

# EFFECT OF ELECTRIC FIELDS ON THE RHEOLOGICAL PROPERTIES OF THE ISOTROPIC PHASE OF PHIC/p-XYLENE SOLUTIONS

TODD J. MENNA, FRANK E. FILISKO, RACHEL A. LYNCH

Materials Science and Engineering, University of Michigan, Ann Arbor, 48109, USA

Email: tmenna@exponent.com  
Fax: x1.630.274.3299

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## ABSTRACT:

The effect of high ac electric fields upon a liquid crystalline polymer solution, poly(n-hexyl isocyanate) in p-xylene, is examined. The results show that the solutions exhibit an increase in rheological properties proportional to the strength of the field at concentrations well below those exhibiting liquid crystalline behavior. The effects of frequency and field strength are examined as a means to explain this previously unreported phenomenon.

## ZUSAMMENFASSUNG:

Der Einfluss von hohen oszillierenden elektrischen Feldern auf eine Lösung flüssigkristalliner Polymere (Poly(n-hexylisocyanat) in p-Xylo) wird untersucht. Die Ergebnisse zeigen, dass bei den Lösungen ein Ansteigen der rheologischen Eigenschaften proportional zur Feldstärke bei Konzentrationen deutlich unterhalb den Konzentrationen auftritt, die bei Flüssigkristallen gemessen werden. Die Einflüsse der Frequenz und der Feldstärke werden untersucht, um diese bisher unbeschriebenen Phänomene zu erklären.

## RÉSUMÉ:

L'effet de puissants champs électriques alternatifs sur une solution de polymère cristal liquide, le poly(n-hexyl isocyanate) dans du p-xylene, est examiné. Les résultats montrent que les solutions présentent une augmentation des propriétés rhéologiques proportionnelle à la force du champ, à des concentrations bien inférieures à celles correspondant au comportement cristal liquide. Les effets de la fréquence et de la force du champ sont étudiés afin d'expliquer ce phénomène qui n'a jusqu'à présent jamais été reporté.

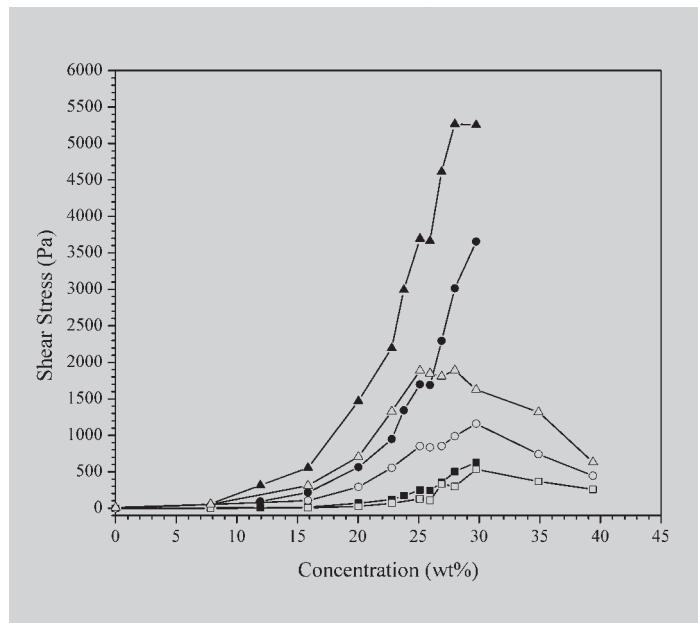
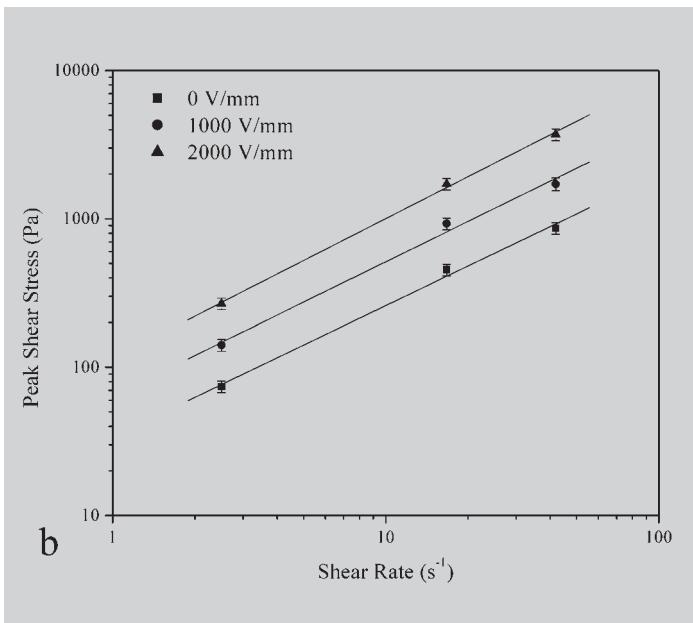
## 1 INTRODUCTION

