

2

DTIC FILE COPY

Office of Naval Research

Contract N0014-85-K-0632

R & T Code 413c014

Technical Report No. 20

AD-A222 255

"MISCIBILITY AND PHASE BEHAVIOR OF PEAN/PEO BLENDS"

by

J. A. Moore and Ji Heung Kim

To Be Published in
Polymer Preprints
Fall 1990 ACS Meeting
Washington, DC

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180-3590

May 31, 1990

DTIC
ELECTE
JUN 05 1990
S E D
B

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

90 06 04 181

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release distribution unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION ONR		
6c. ADDRESS (City, State, and ZIP Code)		7b. ADDRESS (City, State, and ZIP Code) Department of Navy Arlington, VA 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) Department of Navy Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO. N-0014-85-K 0632	PROJECT NO.	
		TASK NO. 625-826	WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) TECH. REP. #20 MISCIBILITY AND PHASE BEHAVIOR OF POLY(ENAMINONITRILE)/PEO BLENDS. (Unclassified)				
12. PERSONAL AUTHOR(S) J.A. MOORE & JI HEUNG KIM				
13a. TYPE OF REPORT Publication	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) May 31, 1990	15. PAGE COUNT	
16. SUPPLEMENTARY NOTATION POLYMER PREPRINTS, DIV. POLYM. CHEM./AMER. CHEM. SOC.				
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP			SUB-GROUP
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Recently, we have been synthesizing and studying the properties of poly(enaminonitriles), a novel class of polymers which exhibit the thermal stability of aramides but are readily soluble in simple, volatile solvents such as THF and ciglyme, as well as in polar, aprotic solvents. Spectroscopic evidence supports specific hydrogen bonded interactions between the NH-groups of the enaminonitrile unit and the oxygen atoms in the ether. Ether solutions exhibit lower critical solution temperature behavior. For the glymes, the critical temperature for phase separation increases as the number -CH2-CH2-O- units increases from one to eleven. A similar tendency is observed for blends with poly(ethyleneoxide) up to PEO contents of 50 wt-%. DSC, FT-IR and light scattering data will be presented and discussed.				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Kenneth J. Wynne		22b. TELEPHONE (Include Area Code) (202) 696-4410	22c. OFFICE SYMBOL	

Miscibility and Phase Behavior of Poly(enaminonitrile)/PEO Blends

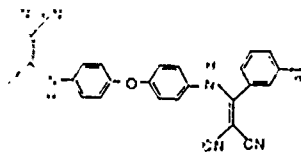
J.A. Moore & Ji-Heung Kim
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, NY 12180-3590

INTRODUCTION

Polyenaminonitriles (PEANs) are novel, high molecular weight, film-forming polymers which have excellent thermal stability and good mechanical properties. Recently, we reported that one of these polymers forms blends with several strong proton accepting polymers such as poly(4-vinyl pyridine), poly(ethyl oxazoline) and poly(N-vinyl pyrrolidone). Poly(ethylene oxide) is a relatively weakly self-associated polymer that contains sites, the oxygen atoms, which are capable of forming a strong interaction (hydrogen bonding) with PEAN even though PEO is an easily crystallizable polymer. The good solubility of PEAN in a series of polyether solvents and the existence of lower critical solution temperatures (LCST) for these solutions also suggest favorable interactions between these two components.¹ In this paper, we study the miscibility and phase behavior of PEO/PEAN blends. Differential Scanning Calorimetry (DSC) and optical microscopy were used to investigate miscibility and phase separation. FT-IR was used to study the molecular interaction involved in this blend system.

EXPERIMENTAL

Materials Polyenaminonitrile (see structure shown below) was prepared through condensation polymerization of 1,3-bis(1-chloro-2,2'-dicyanovinyl)benzene with oxydianiline using the procedure we have developed.² Intrinsic viscosity in DMF at 25°C was 0.47 dl/g. PEO with an average molecular weight of 100,000 Daltons was purchased from Aldrich Chemical Company



Preparation of Blends Blends were prepared by solution casting from DMF. The solvent was evaporated slowly under N₂ flow at 60°C. The resulting films were further dried in vacuo at 100°C for 2 days and then slowly cooled to room temperature and stored in a desiccator prior to measurement. The samples for FT-IR analysis were cast on NaCl plates using the same procedure.

Calorimetric Measurements Glass transition temperatures and heats of demixing were determined in a Perkin-Elmer System 7 differential scanning calorimeter. A heating rate of 5 K/min was used. The glass transition temperature was taken as the midpoint of the heat capacity change.

The phase diagram was established by means of DSC and microscopic observation of the onset of phase separation.

