GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: October 19, 1978

Project Title: Gaseous Polymer Solutions
Green card

Co-Project Nos.: E-27-671/G-41-673

Co-Project Directors: Dr. John L. Lundberg/Dr. Donald C. O'Shea

Sponsor: National Science Foundation

Agreement Period: From 9/1/78 Until ~~2/29/80~~ ~~81~~ 7/31/82
(Grant Period -- includes flexibility period)

Type Agreement: Grant No. DMR78-17929

Amount:

	TE	PHYSICS	TOTALS
NSF	$37,381 (E-27-671)	$ 8,884 (G-41-673)	$46,265
GIT	5,878 (E-27-319)	5,877 (G-41-317)	11,755
TOTALS	$43,259	$14,761	$58,020

Reports Required: Progress Report (submit w/request for continued support); Final Project Report

Sponsor Contact Person (s):

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National Science Foundation
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(Grants Manager)
Ms. Mary Frances O'Connell
Grants Specialist - Area 4
MPE/BBS/SE Branch
Division of Grants and Contracts
National Science Foundation
Washington, D. C. 20550
(202) 632-2858

Defense Priority Rating: n/a

Assigned to: Textile Engineering/Physics (School/Laboratory)

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CA-3 (3/76)

5R454
5-23-83

GEORGIA INSTITUTE OF TECHNOLOGY **OFFICE OF CONTRACT ADMINISTRATION**

SPONSORED PROJECT TERMINATION SHEET

Date June 15, 1983

Project Title: Gaseous Polymer Solutions

Project No: E-27-671

Project Director: Dr. J. L. Lundberg

Sponsor: National Science Foundation

Effective Termination Date: 7/31/82

Clearance of Accounting Charges: 10/31/82

Grant/Contract Closeout Actions Remaining:

- [ ] Final Invoice and Closing Documents
- [X] Final ~~Fiscal~~ Acctg. Report (FCTR)
- [X] Final Report of Inventions
- [X] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other ______________________

Assigned to: Textile Eng./Physics (School/~~Laboratory~~)

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FORM OCA 10:781

NOTICE OF RESEARCH PROJECT

SCIENCE INFORMATION EXCHANGE

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PROJECT SUMMARY

SIE PROJECT NO.
NSF AWARD NO.

FOR NSF USE ONLY

DIRECTORATE/DIVISION	PROGRAM OR SECTION	PROPOSAL NO.	F.Y.

NAME OF INSTITUTION (INCLUDE BRANCH/CAMPUS AND SCHOOL OR DIVISION)

Georgia Institute of Technology

ADDRESS (INCLUDE DEPARTMENT)

School of Textile Engineering
225 North Avenue, NW
Atlanta, Georgia 30332

PRINCIPAL INVESTIGATOR(S)

John L. Lundberg, Donald C. O'Shea

TITLE OF PROJECT

Gaseous Polymer Solutions

TECHNICAL ABSTRACT (LIMIT TO 22 PICA OR 18 ELITE TYPEWRITTEN LINES)

Solubilities measured for 23 polymer - gas systems show that common, industrial polymers are sufficiently soluble in gases such as carbon dioxide, ethane, propane and butane that such solutions may be useful for transporting and forming polymers. Some of these solubility measurements will be checked and extended to higher and lower concentrations of polymers in gases. Solubilities of polymers likely to be easily soluble in gases will be measured; these include polydimethylsiloxane, poly(ethylene glycol), and polybutadiene in propane and butane. Solubilities of these polymers and others in carbon dioxide will be measured. Angular dependence of irradiance of elastically scattered light will be measured on solutions of polyisobutylene in butane and other gas - polymer systems as functions of pressure, temperature, and concentration at relatively low pressures ($p \lesssim 135$ atm). Results will be interperted in terms of polymer solution theories and the theory of scattering from inhomogeneous media. Inelastic light scattering (Brillouin spectra) in solutions of polyisobutylene in butane and other systems will be measured. Velocities of sound, moduli of elasticity and viscosities at high frequencies will be determined. Viscosities at frequencies approaching zero will be measured by the falling bob technique. Judging from turbulence observed near the critical region of polyisobutylene dissolved in butane, these viscosities should be low.

