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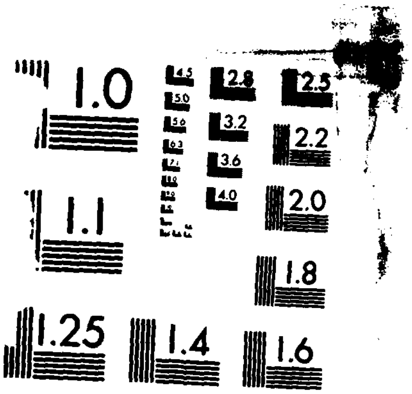
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THE INFLUENCE OF SUB TG ANNEALING ON THE PROPERTIES OF POLYMERS ABOVE AND BELOW TG.

FINAL REPORT

JOHN J. AKLONIS

DECEMBER 10, 1985

U.S. ARMY RESEARCH OFFICE

CONTRACT NUMBER DAAG 29-83-K--0034

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES, CA 90089

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Cont'd

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

We have constructed an instrument which can be used to measure the polarization of fluorescence of quenched polymer glasses at elevated temperatures.

Using this instrument we have investigated changes in fluorescence depolarization associated with thermal aging of several polymer glasses. Our results are much different than what has been observed earlier where the optical experiments were done at room temperature. We have concluded that, in the previous work, macro-

Cont

20. Abstract (continued)

scopic orientation of the samples was induced via the severe quenching conditions and that the unexpected extremes of time and temperature necessary to erase the influence of sub Tg annealing were, in fact, associated with relaxation of this macroscopic ordering.

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The document contains the DD Form 1473, the introduction, a drawing, and Appendix 3 starts at Page 54. The document is complete.
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Introduction.

One of the fundamental tenets of all kinetic treatments of the glass transitions is that changes in viscosity occur as glasses age or anneal below the glass transition temperature even under isothermal conditions. To explain these experimental results it is necessary to assume that these changes are large, i.e., orders of magnitude under ordinarily employed experimental conditions. However, since the viscosity of glasses is always so high, (these materials are solids) even such large changes in the viscosity can go undetected.

To probe these predicted large viscosity variations, we investigated changes in the effective local or micro viscosity of polymeric glasses doped with fluorescent dye molecules at very low concentrations. We reasoned that changes in viscosity of the glass will influence the local environment of the dye molecules and will be reflected as changes in rotational relaxation times or tumbling rates of the dye. These can be measured by monitoring the polarization of fluorescence emission of the dye molecules.

Our previous results can be explained with reference to figure 1, a schematic plot of volume versus temperature for a glass forming system. The solid line represents equilibrium liquid behavior. It is well known that if a polymer is rapidly cooled from above its glass transition temperature to below the glass transition temperature, the volume realized is above the equilibrium volume as shown by the dashed line. If the sample is allowed to age at the temperature T_1 below Tg, volume will contract on a timescale which depends in a sensitive way on the quenching conditions and on the exact temperature T_1. In the past, we argued that the microviscosity of glass systems should change substantially, i.e., by orders of magnitude, during this volume adjustment period. In order to monitor this viscosity change, we measured fluorescence depolarization and observed the predicted effect. In carrying out these previous experiments, we were forced to subject our samples to yet another quench. Since our fluorescence depolarization measurements were actually carried out at room temprature, our experimental techniques involved an initial quench from above Tg to room temperature, carrying out fluorescence depolarization measurements at room temperature, then warming the sample back to a temperature near the glass transition temperature where the annealing timescale was shortened, cooling the sample to room temperature to measure any changes in fluorescent depolarization behavior, etc. Our material was polystyrene with a glass transition temperature of 100°C, and the quenches from 130 or 140°C to room temperature were rather drastic.

In our initial experiments, what was most fascinating was our observation that the effects of annealing at temperatures below Tg caused measurable changes in the behavior of the polymer glass as measured by fluorescent depolarization at temperatures well above Tg! We found that even at temperatures 30° degrees above Tg and higher, equilibrium was not established on the minute or second timescale expected but rather dragged out on the ourageously long timescale of hours or tens of hours at the various high temperatures. This result was entirely unexpected and led us to propose a more careful experiment. The proposal was funded by the ARO.

Experimental Results.

In carrying out these experiments, we had always been suspicious of the necessity to subject the sample to such an extreme temperature jump. Thus, the very first step in our funded research involved building an experimental chamber in which fluorescent depolarization measurement of glasses could be carried out at elevated temperatures. For polystrene, this meant that a sample equilibrated at perhaps 130°C could be quenched to 95°C a much more modest experiment. The sample was then kept at 95°C and changes in fluorescence depolarization monitored as a function of time. The expected changes in microviscosity were not observed in these experiments. At this point, we changed our experimental technique such that the sample was subjected to temperature changes, both heating and cooling, at slow and reasonably constant rate. The results of these experiments are given in the attached appendix.

The results of our initial experiments and the experiments reported herein are very different. It is our opinion that the initial results arose because of the extremes of the quenching conditions involved in the experiments. Under these conditions, it is to be expected that macroscopic orientation of the sample associated with thermally induced stresses would result. This orientation would cause long range molecular order. It is well known that such long range molecular order, which can be induced by a variety of methods, for high molecular weight materials will only relax on a very long time scale at temperatures well above the glass transition temperature. We now believe that the relaxation we observed initially was of this thermally induced orientation. With the much more modest quenches used in the current experiment this phenomenon was not observed.

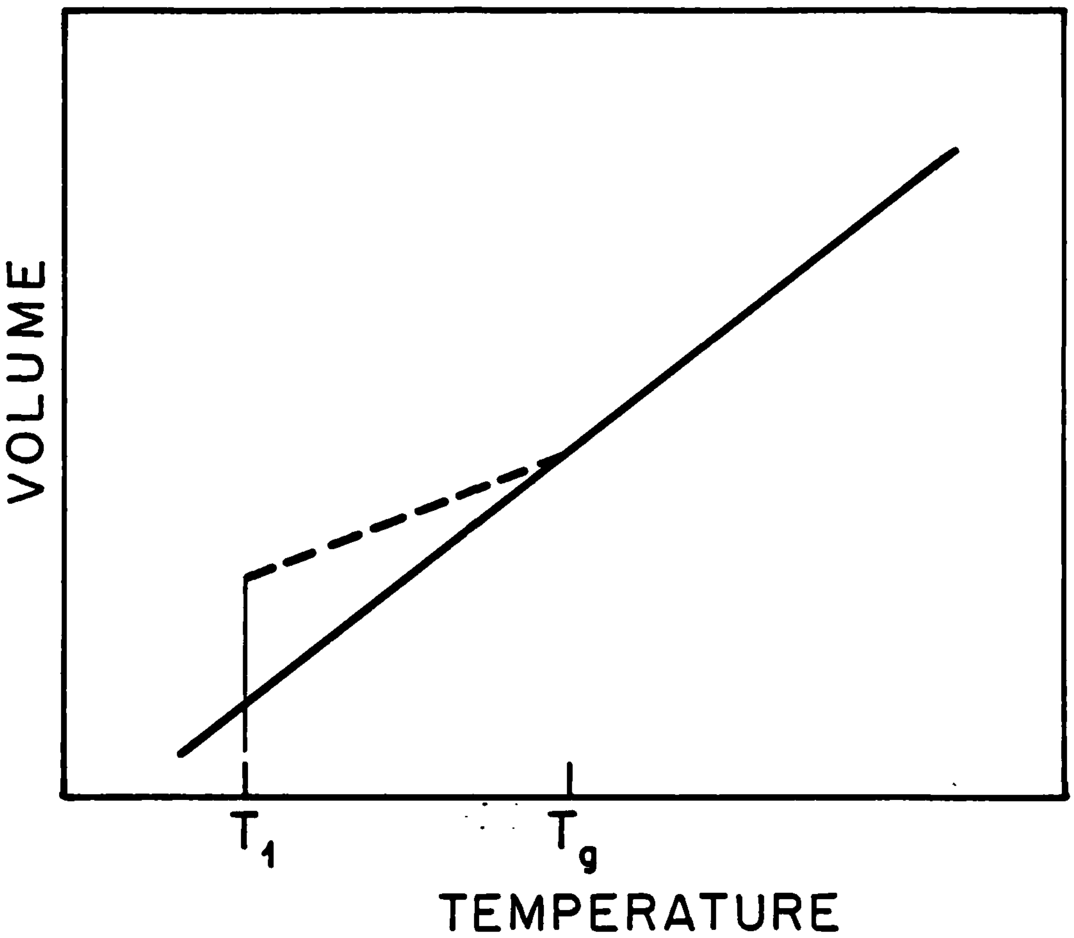
In order to further substantiate our contention that substantial order is induced in a polymeric sample under our type of quenching conditions, we fabricated 1/2 inch cubes of polystyrene and subjected them to the quench used initially. Under these conditions, a large bubble was often found to form at the geometric center of the cube. This bubble does not represent degassing or any similar phenomenon but it does arise from cohesive failure of the material under the strain field generated by quenching the polymeric material. The size of the bubble is easily rationalized in terms of known differences in coefficients of expansion of the liquid polymer and the glassy polymer. The orientation induced in the sample via this stress field will, in fact, only relax under high temperature and long term annealing. Short term excursions but a few degrees above the glass transition temperature will have little or no effect on relaxing the induced orientation.

Conclusion.

Our conclusion is that the strange effects observed in our previous work were associated with orientation and locked in stresses induced in our sample through rapid quenching. The behavior was not reproduced when more moderate thermal quenching schemes were employed. From a practical point of view, these severe quenches may, in fact, be of significance in modifying or controlling behavior of small molecules in glasses. However from the purely scientific point of view, we have little to gain in furthering our exploration in this area.

It should be noted, however, that many others are using similar rapid quenching procedures on macroscopic samples when invesigating the aging of polymers. At this point, we wonder if such quenches are not complicating the behavior which is actually observed.

The experimental work associated with this project was carried out by Dr. Huey-Ling Ding and resulted in a dissertation. I have affixed the final two chapters of her dissertation to this final report. In these chapters one can find a summary of her experimental results as well as her conclusions concerning the results of the experiments she carried out.