The response of a liquid crystalline material to an externally applied shear is a subject of continuous study over the last half century. Numerous researchers have chosen to study the responses either theoretically or morphologically, but most have studied the material in either the fully liquid crystalline phase or the biphasic, in which liquid crystalline droplets exist in an isotropic matrix [1 - 6]. Concentration studies have been preformed, but little is said about the behavior of the materials at concentrations below the isotropic-nematic transition point (7, 8, 4). Likewise, studies of the electrorheological (ER) response of these materials have dealt with the material in either the biphasic or the nematic state [9 - 12], with little emphasis on the response of the isotropic behavior. Yet it has been observed [13 - 15] that not only do these phases exhibit ER activity, but that the isotropic phase does as well, at concentrations well below the phase transition point. The rationale [16 - 18] for these rheological effects cannot be used simp-

ly because the necessary secondary structures do not exist.

Bjornstahl [19] was one of the first to show the influence of an electric field on the viscosity of the nematic phase of a thermotropic p-azoxyphenetol. More recently, Tse and Shine [11] reported incidences of lyotropic liquid crystalline solutions being rheologically active in the presence of electric fields. Their work on poly(n-hexyl isocyanate) (PHIC) introduced a rather unique situation in that it represented one of the first cases where a homogeneous solution other than a suspension was determined electrorheologically active. Other polymers, most notably poly- $\gamma$ -benzyl-L-glutamate (PBLG) [20] and side chain liquid crystals [21, 22] have also been utilized, yet PHIC has distinct advantages with regard to its high solubility in nonpolar solvents while keeping the solution viscosity low [23].

In this paper we illustrate the response of a lyotropic liquid crystalline polymer, poly(n-hexyl isocyanate), isotropic solution not only to shear, but also with concurrent applied electric field.



2000 V/mm field strengths, respectively, indicating a shear thinning behavior. Although not shown, the power law exponents increase asymptotically towards a value of one with increasing field strength, i.e. the solution approaches Newtonian behavior.

#### 4 FREQUENCY EFFECT

Data presented in Fig. 4 shows the effect of a change in field frequency on the shear stress of the material. This comparison is made using the 2000 V/mm, 100 Hz data from Fig. 1c and that at 1000Hz at the same field. Solid data points represent the data at 100Hz while hollow points represent 1000Hz samples.

While the data at 1000 Hz fields shows the same qualitative trends as those at 100 Hz, there is a significant difference quantitatively. In general, the relative positions of the peak stresses remain the same yet the corresponding shear stresses are lower at the higher field frequency, increasingly so as the shear rate is increased. As a note, data taken at frequencies intermediate of these frequencies show similar trends. Reductions in shear stress seen by changing the field frequency from 100 to 1000 Hz are 15.4, 68.3 and 64.1% for the 2.5, 16.7, and 41.9 s<sup>-1</sup> shear rates, respectively.