1. Proposal Folder
2. Program Suspense
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Summary of Progress

1) Solubility studies

Dr. Sabz Ali, postdoctoral fellow, has measured the solubilities of polymers in gases for 18 gas - polymer systems by observing pressures and temperatures of critical opalescence. Mass of gas present at phase separation is calculated from observed pressure assuming the compressibility of the gas in solution is the same as in the pure gas at the same pressure and temperature, the known mass of polymer in the pressure vessel is dissolved, and the partial pressure of the polymer is negligible. Solubilities (in weight fractions of polymers), pressure and temperature ranges, and densities of solutions estimated in this and earlier work are as follows:

Polymer or Polymer of	Gas	T_c °C	P_c atm	dc g/cc	Wt fract polymer	Pressure atm	Temp °C	Density g/cc	P/P_c) T/T_c)
Nylon-6	CO_2	31	73	.47	.138-.165	402-511	233-241	.49-.59	$3.3_1-4.1_5$
Butene-1	CO_2	31	73	.47	.063-.378	294-913	131-150	.53-.91	$2.9_0-9.4_2$
PIB (loMW)	CO_2	31	73	.47	.056-.069	425-439	120-178	.59-.72	$3.9_3-4.6_5$
PIB (hiMW)	CO_2	31	73	.47	.049-.057	603-615	121-177	.70-.82	$5.5_9-6.5_2$
Propylene	CO_2	31	73	.47	.067-.381	453-954	163-208	.60-.87	$4.3_3-8.2_7$
Styrene	CO_2	31	73	.47	.015-.061	666-688	100-144	.79-.91	$6.7_6-7.6_7$
PVC	CO_2	31	73	.47	.036-.212	810-898	88-113	.91-1.02	$8.7_5-10.3_1$
PIB (loMW)	Ethane	32	49	.21	.082-.597	55-163	100-200	.09-.32	$0.8_5-2.7_6$
PIB (hiMW)	Ethane	32	49	.21	.109-.154	260-275	100-200	.26-.36	$3.4_7-4.6_6$
Styrene	Ethane	32	49	.21	.070-.411	187-382	100-201	.26-.47	$3.1_7-4.6_5$
Propylene	Ethane	32	49	.21	.040-.405	307-415	160-200	.27-.45	$4.1_1-6.1_5$
PMMA	Ethane	32	49	.21	.050-.348	400-418	160-188	.18-.36	$5.5_5-6.0_9$
PVC	Propane	97	42	.22	.075-.321	55-129	100-141	.30-.51	$1.3_0-2.7_6$
Ethylene	Propane	97	42	.22	.077-.250	409-431	100-181	.44-.55	$7.9_2-10.1_0$
Ethylene	Propane	97	42	.22	.056-.296	409-432	100-181	.44-.58	$7.9_4-10.1_3$
PVC	Butane	152	38	.23	.099	46	155	.37	1.2
PMMA	Butane	152	38	.23	.059-.198	51-85	155-200	.30-.53	$1.3_6-2.0_4$
PIB (loMW)	Butane	152	38	.23	.202-.314	65-109	155-200	.41-.59	$1.8_3-2.6_8$
PIB (hiMW)	Butane	152	38	.23	.167-.318	60-118	155-200	.36-.60	$1.5_8-2.8_0$
Styrene	Butane	152	38	.23	.130-.294	88-123	155-201	.40-.58	$2.3_3-2.9_2$
Butene-1	Butane	152	38	.23	.051-.199	108-138	171-198	.40-.46	$2.6_1-3.5_2$
Propylene	Butane	152	38	.23	.050-.22	119-157	166-190	.44-.53	$3.0_7-3.8_5$
Propylene	Butane	152	38	.23	.036-.217	115-203	155-189	.30-.56	$3.0_5-4.8_8$

Common to all studies of solubilities reported to date is the visual observation of phase separation (1,2,3). In high pressure vessels used in these studies, not all of the interior volumes can be seen through the windows. Therefore, the assumption that polymer in the pressure vessel is dissolved completely cannot be verified by direct, visual observation. Repeatability of measurements and consistency of solubility estimates are used to substantiate this assumption. In our light scattering studies, we can see the whole volume in the pressure cell; hence, we can verify that all polymer is dissolved (for gas polymer systems at pressures up to about 135 atm, the bursting limit of windows on this cell). At present we are checking solubility measurements comparing measurements in the light scattering and solubility measurement pressure cells.