VOLUME
T_1
T_g
TEMPERATURE

Appendix

Variations of Microviscosity with Temperature in Polymers as measured by Fluorescence Depolarization

Chapters 3 and 4

Dissertation of Dr. H. L. Ding
University of Southern California
Los Angeles, CA
1985

CHAPTER 3

EXPERIMENTS AND RESULTS

§3.1 Sample Preparation

The polymers employed in this research are polystyrene and polymethyl methacrylate which are polymerized from their monomers. For the convenience of experiments, the monomers chosen must be easily polymerized, be transparent in the visible and near U.V. region in the spectrum and the glass temperatures of these polymers must be high enough so that experiment can be done at or above room temperature.

Methyl methacrylate is purchased from J. T. Baker Chemical Company, Phillipsburg, New Jersey; -- Baker grade stabilized with tert-butylpyrocatechol. Styrene is from Alfa products, Danvers, Massachusettes. In order to get rid of impurities and stabilizer before polymerization, both styrene and methyl methacrylate are purified by the following procedures. They are washed with equal volume of 10% NaOH solution. Then, the heavier aqueous phase is discarded. The monomer layer is repeatedly washed with NaOH solution until it appears to be clear. Then, the washed monomer is then repeatedly neutralized by deionized water until the pink litmus paper does not turn purple. The neutralized monomer is dried by adding 100 g/l of anhydrous Na_2SO_4 and then allowed to stand for 30 minutes.

With the fluorescence depolarization measurements, a great caution should be taken in the preparation of samples. The polymeric glass employed must have smooth and shiny surfaces to minimize the scattering of incient light. Therefore, a pyrex window is sealed with a 7mm diameter glass tube to make a good surface ampoule. The monomers are degassed and then vacuum distilled into the ampoule which contains one granule (about 10^{-4}g) of benzoyl peroxide as initiator and about 10^{-5}wt% of dye.

The selection of dye molecules for this experiment is also important. The dye must not react either with the monomers or polymers, and it must fluoresce and absorb in a range accessible to our apparatus. The overlapping between the absorption and emission spectrum must be minimized so that internal energy transfer will be limited, also, the absorption band of the guest (dye) molecules should be far away enough from the absorption band of the host (polymer) molecules to prevent energy transfer. The amount of dye incorporated within the sample is also minimized to the limit that the investigation can be easily performed and the energy transfer between dye molecules does not occur. The dyes employed for this research are anthracene, perylene, 9-vinylanthracene and 9,10 - diphenylanthracene, which are purchased from Aldrich Chemical Company, Milwaukee, Wisconsin.

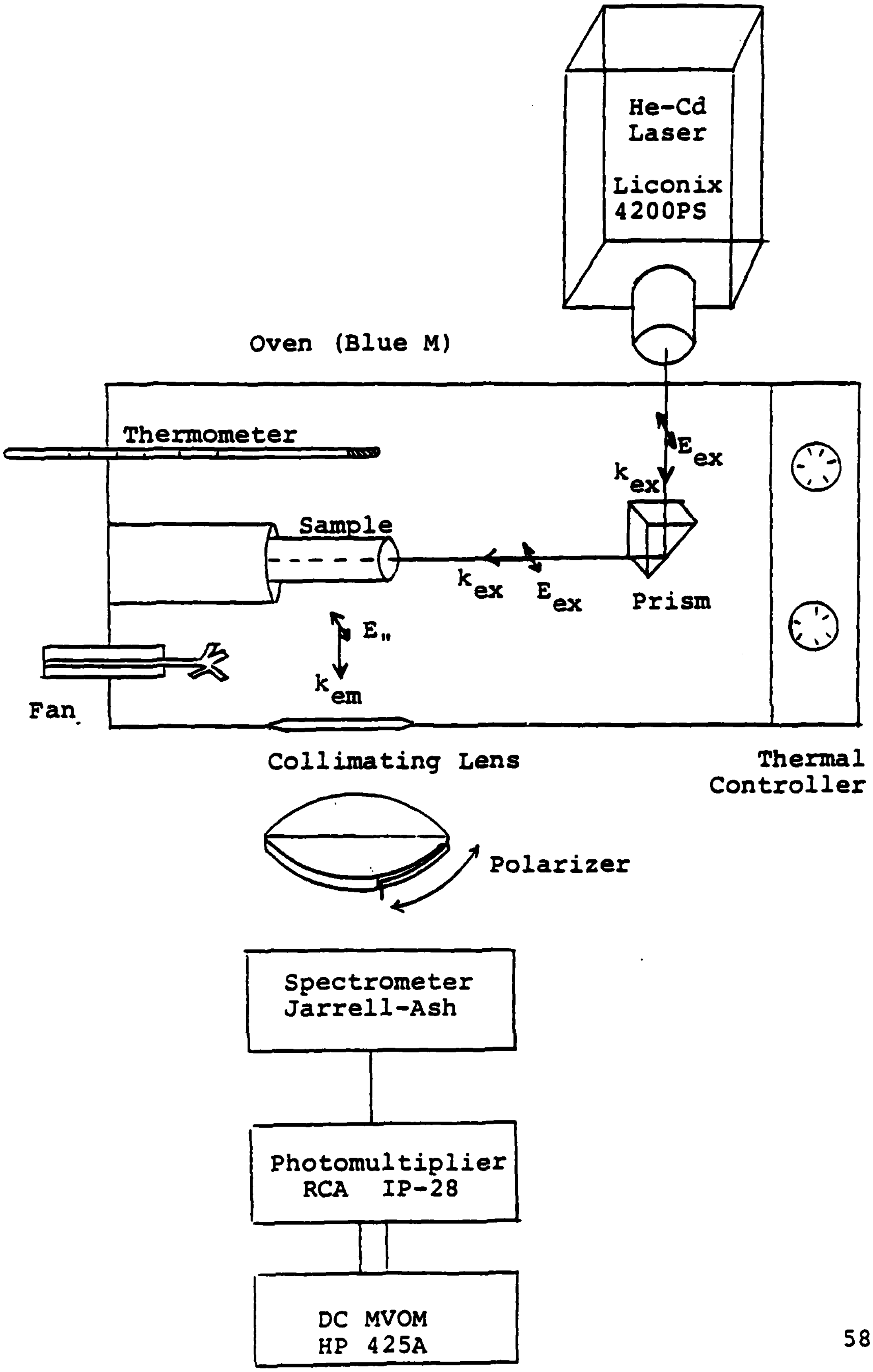
The ampoule which contains initiator, dye, and distilled monomer is then sealed under vacuum and heated in an oven with initial temperature 70°C for one day. Then, the oven temperature is increased to 120°C for several days to complete polymerization. After cooling, a clear shiny cylindrical sample about 2cm long, 7mm in diameter is then obtained within the pyrex glass.

One of the samples contained 15% Dioctyl Phthalate, DOP, which acted as plasticizer to depress T_g, and was purchased from Aldrich Chemical Company. The DOP is pipetted into the ampoule containing degassed monomer and dye.

§3.2 Fluorescence Depolarization Measurements

The apparatus used is shown in figure 15. The exciting light source is a Liconix 4210NB/UV Helium Cadmium Laser with removable, adjustable mirrors for easy conversion from blue (441.6 nm) to ultra violet (325 nm). The power supply for this Laser is Liconix 4200PS. The polarized exciting beam passes through a right angle

Figure 15 Experimental Apparutus


He-Cd
Laser
Liconix
4200PS
Oven (Blue M)
Thermometer
E_{ex}
k_{ex}
Sample
k_{ex}
E_{ex}
Prism
$E_{\parallel}$
k_{em}
Fan
Collimating Lens
Thermal
Controller
Polarizer
Spectrometer
Jarrell-Ash
Photomultiplier
RCA IP-28
DC MVOM
HP 425A

prism and focuses on the center bottom of the cylindrical sample. The stability of laser power is measured by a power meter (RK5100) from Laser Precision Corp. The polymeric sample is thermally controlled by a Blue M heating oven. The emitted light is collimated into a rotatable polarizer, which is placed at such a position that $I_{\parallel}$ detected is parallel to the electric vector of the incident polarized beam and $I_{\perp}$ is perpendicular to it.

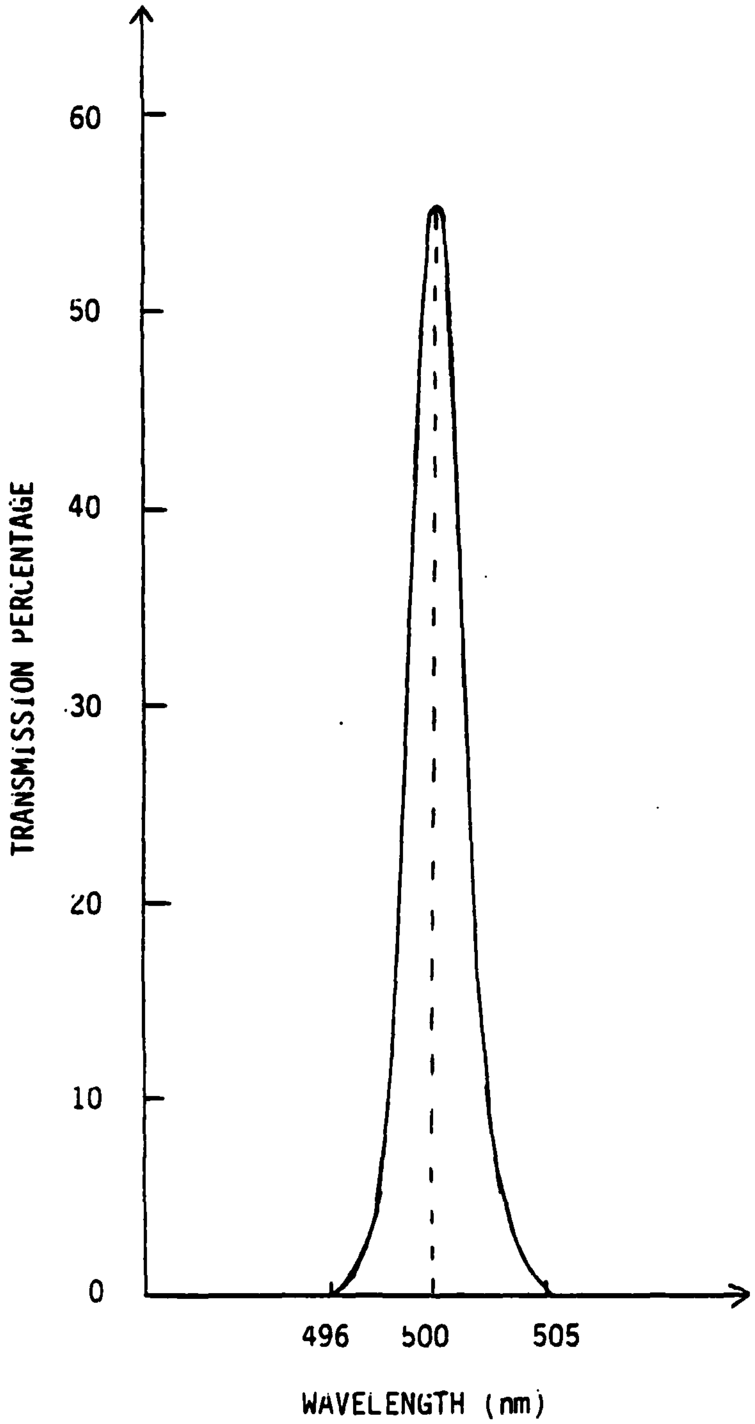
The emission spectrum is taken by a Jarrel-Ash 82-410 spectrometer, and then amplified by a RCA 1P28 photomultiplier. The output of the photomultiplier is read on an HP425A DC microvoltmeter (by Hewlett Packard). Reflection gratings are employed in spectrometers. Since gratings have various preferences for certain polarization directions of linearly polarized light such spectrometers are unsuitable for fluorescence depolarization measurement. In order to measure accurate polarizations, the spectrometer is replaced by a narrow band interference filter which transmits only a narrow spectral band around a given center wavelength. This center wavelength is chosen at maximum peak of the emission spectrum of the fluorescent dye. A typical transmission curve for the narrow band interference filter with peak wavelength 500nm (Model No. 5434, Oriel

Corporation, Stanford, Connecticut) is shown in figure 16.