#### 5 DISCUSSION

The most significant finding in these results is that isotropic solutions, at concentrations well below the nematic transition concentration, exhibit electrorheological behavior. Heretofore, it is to our knowledge that this observation has previously gone unmentioned in the literature. However, there is evidence that solutions at the nematic transition concentration exhibit elec-

trorheological behavior [30], with results similar to those presented here.

The viscosity and shear stress of the isotropic solutions increase proportionally to the strength of an applied high electric field, while at constant electric field strengths, these properties decrease proportionally with the frequency of the electric field. The rheological behavior of the isotropic solutions is noted to approach that of Newtonian as the electric field is increased, as determined by the change in the power law exponent, effectively moving the defined behavior from Region III to Region II of the flow behavior of liquid crystals denoted by Onogi et al. [31] and Asada et al.[1]. This behavior is consistent with that seen for side-chain liquid crystals [32].

#### REFERENCES

- [1] Asada T, Tanaka T et al.: Rheology of Liquid Crystalline Solutions of *a*-Helix Polyopeptides, *J. Appl. Polym. Sci.: Appl. Pol. Symp.* 41 (1985) 229-239.
- [2] Khokhlov AR, Semenov AN: Influence of External Field on the Liquid-Crystalline Ordering in Solutions of Stiff-Chain Macromolecules, *Macromol.* 15 (1982) 1272-1277.
- [3] Ding J, Fang H et al.: Loop-like light extinction in the precipitation film of a presheared lyotropic polymeric liquid crystal, *Polymer* 37 (1996) 3537-3541.
- [4] Aharoni SM: Rigid Backbone Polymers. XI. Solution Phase-Viscosity Relationship, *J. Polym. Sci. Polym. Phys.* 18 (1980) 1439-1453.
- [5] Farhoudi Y, Rey AD: Shear flows of nematic polymers. I. Orienting modes, bifurcations, and steady state rheological predictions, *J. Rheol.* 37 (1993) 289-314.
- [6] Larson RG: Roll-cell instabilities in shearing flows of nematic polymers, *J. Rheol.* 37(2) (1993) 175-196.
- [7] Porter RS, Johnson JF: The Rheology of Liquid Crystals in Rheology: Theory and Applications, edited by Eirich FR (1967) 317-345.

**Figure 4 (right):**  
Shear stress-concentration curves at a constant field strength of 2000 V/mm  
(■ 2.5 s<sup>-1</sup>, 100 Hz; □ 2.5 s<sup>-1</sup>, 1000 Hz;  
● 16.7 s<sup>-1</sup>, 100 Hz; ○ 16.7 s<sup>-1</sup>, 1000 Hz;  
▲ 41.9 s<sup>-1</sup>, 100 Hz; △ 41.9 s<sup>-1</sup>, 1000 Hz).

