concentration.

value of an order of magnitude larger than K_2 and K_3 values [9].

From Table 1, we also notice that, the effect of C_{PS} *on the average elastic energy*; $<K> = (K_1 + K_2 + K_3)/3$, of the 5CB is an increasing linear trend, from 6.9×10^{-7} dyne (at $C_{PS} = 0\%$) to 9.5×10^{-7} dyne (at $C_{PS} = 5\%$). We found that the order parameter obtained from turbidiy data gives a constant value of about 0.32 for all studied MW of PS. In contrast to the polymeric systems, it is well established that $K_1 < K_3$ and K_1/K_3 ratio increases with increasing length of flexible terminal alkyl chains in a homologous series of low mass nematics [22,23].

3.2.2. Molecular weight effect:

In Table 2 and Fig. 4, we show variations of the three elastic constants of PS/5CB solutions with respect to the molecular weight (MW_{PS}) of PS. Although the trends of the MW_{PS}-dependencies of K_i is qualitatively similar to those found for the C_{PS}-dependencies (see Fig. 3), their behavior is, however, linear in the entire range of the studied MW_{PS}. Here, we also found that the $K_1 \gg K_3 > K_2$ inequalities to be similar to those with concentration, where the MW_{PS}-dependence of K_1 is strong and that of K_2 and K_3 are almost constant. In another words, where K_1 in PS/5CB solutions becomes large as a result of PS, the order of magnitude of K_2 and K_3 do not differ markedly from those of the conventional low molar mass nematics. By increasing the MW_{PS}, K_1 diverges by about five times, K_3 is decreased by a factor of 2 and K_2 is practically unaffected. Variations of K_1 and K_3 with MW_{PS} are comparable with those at the lower limit of C_{PS} range where the trends are still linear. This indicates that, at $C_{PS} = 1\%$, the studied molecular weights of PS are still below the saturation limit and the flexibility of the chain structure is still freely fluctuating within the uniaxial nematic solvent. Similar correlations between the elastic constants and molecular weight were found in the polypeptide solutions [15] and, in agreement with the theoretical predictions [1,2], one can observe again a clear manifestation of the effect of macromolecular chain flexibility of PS on the elasticities of 5CB solvent.

The present experimental data are, however, in better accord with the theoretical model which predicts the K_1 scaling with PS chain length [2] rather than with the square of the chain length [1]. This suggests that an entropic, rather than elastic, contribution is dominant. The effect of MW_{PS} on K_1/K_3 ratio is evident, where one notices (see Table 2) its linear increase by a factor of 12, from pure nematic solvent to the solution at $MW_{PS} = 10300$. From Table 2, we also find that $<K>$ values of PS/5CB solutions exhibit an increasing trend at higher MW_{PS} range between 3100 and 10300, but at lower $MW_{PS} = 485–1050$ range, $<K>$ first decreases with molecular weight, mostly at the expense of K_3 values. Considering that all measurements were done at the same ΔT and the molecular weight of 5CB ($MW_{5CB} = 249$) is about half of $MW_{PS} = 485$ (the lowest utilized molecular weight of PS), the lower value of $<K>$ (or K_3) in the latter should be a direct effect of the molecular flexibility of styrenic chemical structure.

4. Conclusion

We studied the three Frank's constants in dilute solutions of PS and 5CB. We observed a systematic variation of the elastic constants of 5CB with the concentration and molecular weight of PS. Among the three elastic constants, K_1 was the most sensitive moduli with respect to changes in the concentration and chain length of PS. The effect of macromolecular chain felxibility was evidenced by large divergences of K_1 and K_1/K_3 ratios. In all solutions, we found that K_3 decreased, whereas K_2 remained invariant with concentration and molecular weight of PS solute. All results were in accord with the theoretical models, that the flexibility of polymer chain would induce a large divergence of K_1 modulus. As the Frank's elastic moduli are bulk properties it could sensibly manifest the polymer chain structure and conformation in the aligned nematic phase. It is possible to utilize the LSAT method to study and quantify the effects of physico-chemical parameters on the polymer chain structure in polymer-nematic systems by monitoring the elastic constants. In the future report, we wil present the results of our experimental work on the elastic constants of poly(carbonate)/5CB solutions.

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