§3.3 Thermal Treatment

In the early stages of our experiment, we did not have facilities to do the fluorescence depolarization measurement at elevated temperature. We annealed the polymeric sample in an oil bath for various times and quenched it to room temperature, and then did the measurement by assuming that the viscosity ratio for different annealing times at the T_{anneal} is the same as the ratio measured at room temperature. However, there are several shortcomings of this treatment; (i) the quenching rate is difficult to control; (ii) quick quenching enhanced formation of microbubbles within the polymeric sample and the bubbles scattered light complicates the measurements; (iii) the temperature of the inside and outside of the sample would vary greatly during quick quenching and this temperature gradient might induce birefringence within the sample. In this case, the probe would be partly oriented (in the birefringence region) and partly unoriented (in the amorphous region), and this could mislead the results. Thus an oven is designed for the purpose of thermal control.

Figure 16 Typical Transmission Curve for Narrow Band Interference Filter with Transmission Wavelength 500nm



TRANSMISSION PERCENTAGE
60
50
40
30
20
10
0
496
500
505
WAVELENGTH (nm)

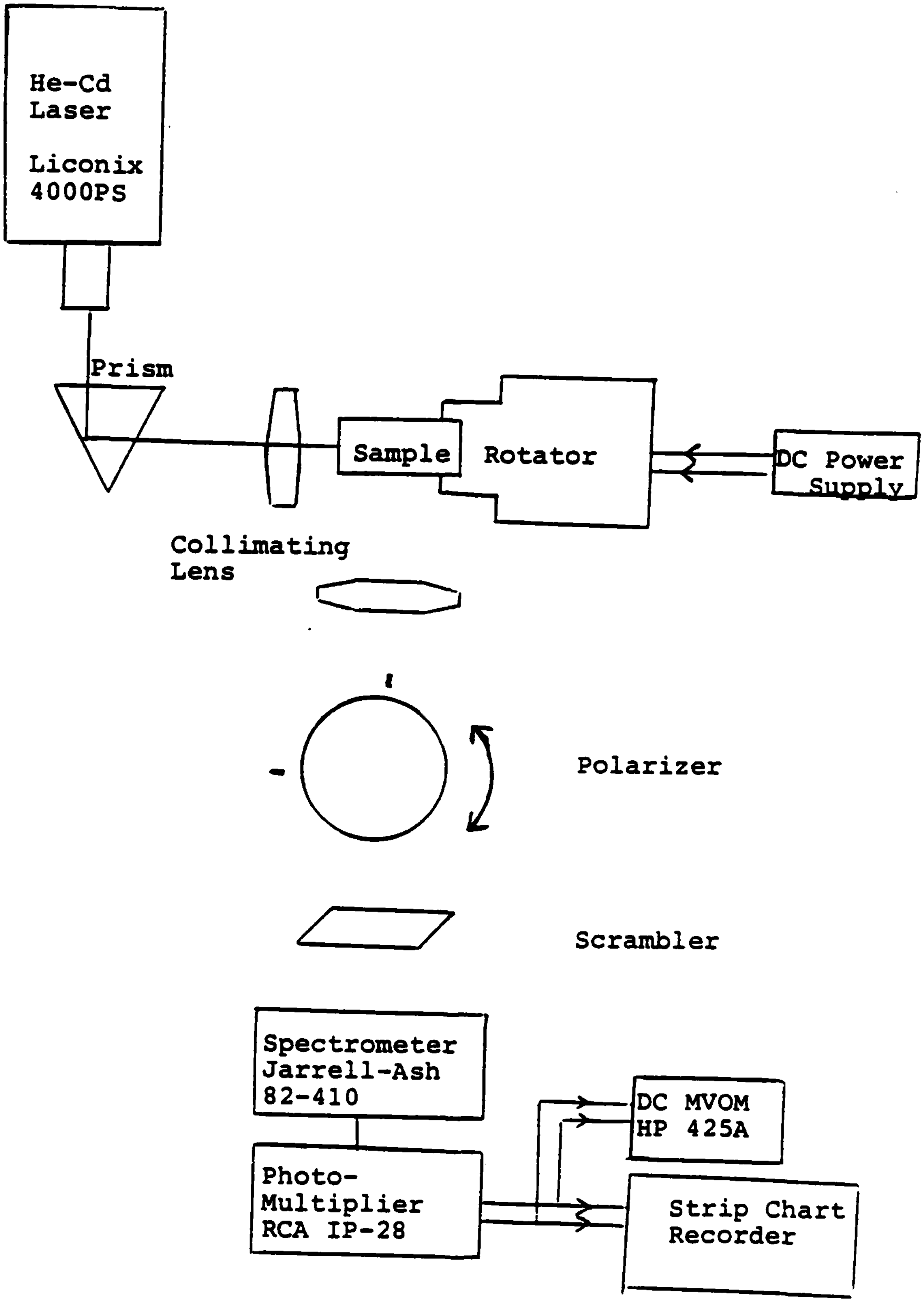
In this research we studied both the temperature dependence of the viscosity and the isothermal viscosity variation of the dye molecules dispersed in the polymer matrix. To measure the temperature dependence of the viscosity, the thermal treatment is conducted as following: the sample is heated to a temperature, T_h, above T_g for a certain time, t_h, to erase thermal history, and then cooled down at about 1.5°/min in air, during which time the polarization measurements are taken. Similar treatments are made with varying T_h and t_h. For the isothermal viscosity variation, the sample is air quenched from T_h, which is above T_g, to T_{gl}, which is close to and lower than T_g where relaxation toward equilibrium is expected to occur. The measurements are then taken while annealing.

§3.4 Previous Work

The studies of isothermal viscosity variation in polymers as measured by fluorescence depolarization have previously been done by Been-Jon King Wood in this lab. [43] The experimental setup for her measurement is shown in figure 17. I had redone the measurement with the same apparatus and found out that there were several drawbacks with this setup which will lead to an incorrect result:

(1) The exciting beam is vertically polarized. After

Figure 17 Experimental Setup by B. J. King Wood


He-Cd
Laser
Liconix
4000PS
Prism
Sample
Rotator
DC Power Supply
Collimating Lens
Polarizer
Scrambler
Spectrometer
Jarrell-Ash
82-410
Photo-
Multiplier
RCA IP-28
DC MVOM
HP 425A
Strip Chart
Recorder

reflected by the prism, the electric vector of the exciting beam is perpendicular to the plane of rotatable polarizer, and the measured $I_\parallel$ should be equal to $I_\perp$, i.e. P=0, irrespective of the local viscosity of the medium. (2) The differential grating in the spectrometer does have various preference for different direction of light. For the above case, i.e. $I_\parallel=I_\perp$, as measured by this Jellel-Ash 82-410 spectrometer $I_\parallel$ is five times stronger than $I_\perp$. (3) Been-Jon had tried to depolarize the emission light by combining usage of scrambler and spectrometer. As I had mentioned before, she had arranged the incoming beam in an incorrect direction that the measured $I_\parallel$ and $I_\perp$ should be the same. However, as we measure this emission by the scrambler and spectrometer, $I_\parallel$ is still 1.5 times as strong as $I_\perp$, i.e. P=0.20 for measuring a non-polarized light.

I have done the following corrections in order to measure fluorescence depolarization accurately: (1) The scrambler and spectrometer are replaced by an interference filter with a wavelength corresponding to the emission band of dye molecule. And then, I measured the degree of polarization with the same orientation of exciting beam as described above, i.e. vertically polarized light emitted from laser. The measured polarization P=0 which means $I_\parallel=I_\perp$. We are then sure that the interference filter is much more appropriate for this measurement. (2) The laser is then rotated 90° so that the electric vector of exciting beam is horizontally polarized. As reflected by prism, the exciting beam entering the sample is polarized in a direction parallel to the plane of polarizer. And the measured polarization for a polymer solid interior with 9,10-DPA as dye at room temperature is about 0.21.

<3.5 Results

The emission spectra of molecules in the glassy matrixes were taken and compared with the spectra in the Fluorescence Handbook [11], as shown in figure 1 to 4. For convenience of measurements, the emission spectra were taken by a setup similar to figure 15, except that the exciting beam is emitted from a nitrogen laser with exciting wavelength 337nm, and a strip chart recorder is connected to the output of photomultiplier. The emission spectra are not affected by the different exciting frequency for anthracene, 9-VA and 9,10-DPA. However, perylene absorbs at wavelength longer than 330 nm (30300 cm^{-1}), it has a low molar extinction coefficient as excited by He-Cd laser with an exciting beam 325 nm. The fluorescence spectra of anthracene, perylene, 9-VA, and 9,10-DPA respectively dispersed in polystyrene with concentration of 10^{-5} wt% are shown in figure 18 to 21. And, 10^{-3} wt% of 9-VA in PS is shown in figure 22, for this higher concentration of 9-VA in polymers, an excimer emission is seen; which shows a structureless band at longer wavelength. And the emission spectrum of pure polystyrene without dye as excited by 337nm UV light is also shown in figure 23. Apparently, the emission band of polystyrene is partially overlapped by the emission bands of these fluorescent dyes and this might interfere with the polarization measurement. Thus, polymethyl methacrylate, with no absorption in UV region, is a better polymeric matrix for this study. The emission spectra of 10^{-5} wt% of perylene, 9,10-DPA and 9-VA respectively dispersed in PMMA glass are shown in figure 24 to 26. 9-VA appeared to be a free probe dispersed in PS or PMMA, this is proved by the gel permeation chromatography measurement; a strong absorption of 370nm UV light at low molecular weight region (about 10^2 g/mole) is observed by UV detector. Anthracene has a very low fluorescence quantum yield. And, perylene absorbs very slightly in the region of 325nm as excited by Helium-Cadmium laser. 9,10-DPA appears to be the most applicable probe here among these dyes we have chosen.

