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POLYMERS(U) DUKE UNIV DURHAM NC DEPT OF CHEMISTRY
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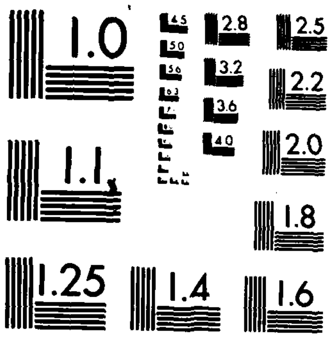

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ELECTROHYDRODYNAMIC AND FLOW INSTABILITIES IN NEMATIC POLYMERS

WILLIAM R. KRIGBAUM

FINAL REPORT

JANUARY 28, 1984

DAAG 29-81-K-0023

DUKE UNIVERSITY

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
1984-KGMB

2. GOVT ACCESSION NO.
AD-A137 812

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Electrohydrodynamic and Flow Instabilities in Nematic Polymers

5. TYPE OF REPORT & PERIOD COVERED
Final Report
80-12-01 through 83-11-30

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
William R. Krigbaum

8. CONTRACT OR GRANT NUMBER(s)
DAAG-29-81-K-0023

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Chemistry
Duke University
Durham, NC 27706

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

12. REPORT DATE
January 28, 1984

13. NUMBER OF PAGES
7

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report)
unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Electrahydrodynamic instabilities, nematic polymers, Williams domains, Fluctuating Williams Domains, Variable grating mode, Broad domains, Dynamic scattering mode, High field turbulence, Persistence length.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A nematic phase interacts more strongly with an external field than does an ordinary liquid because the molecules in the nematic phase interact cooperatively. We have investigated a variety of thermotropic polymers to ascertain which of the instabilities reported for low molecular weight nematogens are also exhibited by polymers having mesogenic units as part of the main chain, and the conditions under which these occur. The higher viscosity of a polymeric mesophase leads to longer domain formation times, but it does offer some advantages which can be exploited under certain circumstances.

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FINAL REPORT

We proposed to investigate electrohydrodynamic and flow instabilities in polymeric nematic phases, to attempt an evaluation of the elastic constants for one thermotropic polymer, and to explore the possibility of obtaining molecular alignment in a polymeric nematic phase by surface effects and external fields. We continue to believe that all of these areas are important and merit investigation, but our proposal was too optimistic in terms of what could be accomplished during the grant period. In fact, the full grant period was utilized for a thorough investigation of the effect of electric fields on nematic polymers. We did explore, during the course of this work, the possibility of achieving alignment of a nematic phase on rubbed glass surfaces.

A nematic phase interacts more strongly with an external field than does an ordinary liquid because the molecules in the nematic phase interact cooperatively. For low molecular weight nematogens, theoretical treatments[1-11] indicate that different mechanisms operate in the conduction regime below the critical frequency f_c, and in the dielectric regime at higher frequencies. We have investigated a variety of thermotropic polymers to ascertain which of the instabilities reported for low molecular weight nematogens are also exhibited by polymers having mesogenic units as part of the main chain, and the conditions under which these occur. The higher viscosity of a polymeric mesophase leads to longer domain formation times, but it does offer some advantages which can be exploited under certain circumstances.

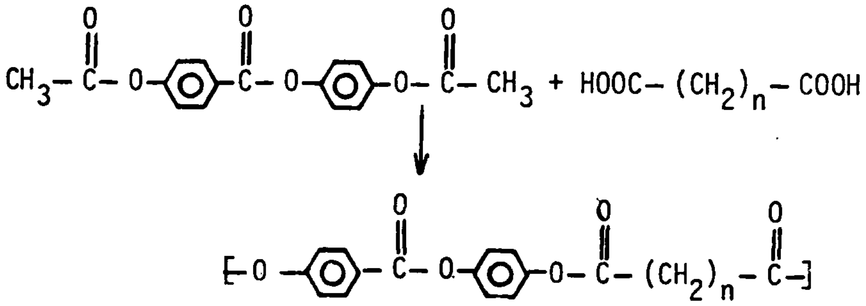
We first investigated[12,13] a high molecular weight sample of Tennessee Eastman T2/60, a copolyester having 40% ethylene terephthalate units and 60% oxybenzoate units. We observed Williams domains very similar to those seen in the nematic phase of the low molecular weight nematogen p-azoxyanisole (PAA). However, even under the most favorable conditions (dc voltage and relatively high temperatures) the domain formation time was the order of hours, as compared to tenths of hundredths of a second for PAA. On the other hand, the long relaxation time offered the advantage that the instability pattern could be preserved in the crystalline polymer by quenching. One expects to find the conduction regime at frequencies below f_c, but this instability can be quenched by reducing the sample thickness (which reduces the bend relaxation time). Under these conditions the variable grating mode could be observed in both T2/60 and PAA. A high field turbulence, again resembling that seen in PAA, appeared in T2/60 with a formation time of less than a minute. The same behavior was not observed for T2/30, which is not nematogenic. This finding, along with the short formation time, led us to suggest this as a useful diagnostic test for a polymeric nematic phase. Neither the dynamic scattering mode (DSM) nor the chevron pattern werte found for T2/60, and we were not successful in attempts to obtain an aligned sample of the nematic phase of T2/60 by the Chatelain rubbing technique.