The morphology of the phase-separated structure was observed on a hot-stage optical microscope. FT-IR spectra were recorded on a Perkin-Elmer Model 1800 spectrometer at a resolution of 2 cm⁻¹. A minimum of 64 scans were signal-averaged.

RESULTS and DISCUSSION

Films of blends containing 10, 20, 30, 50, 65, 70 and 80 wt% PEO blend film prepared as described above. Up to 50 wt% PEO, cast films were transparent, but films containing more than 50 wt% PEO were turbid because of the development of crystallites of PEO in the blend film. DSC began to show the melting endotherm of PEO with growing peak intensity as the PEO content increased from 65 wt% PEO. These blends containing more than 50 wt% PEO may be viewed in terms of crystallites of PEO embedded in a mixed amorphous matrix of PEAN and PEO. to a first approximation. The T_g vs composition curve up to 50 wt% PEO is shown in Figure 1. All the points fell almost on the weight average line between the limiting values of T_g, suggesting miscibility between these two polymers. Besides the glass transition, another composition-dependent endothermic transition was observed at higher temperature which turned out to be a transition associated with phase separation. Figure 2 shows a DSC trace resulting from a continuous increase of the temperature from the homogeneously mixed state to the phase separated range. It is obvious that phase separation is associated with an endothermic process in this blend. Hot-stage microscopy showed the separation process clearly at the same temperature with the one observed in DSC. The initially clear film became opaque after separation and went back to clear when the sample film was cooled, i.e., the process was reversible. A partial phase diagram was determined from DSC and microscopic observations of the onset of phase separation as shown in Figure 1. This lower critical solution temperature (LCST) behavior further substantiates miscible behavior at temperatures below the cloud point and suggests that these polymers are miscible as a result of an exothermic interaction. A highly interconnected two-phase morphology with uniform domain size is seen in the micrograph of a 50/50 (PEAN/PEO) blend as shown in Figure 3. In this system, phase redissolution occurred relatively rapidly and reheating the sample reproduced the original separation process.

Recently, several authors^{3,4,5} have studied the heat of demixing associated with LCST phase behavior by DSC. From the DSC of 50/50 (PEAN/PEO) blend under different heating rate (5K/min to 40K/min), the onset temperature of the endothermic peak was found to shift to higher temperature with increasing rate as has been observed by other authors.^{3,5} Heats of demixing were determined from the area under the endothermic peaks. At lower heating rates, the area decreases dramatically and precise measurement becomes difficult. Within the heating rate range from 5 K/min to 40 K/min, ΔH_{demix} was found to be 5.0 ± 0.5 J/g approximately and it seems that the heat of demixing does not change much depending on the heating rate in this system. More data about this subject are being collected.

FT-IR spectrometry was used to study the specific hydrogen bonding interaction involved in this blend. FT-IR spectrum of the -NH stretching region of PEAN is shown in Figure 4. As the concentration of PEO is increased in the blend, the infra-red band at 3360 cm^{-1} attributed to relatively 'free' -NH groups decreases and almost completely disappears at 50 wt% PEO. The broad band originally centered at 3240 cm^{-1} is shifted to lower frequency with increasing intensity. This result implies a strong hydrogen bonding interaction between the enamine hydrogen on the PEAN backbone and oxygen atom in PEO. The IR bands of the -NH stretching region of blend films above 50 wt% PEO were almost the same as that of the 50wt% PEO sample.

CONCLUSIONS

PEAN forms a miscible blend with PEO in the amorphous state as determined by optical clarity and a single glass transition temperature changing smoothly with composition. This blend shows phase separation at higher temperature because of the presence of lower critical solution temperature behavior. The phase separation is associated with an endothermic process. The phase diagram was obtained by means of DSC and microscopic observation of the onset of phase separation. Hydrogen bonding evidenced by FT-IR seems to be the strong interaction responsible for the miscibility of this blend system.

REFERENCES

1. J.A. Moore, Ji Heung Kim, Proc. Polym. Mat. Sci. Eng., 1989, 61, 679
2. J.A. Moore, D.R. Robello, Macromolecules, 1989, 22, 1084
3. C. Uriarte, J.I. Eguiazabal, M. Llanos, J.I. Iribarren, and J.I. Iruiñ, Macromolecules, 1987, 20, 3038
4. A. Natansohn, J. Polym. Sci., Polym. Lett. Ed., 1985, 23, 305
5. M. Evert, R.W. Garbella, J.H. Wendorff, Macromol. Chem., Rapid Commun., 1986, 7, 65

ACKNOWLEDGMENT

This work was supported by the Office of Naval Research

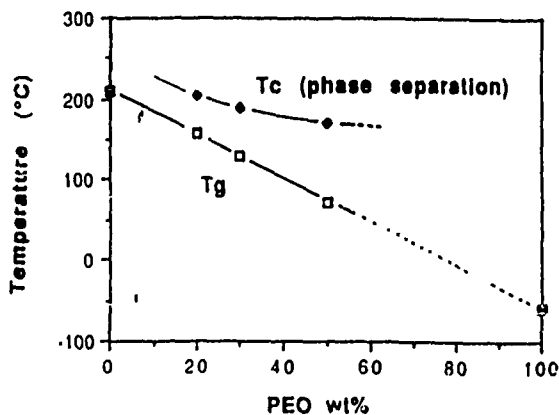


Figure 1. The phase diagram and T_g-composition curve of PEO/PEAN blend.