As explained before, for polarization measurements, grating spectrometers are not suitable so that we

Figure 18 Fluorescence Spectrum of 10^{-5} wt% of Anthracene Dispersed Polystyrene Excited by 337nm UV Light

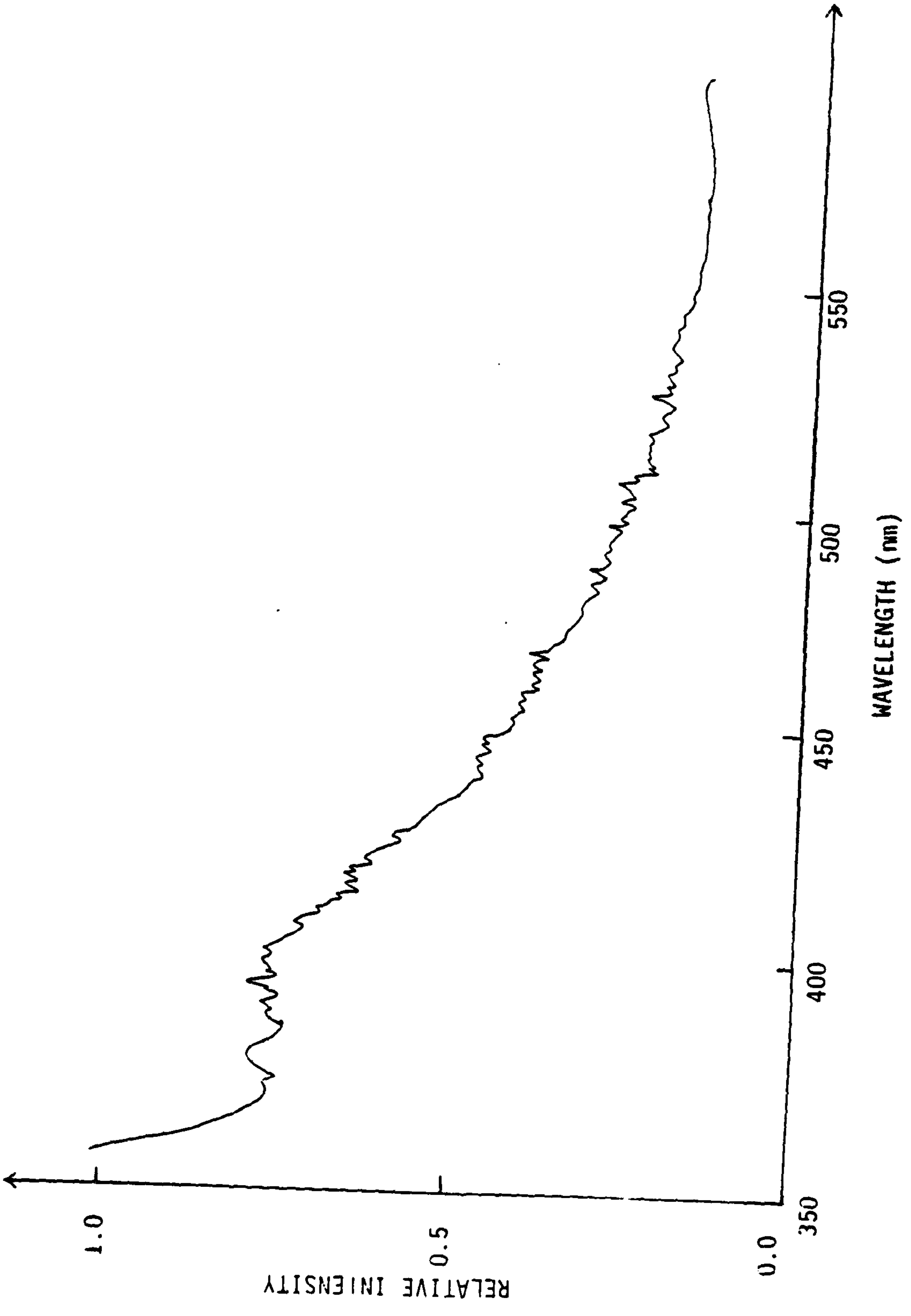

RELATIVE INTENSITY
1.0
0.5
0.0
350
400
450
500
550
WAVELENGTH (nm)

Figure 19 Fluorescence Spectrum of 10^{-5} wt% of Perylene Dispersed in Polystyrene as Excited by 337nm UV Light

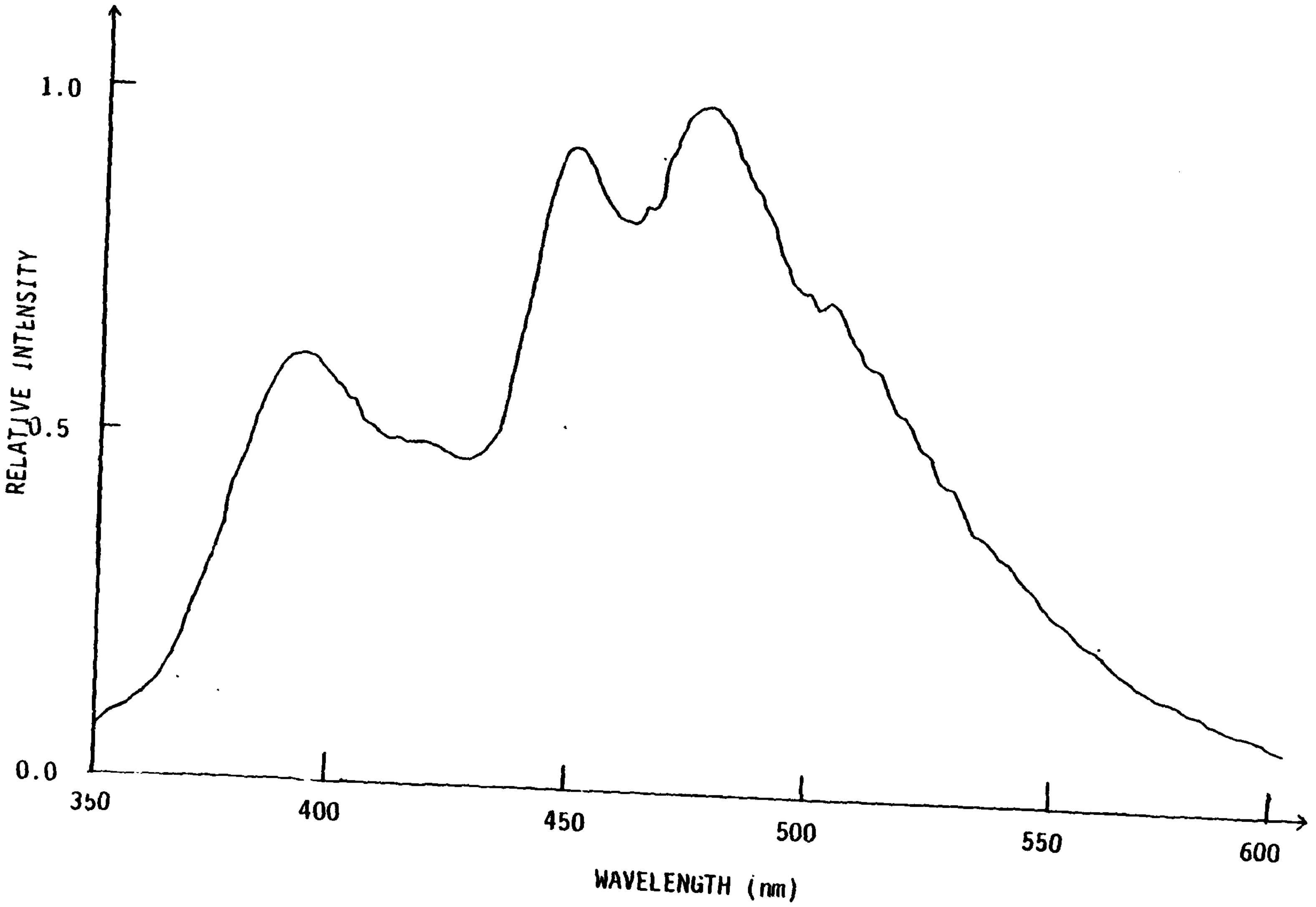

RELATIVE INTENSITY
1.0
0.5
0.0
350
400
450
500
550
600
WAVELENGTH (nm)

Figure 20 Fluorescence Spectrum of 10-5 wt% of 9,10-Divinylanthracene Dispersed in Polystyrene as Excited by 337nm UV Light