- [8] Hermans J: The Viscosity of Concentrated Solutions of Rigid Rodlike Molecules (poly- $\gamma$ -benzyl-L-glutamate in m-cresol), *J. Colloid Sci.* 17 (1962) 638-648.
- [9] Lacey D, Malins C et al.: Investigations into the Use of Liquid Crystalline Materials in Electrorheological Fluids, Proceedings of the 5th International Conference on Electro-Rheological Fluids, Magneto-Rheological Suspensions and Associated Technology, edited by Bullough WA, World Scientific, Singapore (1996) 630-637.
- [10] Yang I-K, Shine AD: Electrorheology of a nematic poly(n-hexyl isocyanate) solution, *J. Rheol.* 36 (1992) 1079-1104.
- [11] Tse K-L, Shine AD: Electrorheology of a nematic poly(n-hexyl isocyanate) solution, *J. Rheol.* 39 (1995) 1021-1040.
- [12] Tanaka K, Akiyama R et al.: Electrorheological Effect of Anisotropic Solution of Poly( $\gamma$ -benzyl-L-glutamate) Induced by Stepwise Electric Fields, *J. Appl. Polym. Sci.* 66 (1997) 1079-1084.
- [13] Quist GP, Filisko FE: ER suspensions with ER active matrix liquids, *Int. J. Mod. Phys. B* 13 (1999) 1675-1681.
- [14] Simões M, Fernandes PR et al.: Induction of orientational order in the isotropic phase of a nematic liquid crystal, *Phys. Rev. E* 64 (2001) 021707.
- [15] Menna TJ, Filisko FE et al.: Response of a Poly(n-hexyl isocyanate)/p-Xylene Solution to Applied High Electric Fields and Shear, presented at the Society of Rheology 74th Annual Meeting, Minneapolis, Minnesota, October 2002.
- [16] Klingenberg DJ, von Swol F et al.: The small shear rate response of electrorheological suspensions. II. Extension beyond the point-dipole limit, *J. Chem. Phys.* 94 (1991) 6170-6178.
- [17] Kume T, Hashimoto T et al.: Rho-Optical Studies of Shear-Induced Structures in Semidilute Polystyrene Solutions, *Macromol.* 30 (1997) 7232-7236.
- [18] Henley S, Filisko FE: Flow profiles of electrorheological suspensions: An alternative model for ER activity, *J. Rheol.* 43 (1999) 1323-1336.
- [19] Bjornstahl Y: The Influence of an Electric Field on the Viscosity of Aleotropic Liquids, *Physics* 6 (1935) 257-264.
- [20] Inoue A, Maniwa S: Electrorheological Behavior of Two Thermotropic and Lyotropic Liquid Crystalline Polymers, *J. Appl. Polym. Sci.* 59 (1996) 797-802.
- [21] Inoue A, Maniwa S: Electrorheological effect of liquid crystalline polymers, *J. Appl. Polym. Sci.* 55 (1995) 113-118.
- [22] Inoue A, Maniwa S et al.: Relation between molecular structure and electrorheological effects in liquid crystalline polymers, *J. Appl. Polym. Sci.* 64 (1997) 303-310.
- [23] Filisko FE: Materials aspects of ER fluids, in Electrorheological Fluids: A Research Needs Assessment, Report DOE/ER/3-172, Department of Energy, Washington, DC (1993) 5.9-1 - 5.9-20.
- [24] Shashoua VE, Sweeny W et al.: The Homopolymerization of Monoisocyanates, *J. Amer. Chem. Soc.* 82 (1959) 866-873.
- [25] Aharoni SM: Rigid Backbone Polymers. 2. Polyisocyanates and Their Liquid-Crystal Behavior, *Macromol.* 12 (1979) 94-103.
- [26] Hopkins A: Master's Thesis. University of Michigan (1993).
- [27] ASTM D 2857-95, Annual Book of ASTM Standards, Vol. 08.02.
- [28] Berger M N, Tidswell BM: Dilute solution viscosity and conformation of poly-n-hexyl isocyanate, *J. Polym. Sci. Polym. Symp.* 42 (1973) 1063-1075.
- [29] Bur AJ, Fetter LJ: Intrinsic Viscosity Measurements on Rodlike Poly(n-butyl isocyanate) and Poly(n-octyl isocyanate), *Macromol.* 6 (1973) 874.
- [30] Yang I-K, Huang I-T: The Electrorheology of Rigid Rod Poly(n-hexyl Isocyanate) Solutions, *J. Polym. Sci. B - Poly. Phys.* 35 (1997) 1217-1224.
- [31] Onogi S, Asada T: Rheology and Rho-Optics of Polymer Liquid Crystals, Proceeding from the Eighth International Congress on Rheology, Naples (1980) 127-147.
- [32] Minigawa K, Kimura et al.: ER Effect on the Normal Stress and Induced Network Structure of Liquid Crystal Polymer, Progress in Electrorheology edited by Havelka KO, Filisko FE, Plenum Press, New York (1995) 263-271.



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