Closeout Notice Date 31-AUG-1998

Project Number E-19-X64 Doch Id 34515

Center Number 10/24-6-R8299-0A0

Project Director LUDOVICE, PETER

Project Unit CHEM ENGR

Sponsor AMERICAN CHEMICAL SOCIETY/POLYMER EDUCATION COMMITTEE

Division Id 5952

Contract Number 28597-G7 Contract Entity GTRC

Prime Contract Number

Title APPLICATION OF STRUCTURE-SPECIFIC MOLECULAR MODELS TO CHARACTERIZE INTER..

Effective Completion Date 31-AUG-1995 (Performance) 31-AUG-1996 (Reports)

| Closeout Action: | Y/N | Date Submitted |
|---|---|---|
| Final Invoice or Copy of Final Invoice | N | |
| Final Report of Inventions and/or Subcontracts | N | |
| Government Property Inventory and Related Certificate | N | |
| Classified Material Certificate | N | |
| Release and Assignment | N | |
| Other | N | |

Comments

Distribution Required:

| | |
|---|---|
| Project Director/Principal Investigator | Y |
| Research Administrative Network | Y |
| Accounting | Y |
| Research Security Department | N |
| Reports Coordinator | Y |
| Research Property Team | Y |
| Supply Services Department/Procurement | Y |
| Georgia Tech Research Corporation | Y |
| Project File | Y |

E-19-X64
n/a

Home of the 1996 Olympic Village
Georgia Institute of Technology
Office of Grants and Contracts Accounting
Risk Management

September 25, 1996

Attn: Mr. Joseph Rogers, Jr.
The Petroleum Research Fund
American Chemical Society
1155 Sixteenth Street, NW
Washington, DC 20036

Re: PRF# 28597-G7

Dear Mr. Rogers:

Enclosed herewith please find the Final ACS-PRF Financial Statement for the above referenced grant. This report covers the period September 1, 1995 through August 31, 1996. There is an unexpended balance on this grant of $0.39. We will not refund this amount unless instructed otherwise by your organization.

If you have any questions, please contact Jill Redmond at (404) 894-6757 or me at (404) 894-2629.

Sincerely,

David V. Welch

David V. Welch
Director

enc.

cc: P. J. Ludovice, PH.D., Chem Eng, 0100
Claudia Clarkson, Chem Eng, 0100
Wanda Simon, OCA, 0420
File: E-19-X64/246R82990A0

**Office of Grants and Contracts Accounting**
190 Bobby Dodd Way
Atlanta, Georgia 30332-0259 U.S.A.
PHONE 404·894·4624 FAX 404·894·5519
RISK MANAGEMENT 404·894·4626

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Instructions on Reverse Side

## ACS-PRF FINANCIAL STATEMENT

PRF# 28597-G7 Inst. Ref.# E-19-X64/ R8299-0A0 Period From: 9-1-95 T 8-31-96

Balance Carried Forward from Last Reporting Period (for *This* or *Previous* Grant) (5,048.33)

Total Payments Received from PRF During *This* Reporting Period _____

| | |
|---|---|
| Stipends to: | |
| a. Principal Investigator (Summer Salary and Fringes) | 2,425.74 |
| b. Graduate Students/Fellows (including benefits) | 2,001.14 |
| c. Undergraduate Students | |
| d. Postdoctoral Fellows (including benefits) | |
| e. Summer Research Fellowship Supplement | |
| f. Undergraduate Research Supplement | |
| g. Others (Specify) | |
| | |
| Tuition (Graduate Students) | |
| Materials and Supplies | 524.40 |
| Equipment | |
| Publication Costs | |
| Travel (Identify costs for field work, if any) | |
| Other Expenses *(Attach itemized list)* | |
| Departmental Allocation (if budgeted) | |
| Total Expenditures During Reporting Period | 4,951.28 |

Balance on Hand at End of Period .39

This is to certify that the expenses reported herein were incurred for education and research in accord with the terms of the approved ACS-PRF grant-in-aid.

P. J. Ludovice, Ph.D.
Name of Principal Investigator

David V. Welch David V. Welch
Financial Officer (typed name and Signature)

Georgia Tech Research Corporation
Grantee Institution

Director, Grants & Contracts Accounting
Official Title

Jill Redmond (404) 894-6757
Contact Person/Telephone

(404) 894-2629 09/25/96
Telephone Date

**********

DO NOT complete this section unless there is a balance in the grant account at the termination date of the current grant agreement. Indicate below how the grant balance will be liquidated.

_____ By refund of unspent and uncommitted funds. The check should be drawn to the order of American Chemical Society-The Petroleum Research Fund, and identified by the PRF grant number.

_____ By use in the completion of the grant project. We hereby request approval by the American Chemical Society of an extension of the grant agreement, without commitment of additional funds, until _____ (Period up to one year, renewable).