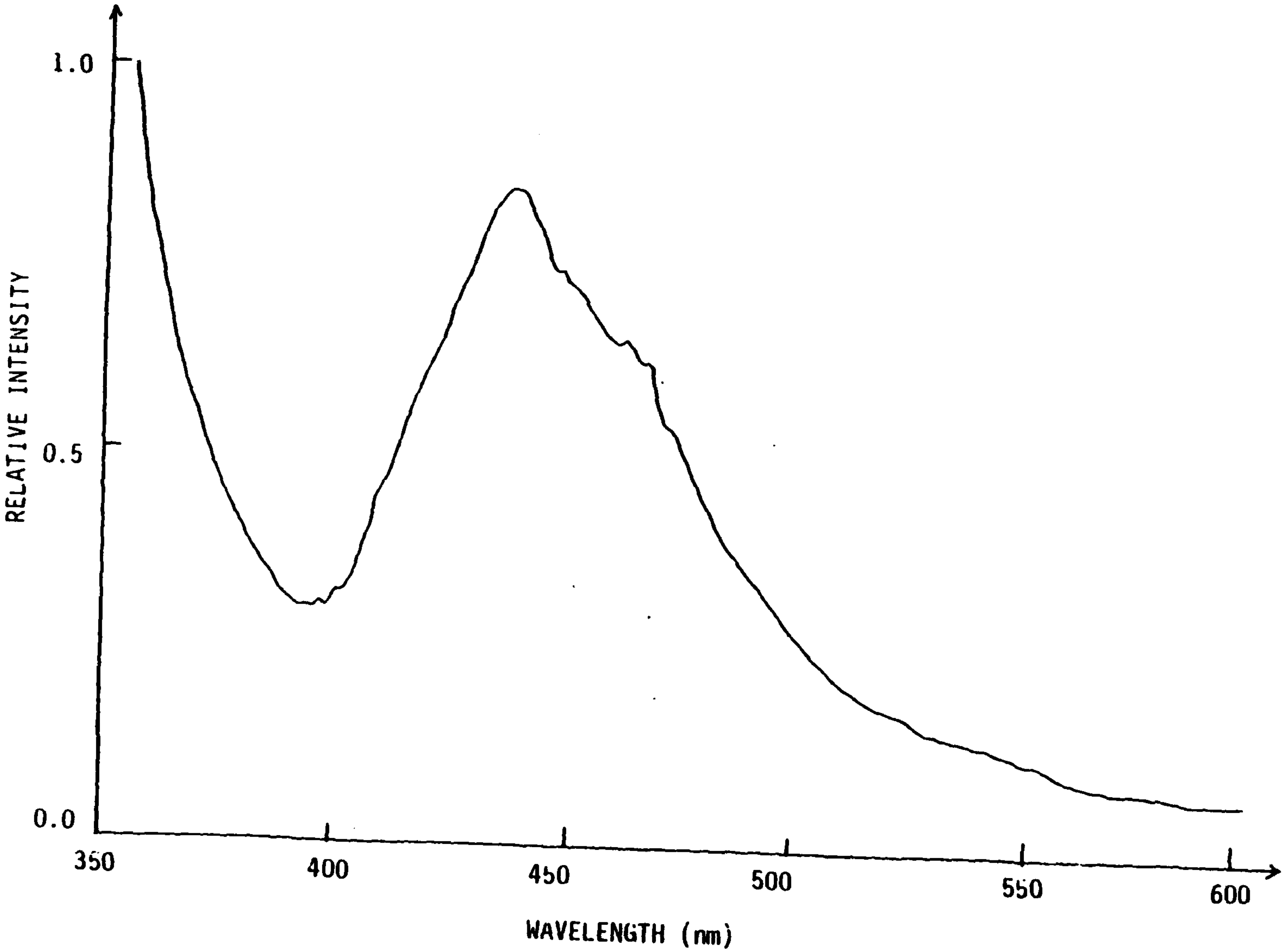

RELATIVE INTENSITY
1.0
0.5
0.0
350
400
450
500
550
600
WAVELENGTH (nm)

Figure 21 Fluorescence Spectrum of 10^{-5} wt% of 9-Vinylanthracene Dispersed in Polystyrene as Excited by 337nm UV Light

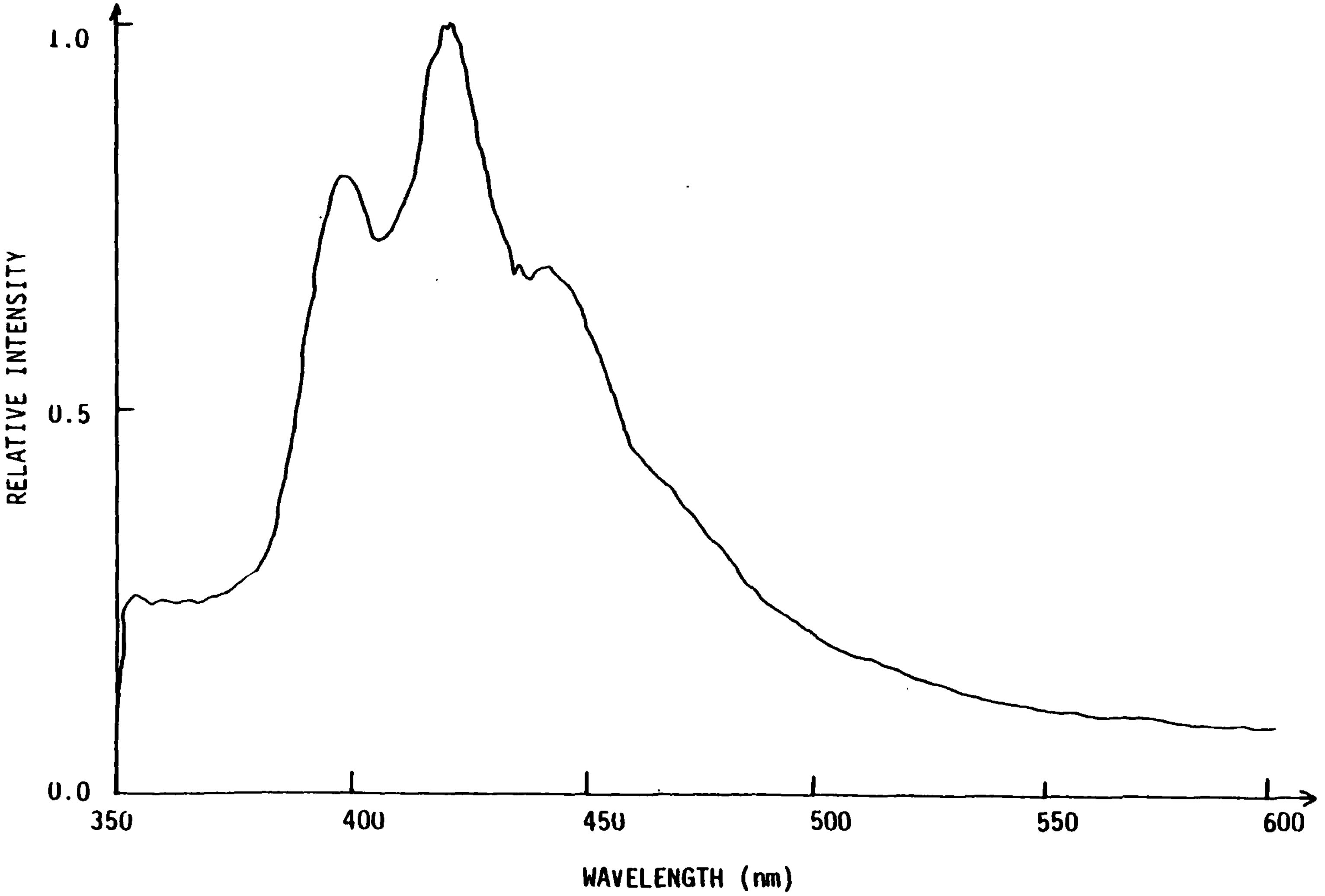

RELATIVE INTENSITY
1.0
0.5
0.0
350
400
450
500
550
600
WAVELENGTH (nm)

Figure 22 Fluorescence Spectrum of 10^{-3} wt% of 9-Vinylanthracene Dispersed in Polystyrene as Excited by 337nm UV Light

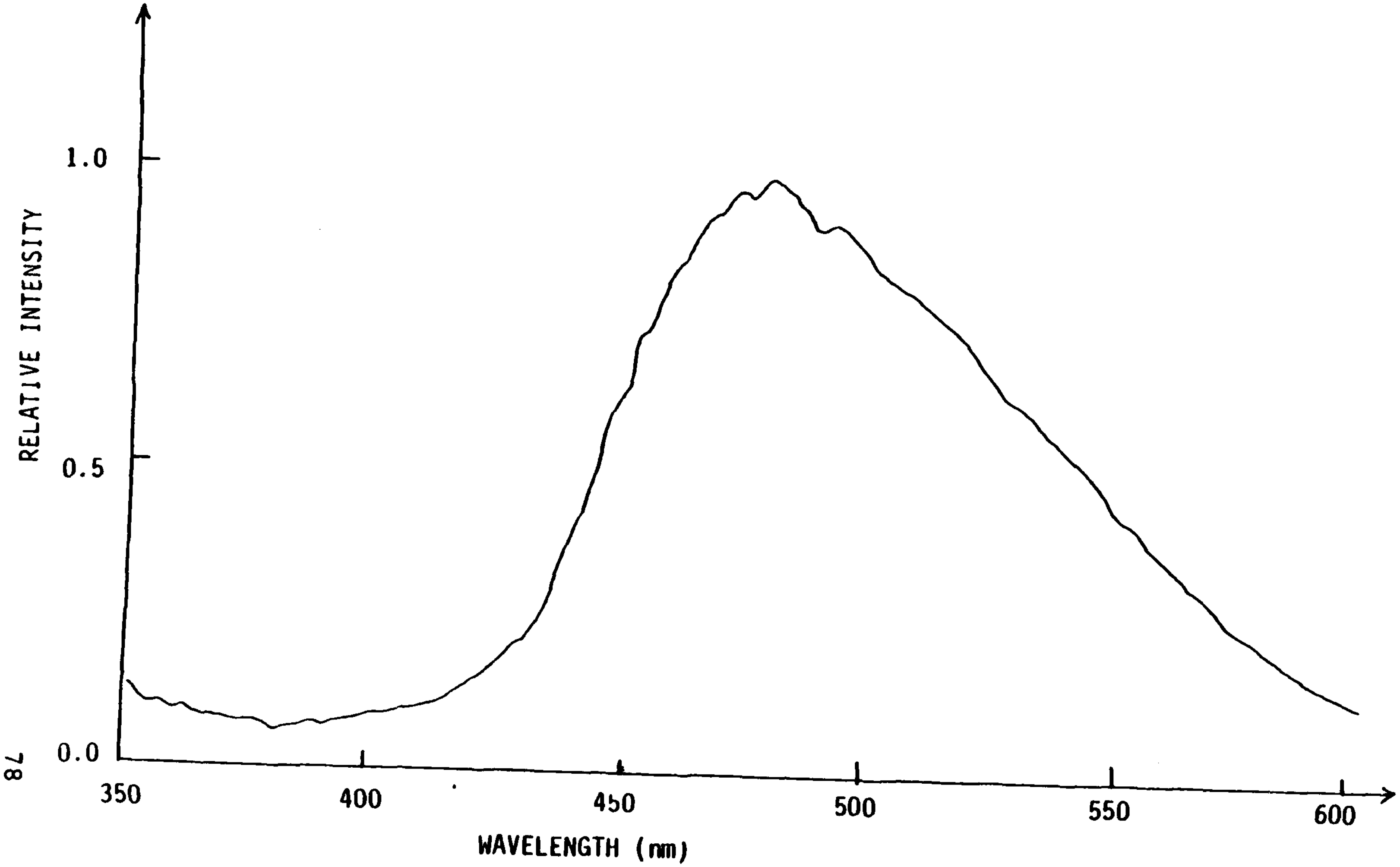

1.0
0.5
0.0
RELATIVE INTENSITY
350
400
450
500
550
600
WAVELENGTH (nm)