We utilized T2/60 for these first studies because it was commercially available; however, this choice had several disadvantages. The crystal melting temperature is high, giving a possibility of degradation, and this polymer has no known nematic-isotropic transition. Also, samples were not available covering a range of molecular weights. Hence, all our subsequent studies were performed using polymers synthesized in this laboratory, which gave a certain degree of control of the transiton temperatures. However, it should be noted that in no case was an attempt made to obtain a carefully purified polymeric sample. Certain of the parameters may have been affected by the presence of conducting impurities.

Our second study [14] involved a low molecular weight polyester synthesized from 4,4′-dihydroxy-α-methyl stilbene and adipic acid. In the conduction regime the nematic phase of this polymer gave a fluctuating Williams domain (FWD) pattern similar to that observed for the low molecular weight nematogen p-methoxybenzylidene-p-n-butylaniline (MBBA). The formation time of FWD for this polymer was only tenths of a second (due to its low molecular weight). Appearance of the FWD pattern was found to be dependent upon voltage, frequency, temperature and sample thickness. This indicates there is a critical field for the FWD effect, rather than a critical voltage as seen for Williams domains. The critical field increased with temperature, and the apparent threshold voltage decreased with temperature and increased with sample thickness. This polymer also gave a DSM pattern not observed for T2/60. Its formation time was several seconds, which allowed us to photograph a precursor pattern. Interestingly, the precursor is more regular than the FWD pattern from which it develops, while the subsequent DSM involves a chaotic, random flow. It has not been possible to photograph the corresponding precursor pattern for low molecular weight nematics due to the much shorter onset time.

We next performed a more systematic investigation[15] of the effect of polymer molecular weight upon instabilities using the polyesters based upon 4′-hydroxyphenyl-4-hydroxycinnamate and dibasic acids. The monomeric analog, 4′-acetoxyphenyl-4-hydroxycinnamate, is a thermotropic nematogen. An electric field was observed to depress both the K-N and N-I transition temperatures of this monomer analog. The latter effect has been treated by Helfrich[16] using continuum theory. The effect of molecular weight was investigated using an homologous series of azelate polyesters. The formation time of Williams domains was short for polymers of low inherent viscosity, but increased to an hour for an inherent viscosity of 0.68 dL/g. Also, the DSM was only observed for polymers having inherent viscosities below 0.61 dL/g. The critical frequency at a given temperature was found to decrease with increasing molecular weight and, for a given molecular weight, to increase rapidly with temperature. Dvorjetski, Silberberg and Wiener-Avnear[17] have shown that the activation energy for ionic conduction, ΔE, can be evaluated from a plot of $\ln f_c$ vs. $1/T$. For three polyesters having inherent viscosities 0.09, 0.24 and 0.27 the activation energies were 0.67, 0.75 and 0.97 ev, as compared with a typical value of 0.6 ev for low molecular weight nematogens. This difference implies that the temperature dependence of f_c will become stronger as the molecular weight increases. With this polymer we were able, for the first time, to obtain an oriented nematic phase by rubbing for the sample having inherent viscosity 0.09 dL/g. At frequencies below f_c this sample exhibited a Williams domain pattern perpendicular to the rubbing direction, while above f_c we observed a broader domain pattern, also perpendicular to the rubbing direction. The latter pattern has been reported for low molecular weight MBBA by Trufanov, Blinov and Barnik.[18]

Recently our interest was attracted to the polyesters based upon 4′-hydroxyphenyl-4-hydroxybenzoate due to their reported wide nematic range. These polymers have been extensively investigated by Strzelecki and coworkers,[19-23] who prepared them by a transesterification reaction:



We[24] prepared a series of polymers in this way, obtaining properties in reasonable accord with those reported by Strzelecki and coworkers. However, except for the polymer of lowest molecular weight, these exhibited nematic droplets in a less birefringent background. Only the polymer of lowest molecular weight exhibited Williams domains, although the DSM could be seen in polymers having a biphasic structure. It was possible to obtain an ordered nematic phase for the polymer of lowest molecular weight by the rubbing technique, and to observe the broad domain pattern just above the critical frequency. We subsequently prepared this type of polymer by the acid chloride route and this polymer was significantly different in properties. The nematic range was not as broad, and a single nematic phase was observed (even for polymers of higher molecular weight) over a substantial temperature range. We suggest that transesterification with a monomer containing an internal ester linkage will occasionally involve this internal ester group, leading to a copolymer having rigid units of varying lengths. The transesterification polymers had lower melting temperatures, and a biphasic region extending over 50°C, while the corresponding polymer prepared by the acid chloride route had a biphasic region spanning only 9°.

Results of the work supported by ARO were reported in a paper, "The Effects of External Fields on Polymeric Nematic and Cholesteric Mesophases", presented at the seminar "Polymer Liquid Crystals: Science and Technology" held at Santa Margherita Ligure, Italy during the period May 19-23, 1981. This has recently appeared as a chapter in the monograph "Polymer Liquid Crystals".[25] I presented a second paper, "The Effect of Electric Fields on Nematic Phases of Thermotropic Polymers" at the U.S.-Japan Seminar on Polymer Liquid Crystals held in Kyoto during the period June 15-20, 1983. This will appear as a paper[26] in a volume of the Journal of Applied Polymer Science devoted to this meeting.

During our previous ARO grant we undertook a comparison of different methods for the measurement of the persistence length of polymers. Specifically, we selected a single test polymer, a polyamide-hydrazide, and reported results by light scattering[27] and intrinsic viscosity.[28] During the current grant period we extended this study to include a detemination of the persistence length of this polymer by small angle x-ray diffraction.[29]

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Dr. Hirokazu Toriumi	
Mr. Koichi Kubota	
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*Work supported on the ARO grant being reported.

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