_____ By transfer of unspent funds to the investigator's new grant account, ACS-PRF#_____

**********

Please submit to The Petroleum Research Fund, American Chemical Society
1155 Sixteenth Street, N.W., Washington, DC 20036 Telephone (202) 872-6092 8/95

E-19-X64
#1
(New)

Georgia Tech

**Georgia Institute of Technology**
School of Chemical Engineering
Atlanta, Georgia 30332-0100
USA

Peter J. Ludovice
Assistant Professor
404 • 894 • 1835
FAX 404 • 894 • 2866
EMAIL pete.ludovice@che.gatech.edu

September 29, 1995

Mr. Joseph Rogers Jr.
The Petroleum Research Fund
American Chemical Society
1155 Sixteenth Street, NW
Washington, DC 20036

Dear Mr. Rogers:

Enclosed herewith please find the Progress Report and Personnel Statement for ACS-PRF grant # 28597-G7. This material covers the period from September 1, 1994 through August 31, 1995. Please note that the Financial Statement was sent to you previously from Georgia Tech's Office of Contract Administration.

If you have any questions regarding this material please do not hesitate to contact me.

Sincerely,

Peter Ludovice

Peter J. Ludovice

enc.
cc: Wanda Simon, OCA, 0420

PERSONNEL STATEMENT

PRF# 28597-G7 REPORTING PERIOD 9/1/94 TO 8/31/95

GRANTEE INSTITUTION Georgia Tech Research Corporation

PRINCIPAL INVESTIGATOR(S) Peter J. Ludovice

GRANT PROJECT TITLE The Application of Structure Specific Models to Characterize Intermediate Order in Atactic Polyvinyl-chloride

List **undergraduate, graduate, and postdoctoral** co-workers receiving stipends under the above named grant: **DO NOT** list the principal investigator(s).

| NAME | TITLE OR ACADEMIC APPOINTMENT | PREVIOUS EDUCATION AND DEGREES* | COUNTRY OF PERMANENT RESIDENCE | PERIOD OF SUPPORT (MONTHS) | PERCENT OF SUPPORT FROM PRF** | DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD |
|---|---|---|---|---|---|---|
| Jon Van Order | Ph.D Student | B.S. Lehigh Univ. | U. S. A. | 8 | 2/3 | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

List other co-workers on grant project not directly supported with ACS-PRF funds:

| NAME | SOURCE OF SUPPORT | DATES ASSOCIATED WITH GRANT PROJECT |
|---|---|---|
| Rowland McCellan | Undergraduate project for course credit | 3/94 - 8/95 |
| | | |
| | | |
| | | |

*For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph.D. granting institution.

**(during the period stated in preceding column)

Revised 8/95

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 28597-G7

Page 1 of 2 pages.

PREPARED BY

Peter J. Ludovice

Date 9/28/95

Please refer to instructions.

Fill in information requested above for each page.

The report heading, narrative, and all drawings must be prepared within the box.

Please submit one sharp, clear "original" and a copy (Xerox, carbon, etc.) for each page.

28597-67 The Application of Structure Specific Models to Characterize Intermediate Order in Atactic Polyvinylchloride

Peter J. Ludovice, Georgia Tech Research Corporation

Our efforts have focused on the use of molecular modeling to produce models of polymer glasses that contain levels of structural order intermediate between that of crystalline and amorphous states. We have chosen atactic polyvinylchloride (PVC) as a representative example of a polymer glass that contains this intermediate order. During the past one year grant period we have carried out 1.) the validation of an atomic level force field from which we may 2.) develop a structure specific meso-scale model to simulate the intermediate order in polymer glasses.

1.) An atomically detailed polymer model of atactic polyvinylchloride was derived from force field parameters previously calculated using *ab initio* quantum chemistry calculations.[1] We also carried out x-ray diffraction measurements on a well characterized PVC sample whose stereochemical distribution is identical to that of the polymer model. These measurements confirm that the unusual x-ray diffraction pattern is not a manifestation the additives present in commercial samples that represent the vast majority of diffraction analyses reported in the literature. The force field reproduces the local crystalline structure of various stereochemical configurations more accurately than generic force fields

2.) . This force field was then used to map the conformational characteristics of the PVC chain. This conformational information has been transformed to a coarse-grained or meso-scale model based on the interaction of the effective dipole due to the chloride group. Previous simulations suggest that this dipole represents the principle structural characteristic responsible for the formation of PVC's intermediate order.[2] Unlike other meso-scale models, this structural characteristic will be retained to facilitate the formation of intermediate order This more efficient new model should more easily converge to the intermediate order structure unlike the atomically detailed models, which have failed to do so. This new model will be compared

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 28597-G7



PREPARED BY

Peter J. Ludovice

Date 9/28/95

Please refer to instructions.