Solubilities of polymers in gases appear to be sufficient that gaseous solutions can be useful for the transport and fabrication of polymers. The polymers are soluble at temperatures close to or above their softening or melting temperatures. Extrusion of polymers usually is carried out at temperatures substantially above softening or melting points of polymers in order to lower viscosities into workable ranges. Gaseous solutions of polymers should be attractive as transport and facrication media because these can be manipulated at temperatures substantially lower (as much as 100 centigrade degrees). For example, the solubilities of polyvinylchloride in propane and carbon dioxide at temperatures as low as 100^{O}C appear to be sufficient that these solutions may be useful for fabricating polyvinylchloride. Pressures at which polymers dessolve in gases may be expected to be higher the higher the melting or softening temperature of the polymer and the lower the critical temperature of the gas. Therefore, approximate comparison of solubility behaviors may be made by comparing the reduced pressures divided by the reduced temperatures of the gases for ranges of solubility. By this criterion nylon-6 is easily dissolved in CO_2 as are polyisobutylene in ethane and n-butane and polyvinylchloride in propane and n-butane while polyethylene is less readily soluble in propane and n-butane.

2) Elastic light scattering

Gaseous polymer solutions such as polyisolbutylene in n-butane scatter light with the intensity expected from our experience with pure gas - liquid systems and critical miscibility in two component liquid systems. Mr. Kenneth Ko, predoctoral fellow in the School of Textile Engineering, has observed near critical opalescence, turbulence, and diffraction caused by density gradients for solutions of polyisobutylene in n-butane.

Light scattering apparatus, thermostatted scattering cell, and temperature and pressure measuring and data recording systems have been built and calibrated. Present efforts are directed toward preventing precipitation of polymer on the windows of the light cell. Such precipitated polymer interferes with measurements of irradiance of scattered light.

3) Inelastic light scattering

Mr. Eric Kuster, predoctoral fellow in the School of Physics, has constructed a Brillouin spectrophotometer with thermostatted pressure cell and pressure system to produce gaseous polymer solutions and observe Brillouin spectra. Polyisobutylene has been dissolved in butane in the spectrophotometer cell. This requires some stirring, by rolling ball bearings within the cell as it is rocked. Attempts to dissolve the less readily soluble polymers such as polystyrene, polypropylene and polyethylene in carbon dioxide were not successful.

Plans for the Third Year of the Study

1) Solubility studies (S. Ali and J.L. Lundberg)

Solubilities of some polymer - gas systems which may exist at lower pressures will be examined. Possible systems are polydimethylsiloxane, polybutadiene, and polyethylene glycol in propane and butane. Solubilities on systems measured in the past will be checked to determine that all polymer placed in the pressure cell is dissolved.

2) Elastic light scattering (K. Ko and J.L. Lundberg)

Angular dependence of the irradiance of scattered light will be measured at various pressures, temperatures, and concentrations for polyisobutylene in n-butane and other gas - polymer systems at pressures up to about 135 atm. Results will be interpreted using Einstein's equations for light scattering from mixtures (4) and theories of polymer solutions (5,6) and Debye's equation for scattering from inhomogenious media (7).

3) Inelastic light scattering (E. Kuster and D.C. O'Shea)

The Brillouin spectra of solutions of polyisobutylene in n-butane will be measured at various pressures, temperatures and concentrations approaching immiscibility. Measurements will be made on other, readily soluble polymer in gas systems. Sound velocities, moduli of elasticity, and viscosities at ultrasonic frequencies will be calculated.

4) Viscosities (S. Ali and J.L. Lundberg)

Viscosities of a few of these gaseous polymer solutions will be measured using the falling cylinder technique. Apparatus has been assembled and tested and will be refined. Techniques to prevent the cylinder from sticking in polymer to the wall of the pressure vessel before dissolution must be perfected.

References

1. P. Ehrlich and J. J. Kurpen, J. Polymer Sci., A, 1, 3217 (1963); P. Ehrlich, ibid, 3, 131 (1965).

2. T. Swelheim, J. de Swaan Arons and G.A.M. Diepen, Rec. Trav. Chim., 84 261 (1965).

3. R. Konigsveld, G.A.M. Diepen and H.A.G. Chermin, Rec. Trav. Chim., 85, 504 (1966).

4. A. Einstein, Ann. Physik., 33, 1275 (1910); translated by G. Y. Rainich and published in Colloid Chemistry: Theoretical and Applied, Vol. I, Jerome Alexander, Ed. (Chem. Catalog Co., New York, 1926), p. 323.