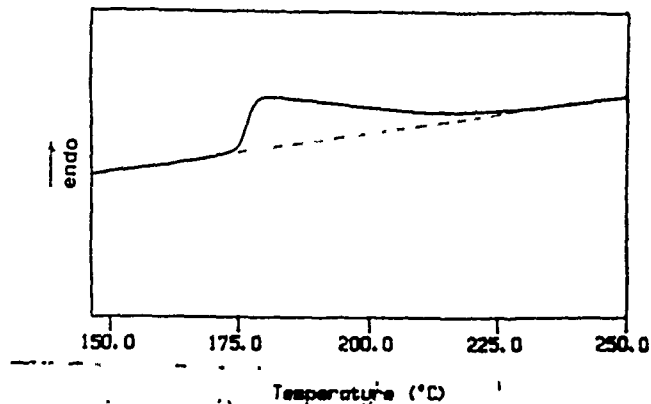


Figure 2. DSC trace characteristic of the phase separation. Blend of 50/50 (PEO/PEAN)

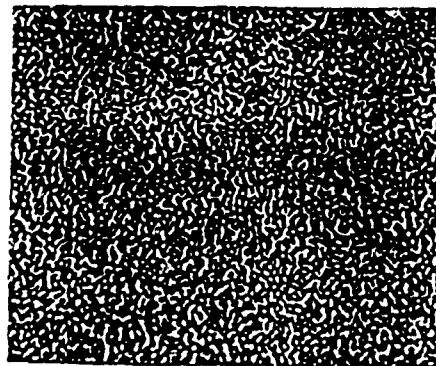


Figure 3. An optical micrograph of the phase separated structure taken on a hot-stage microscope. (X600)

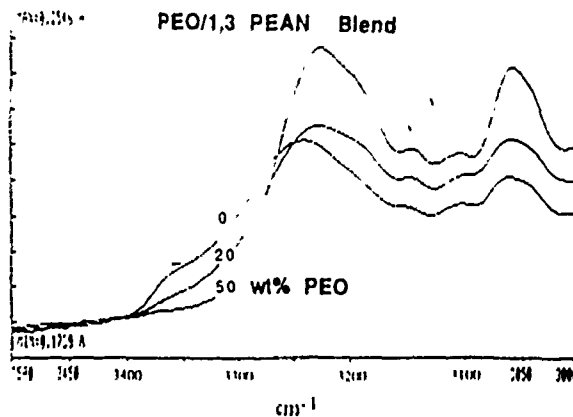


Figure 4. FT-IR spectra of the -NH stretching region of the PEO/PEAN blend

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)
 Chemistry Division, Code 1113
 800 North Quincy Street
 Arlington, Virginia 22217-5000

Dr. Robert Green, Director (1)
 Chemistry Division, Code 385
 Naval Weapons Center
 China Lake, CA 93555-6001

Commanding Officer (1)
 Naval Weapons Support Center
 Dr. Bernard E. Douda
 Crane, Indiana 47522-5050

Chief of Naval Research (1)
 Special Assistant for Marine
 Corps Matters
 Code OOMC
 800 North Quincy Street
 Arlington, VA 22217-5000

Dr. Richard W. Drisko (1)
 Naval Civil Engineering
 Laboratory
 Code L52
 Port Hueneme, CA 93043

Dr. Bernadette Eichinger (1)
 Naval Ship Systems Engineering
 Station
 Code 053
 Philadelphia Naval Base
 Philadelphia, PA 19112

David Taylor Research Center (1)
 Dr. Eugene C. Fischer
 Annapolis, MD 21402-5067

Dr. Sachio Yamamoto (1)
 Naval Ocean Systems Center
 Code 52
 San Diego, CA 92152-5000

Dr. James S. Murday (1)
 Chemistry Division, Code 6100
 Naval Research Laboratory
 Washington, D.C. 20375-5000

Dr. Harold H. Singerman (1)
 David Taylor Research Center
 Code 283
 Annapolis, MD 21402-5067

Defense Technical Information Center (2)
 Building 5, Cameron Station
 Alexandria, VA 22314

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist	and/or Special
A-1	