Figure 23 Fluorescence Spectrum of Pure Polystyrene as Excited by 337nm UV Light

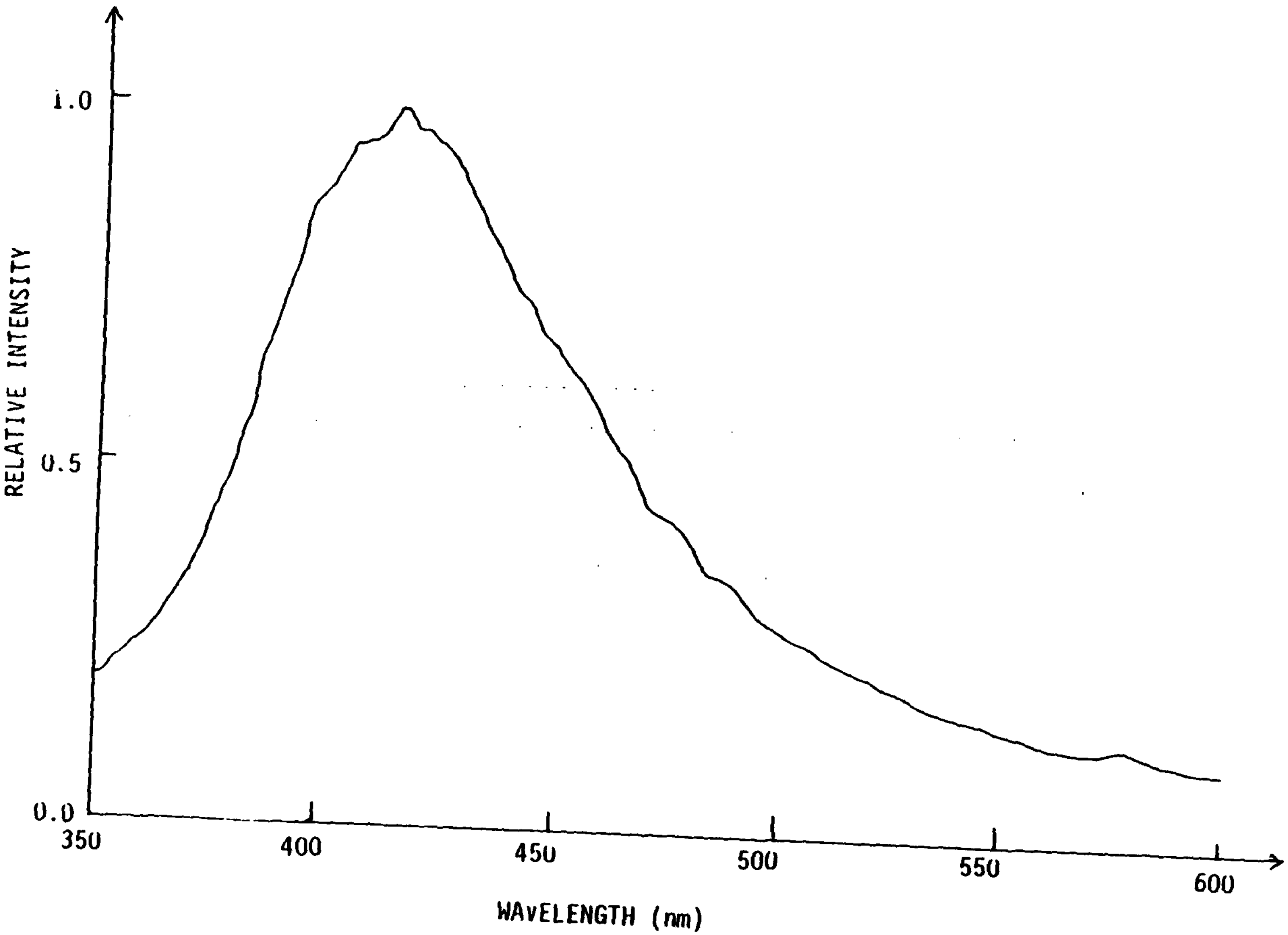

1.0
0.5
0.0
RELATIVE INTENSITY
350
400
450
500
550
600
WAVELENGTH (nm)

Figure 24 Fluorescence Spectrum of 10-5 wt% Perylene Dispersed in PMMA as Excited by 337nm UV Light

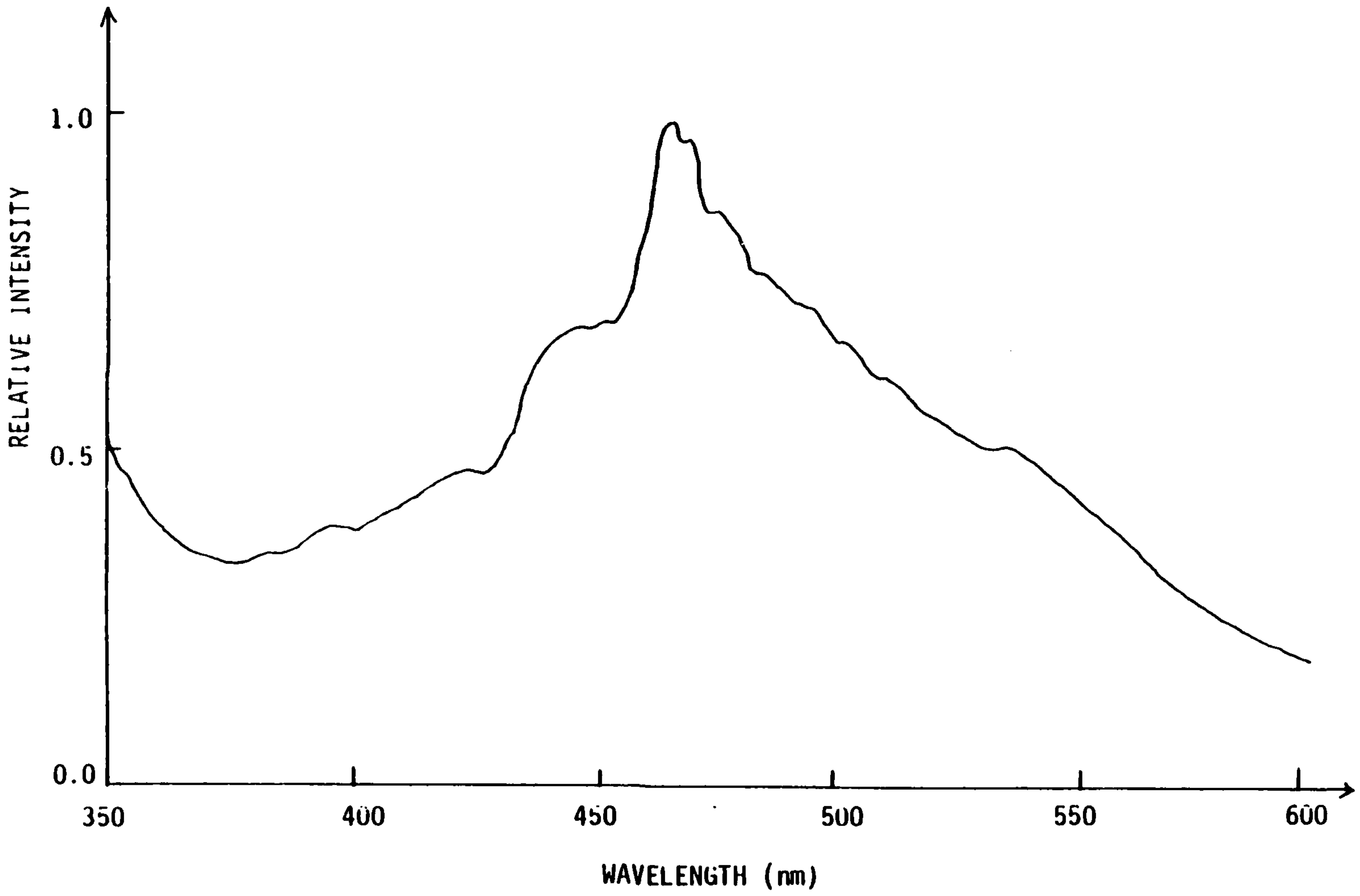

RELATIVE INTENSITY
1.0
0.5
0.0
350
400
450
500
550
600
WAVELENGTH (nm)

Figure 25 Fluorescence Spectrum of 10^{-5} wt% 9,10-Diphenylanthracene Dispersed in PMMA as Excited by 337nm UV Light