5. P. J. Flory, J. Chem. Phys., 9, 660 (1941), ibid, 10, 51 (1942); M. L. Huggins, J. Chem. Phys. 9, 440 (1941); J. Phys. Chem., 46, 15 (1942), Ann. N. Y. Acad. Sci., 43, 1 (1942).

6. B. H. Zimm and J. L. Lundberg, J. Phys. Chem., 60, 425 (1956), J. L. Lundberg, Pure and Appl. Chem., 31, 261 (1972).

7. P. Debye, Physik Z., 28, 135 (1927); P. Debye and A. Bueche, J. Appl. Phys., 20, 518 (1949); P. Debye in Scattering of Radiation by Non-crystalline Media, V. D. Frechette, Ed. (John Wiley and Sons, New York, 1960) p. 1.

Current and Pending Support

	AGENCY	TITLE	GRANT NO.	AMOUNT	PERIOD	ACAD.	SUMMER	LOCATION
J. L. Lundberg	NSF	Gaseous Polymer Solutions	DMR-7817929 DMR-7922660	$94,265	09/01/78- 02/28/81	1	0	Georgia Tech
	NSF	Student Science Training Program	Proposal submitted 8/22/80	40,270		0	2	Georgia Tech
D. C. O'Shea	NSF	Relative Contributions of Scattering Equation Terms to the Resonance Spectra of Synthetic Metalloporphorins	DMR-7907758	43,783	07/01/80 07/10/81	1	1	Georgia Tech
			DMR-8011078	50,935	07/01/81- 07/01/82	1	0	Georgia Tech

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

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PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology 225 North Avenue, NW Atlanta, GA 30332	Polymer Program	DMR-7817929
	4. Award Period From 9/1/78 To 7/31/82	5. Cumulative Award Amount $145,265

6. Project Title

GASEOUS POLYMER SOLUTIONS

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

This study of "Gaseous Polymer Solutions" consisted of measurements of solubilities of polymers in gases (by S. Ali and J. L. Lundberg), elastic scattering of light by gaseous solutions of poly(dimethylsiloxane), PDMS, in butane (by K-Y Ko and J. L. Lundberg), and Brillouin scattering by solutions of PDMS in butane (by E.J. Kuster and D. C. O'Shea).

Polypropylene,polystyrene, and high and low molecular weight polyisobutylenes appear to be reasonably soluble in carbon dioxide, ethane and butane at temperatures above the critical temperatures of the gases and the softening temperatures of the polymers and at pressures above the critical pressures of the gases. Poly(methyl methacrylate) dissolves in butane gas and to some extent in ethane gas under similar conditions. Polyethylene is readily soluble in propane and butane; small amounts of polyisobutylene dissolve in sulfurhexafluoride. Polydimethylsiloxane dissolves quite easily in gaseous butane.

Elastic scattering of light from butane solutions of PDMS (at concentrations up to 0.043 g/cm^3, scattering angles up to 8^o, and of temperatures 0.25^o to 1.25^{o}C above the critical miscibility temperatures of the solutions) can be described quite accurately by Einstein's equation for scattering from a liquid mixture and Huggins' equation for the activity of solvent derived from the lattice theory. Average distances between refractive index fluctuations calculated by fitting scattering data to Debye's equation for scattering from inhomogeneous media suggests that refractive index fluctuation lengths are from about 0.65 to 0.70 μ in these solutions. The concentration fluctuation correlation lengths and ranges of molecular forces, deduced by fitting data to Debye's equation for scattering from solutions near critical immiscibility, are much too high.

Brillouin shifts were measured on a series of PDMS-n-butane mixtures at constant density and composition at temperatures from 110^o to 195^{o}C and pressures from 20 to 110 atm. Brillouin shifts varied from 0.01 to 0.05 cm. The results show that gaseous solutions did form and that for a solution of about 20 percent by weight PDMS the critical temperature is estimated to be 146^{o}C.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM: Check (✓)	Approx. Date
a. Abstracts of Theses				x	9/1/83
b. Publication Citations				x	1/1/84
c. Data on Scientific Collaborators	x				
d. Information on Inventions	x				
e. Technical Description of Project and Results				x	7/1/83
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
John L. Lundberg		5/20/83