Fill in information requested above for each page.

The report heading, narrative, and all drawings must be prepared within the box.

Please submit one sharp, clear "original" and a copy (Xerox, carbon, etc.) for each page.

to the experimental x-ray diffraction results to determine whether it predicts the presence of the intermediate order in PVC.

[1] Smith, G.D.; Ludovice, P.J.; Jaffe, R.L.; Yoon, D.Y. *J. Phys. Chem.*, **99**, 164-172 (1995).

[2] Ludovice, P.J. and Suter, U.W in Computational Modeling of Polymers, pages 401-435, (J. Bicerano, Ed.) Marcel Dekker: New York (1992).

K-19-X64 #2 ~~K-19-X98~~ thesis

28597-67 The Application of Structure Specific Models to Characterize Intermediate Order in Atactic Polyvinylchloride

28597-G7

1 2

Peter J. Ludovice, Georgia Tech Research Corporation

Peter J. Ludovice

9/27/96

Most polymer glasses are generalized as having amorphous structure, however, very subtle differences in their structures produce properties that span several orders of magnitude. The purpose of this work is to analyze how subtle changes in structure, intermediate between that of crystalline and amorphous states, affects properties. Current polymer glass models use randomly generated initial conformations that are equilibrated via Molecular Mechanics (MM) or Molecular Dynamics (MD) algorithms. These models are accurate when the structure of the glass is truly amorphous as indicated by two very broad reflections (the amorphous halo) in their diffraction patterns. For example, these types of models have reproduced the amorphous halo diffraction patterns of atactic polypropylene[1], and bisphenol-A polycarbonate[2].

Part of our work over the last two years has focused on how far these models can be pushed to characterize differences in structure that produce differences in properties. Molecular Mechanics simulations of polycarbonate derivatives were carried out and the resulting structures analyzed using Delauney tessellation.[3] A mean spherical model of gaseous diffusants was applied to calculate the volume available to diffusants of various sizes in the resulting polymer matrices. The reciprocal of this available volume correlated linearly with the experimental diffusivity. The correlations were statistically different (at the 95% confidence level) for two very similar derivatives of polycarbonate.

The above results indicate that current models can be used to analyze structure-property relationships for structural derivatives of the same polymer. However, this does not occur when the polymer contains levels of structural order intermediate between the crystalline and amorphous states. This order is typically characterized by at least one split or shoulder occurring in the first diffraction peak of the amorphous halo. The rest of our work over the previous two year period has focused on production of methods of simulation

28597-G7

2 2

Peter J. Ludovice

9/27/96

for these ordered polymers. This has resulted in 1.) the validation of an atomic level force field and 2.) the development of a structure specific meso-scale model to simulate the intermediate order in polymer glasses.

1.) An atomically detailed polymer model of atactic polyvinylchloride (PVC) was derived from force field parameters previously calculated using *ab initio* quantum chemistry calculations.[4] We have validated that this force field model reproduces the order in crystalline PVC despite the fact that MD simulation of PVC oligomers using this force field did not accurately reproduce the second virial coefficient. This discrepancy is due to the failure of the derived force field to include the long range corrections to the 2nd virial coefficient. PVC was chosen for the initial model because it contains well characterized intermediate order, and current MM models fail to undergo sufficient conformational relaxation so as to accurately reproduce this order.

2.) This force field was then used to map the conformational characteristics of the PVC chain. This conformational information has been transformed to a coarse-grained or meso-scale model based on the interaction of the effective dipole due to the chloride group. A new intramolecular potential energy function has been developed $E(\theta_1,\theta_2,d)$ which is a function of the distance (d) and the orientational angles $(\theta_1,\theta_2)$ between neighboring dipoles. This, coupled with a dipole-dipole, and a soft-sphere intermolecular interaction term in the dipole model is now being used to simulate PVC. The advantage of this new model over detailed atomistic models is that it has lower barriers to energy relaxation thereby allowing better conformational relaxation of bulk polymer models so as to produce the intermediate order. Yet, it retains the structural detail so as to analyze realistic structure-property relationships.

[1] Theodorou, D.N. Ph.D. Thesis, Massachusetts Institute of Technology (1985).

[2] Gentile, F.T.; Suter, U.W. from *Amorphous Polymer Microstructure from Materials Science and Technology: Structure and Properties in Polymers*, (Haaseen, P. and Kramer, E. Eds.) VCH Publishers: Weinheim, Germany, pp. 33-77 (1993).

[3] Gentile, F.T.; Arizzi, S.; Suter, U.W. and Ludovice, P.J. *Ind. Eng. Chem. Research*, **34**(12), 4193-4201 (1995).

[4] Smith, G.D.; Ludovice, P.J.; Jaffe, R.L.; Yoon, D.Y. *J. Phys. Chem.*, **99**, 164-172 (1995).