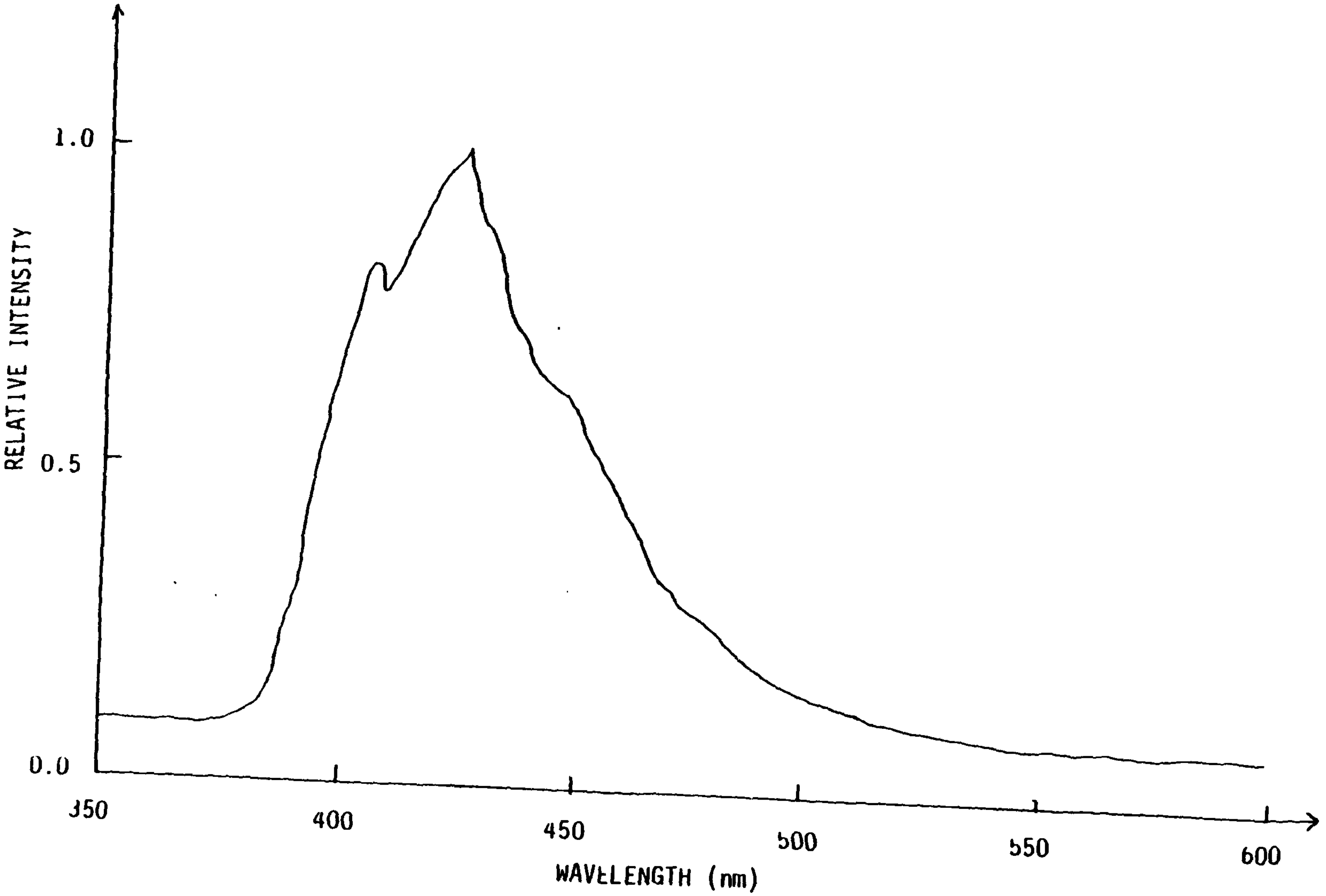
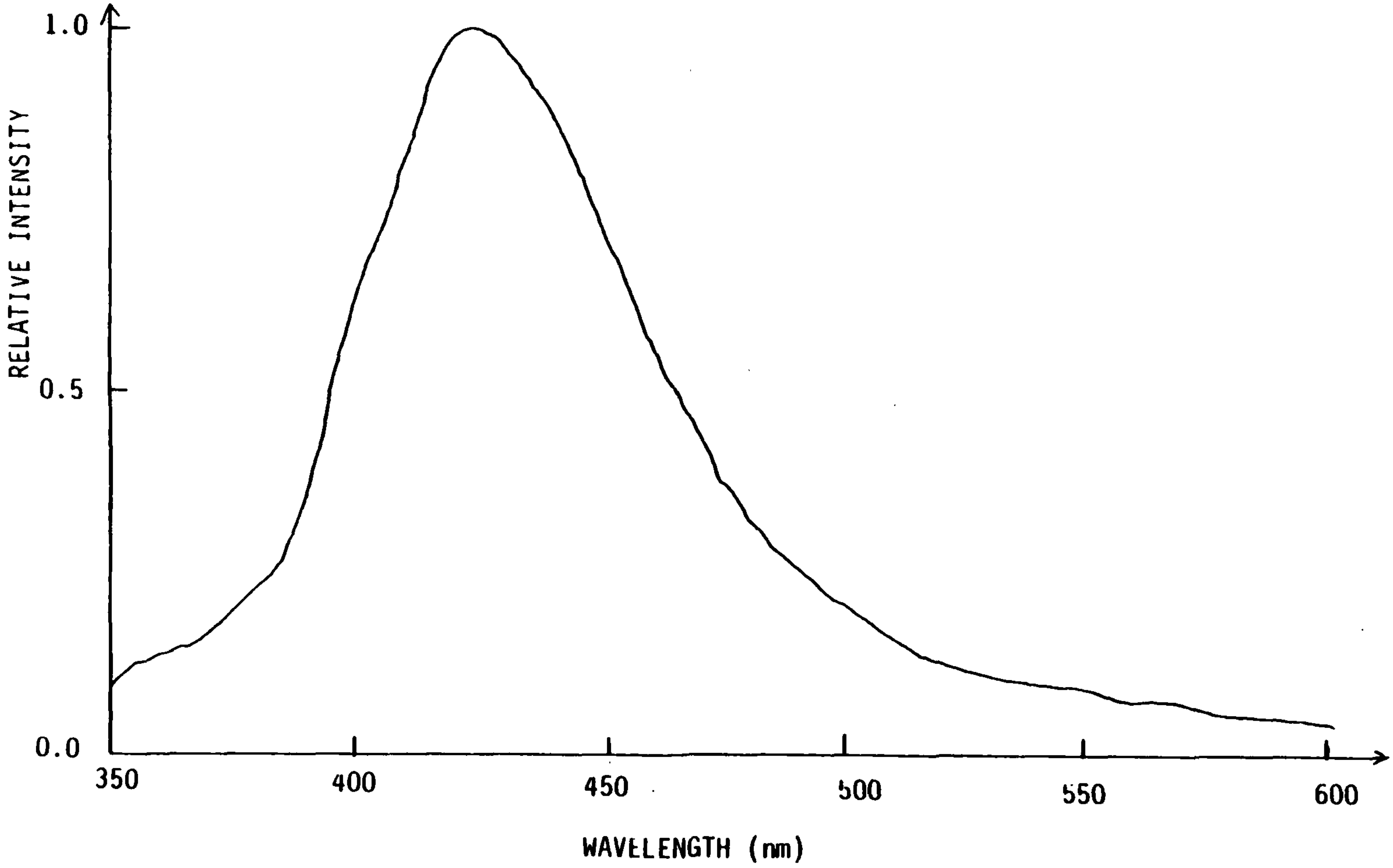

1.0
0.5
0.0
RELATIVE INTENSITY
350
400
450
500
550
600
WAVELENGTH (nm)

Figure 26 Fluorescence Spectrum of 10^{-5} wt% of 9-VA Dispersed in PMMA as Excited by 337nm UV Light


1.0
0.5
0.0
RELATIVE INTENSITY
350
400
450
500
550
600
WAVELENGTH (nm)

substitute a 440nm narrow band interference filter (Oriel Corp., Model No. 5430) for the Jarrell-Ash spectrometer to measure the degree of polarization of polymer containing 9,10-DPA. The transmission spectrum of this 440nm narrow band interference filter is shown in figure 27. The reason we pick 440nm to detect the emission is that at 440nm the intensity of the emission is the highest, thus, $I_\parallel$ and $I_\perp$ can be easily determined as strong signals.

The sample is annealed at temperature higher than T_g to erase previous thermal history. By trial-and-error, the annealing temperature is selected at 120°C for the first series of experiments. The PMMA sample is annealed at 120°C at first, for 40 minutes, and then cooled down at the rate of 1.5 degree per minute. The fluorescence depolarization is measured as a function of temperature, which is shown in figure 28. A transition is observable from these data.

Upon heating, the variation of polarization with temperature is shown in figure 29 with heating rate about 2.0°/min. The transition for heating occurs at 105°C which is much higher temperature than for cooling. Besides the intrinsic feature of glass which response asymmetrically upon heating and cooling, this might also be due to: (1) the difference between cooling and heating

Figure 27 Transmission Spectrum of 440nm Narrow Band Interference Filter

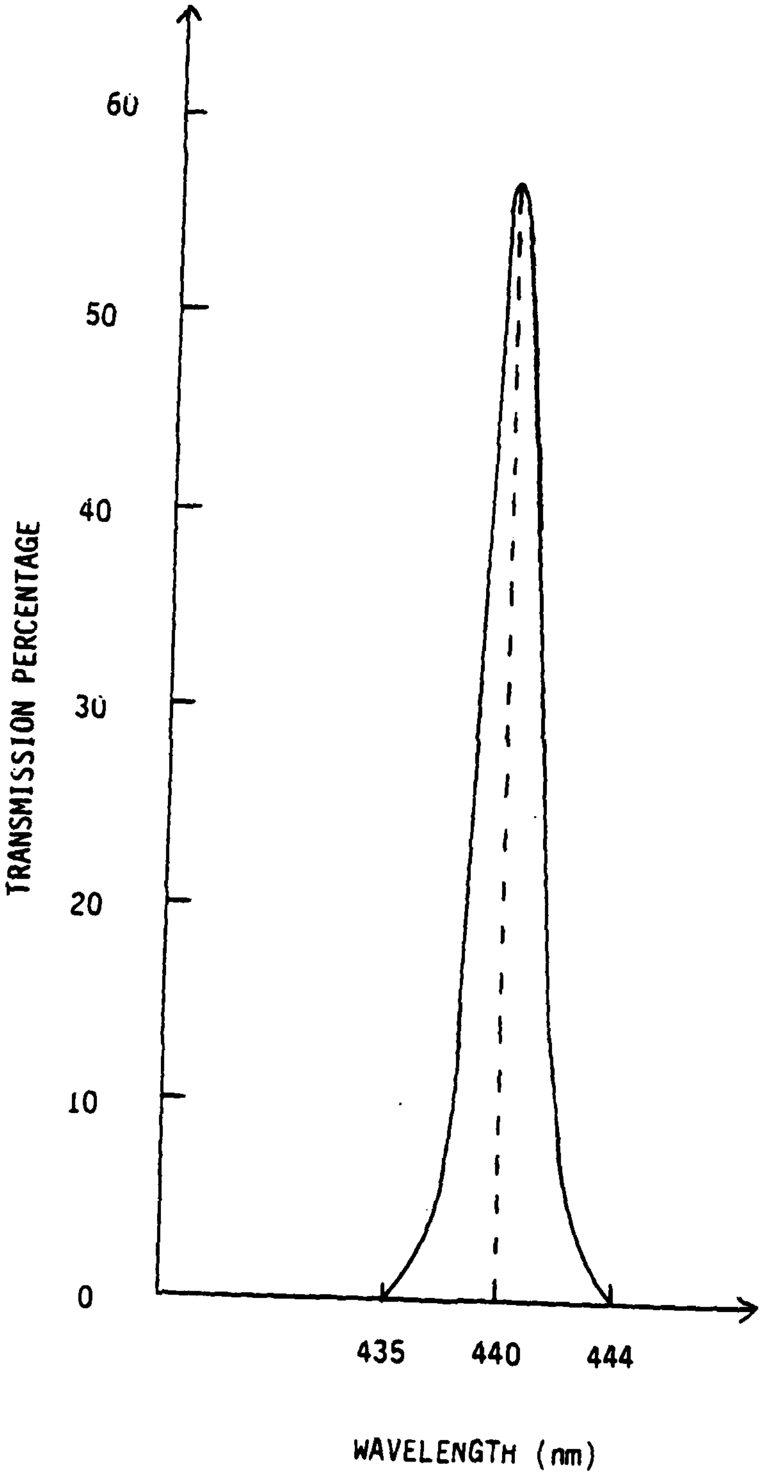
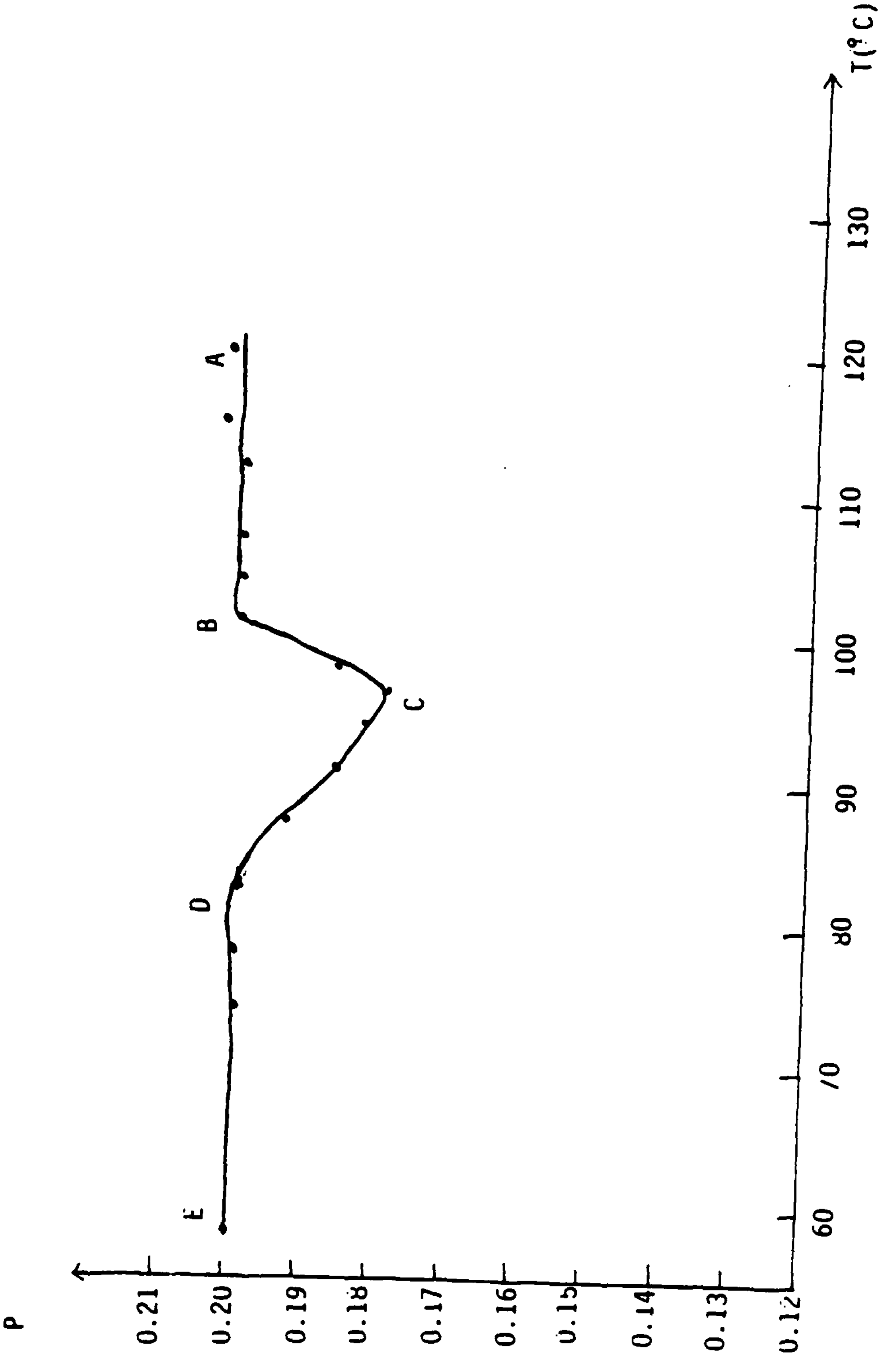
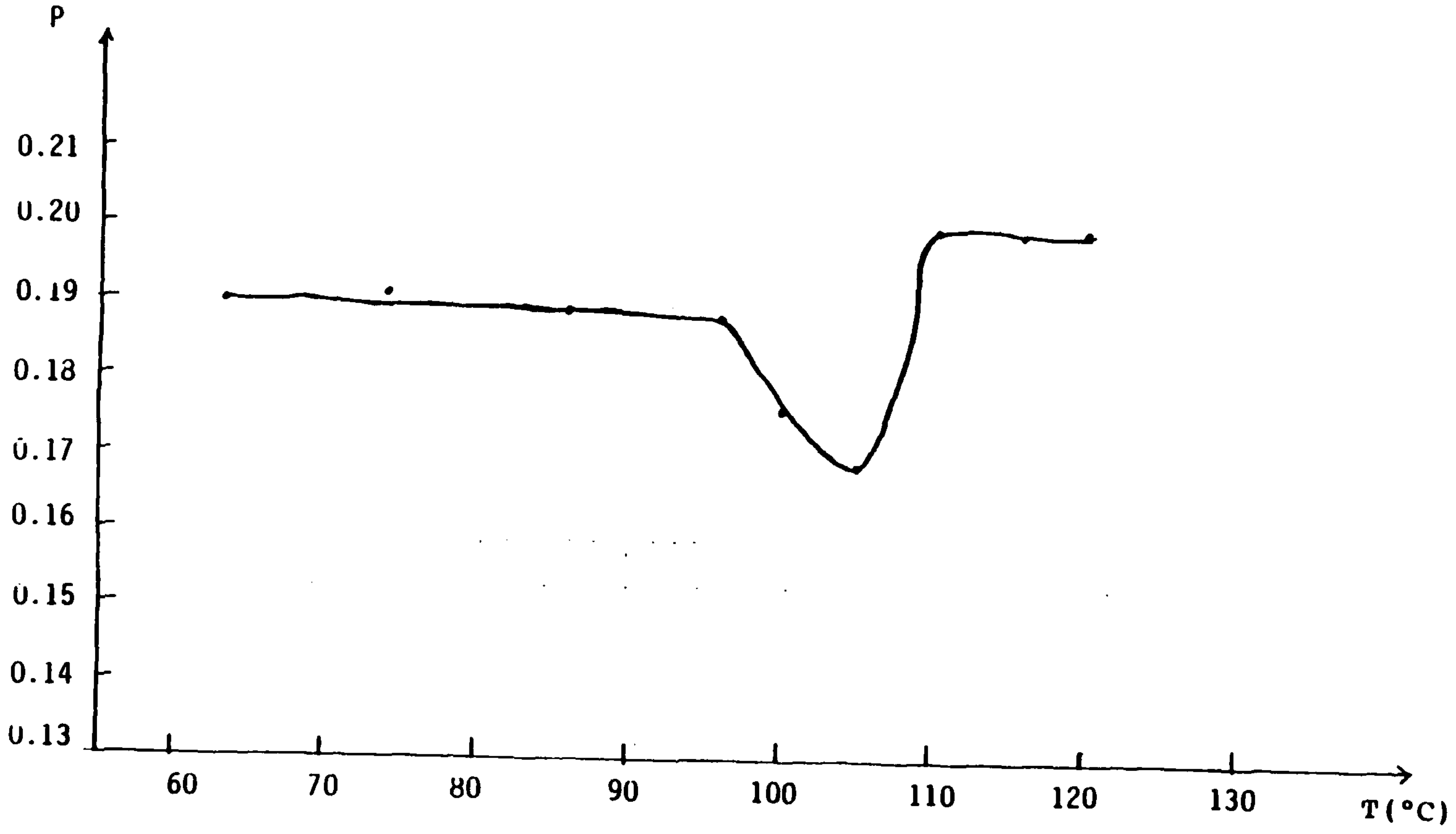

60
50
40
30
20
10
0
TRANSMISSION PERCENTAGE
435
440
444
WAVELENGTH (nm)

Figure 28 Polarization Versus Temperature for PMMA-9,10-DPA Sample which Had Been Annealed at 120°C for 40 Minutes



P
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
60
70
80
90
100
110
120
130
T(°C)
A
B
C
D
E

Figure 29 Polarization Versus Temperature for PMMA-9,10-DPA Sample Heated from Room Temperature to 120°C at the Rate of 2.0°/minute


P
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
60
70
80
90
100
110
120
130
T(°C)

rate, (2) the lag between the temperature of thermometer and of the sample. In order to make sure that the polarization changes at glass transition region, this PMMA sample is measured by Differential Scanning Calorimeter (Perkin-Elmer DSC-4 System). With 10°/min of heating and cooling rate, the result is shown in figure 30 and 31. Glass transitions are seen upon both heating and cooling, the temperature at which the middle of transition occurs is defined as T_g, which is, 108°C for the heating and 97°C for the cooling. The T_g's as measured by DSC are in good agreement with our fluorescence depolarization measurements if we define the temperature with lowest P in the transition region as T_g, i.e. 96°C in figure 28 and 105°C in figure 29. Apparently, the big difference of T_g's as measured upon heating and cooling is mostly due to the asymmetry feature of glass.

Since the experiment is carried out by the air cooling, the cooling rate of the sample is controlled by the temperature of surrounding air. Thus, the initial cooling rate at temperature above T_g is slightly higher than the cooling rate below T_g. The average rate of cooling around glass transition interval, i.e. between 110°C and 85°C in figure 28 is regarded as the cooling rate of the sample in this thesis. However, with our

Figure 30 DSC Measurement of PMMA Sample with Heating Rate 10°/minute

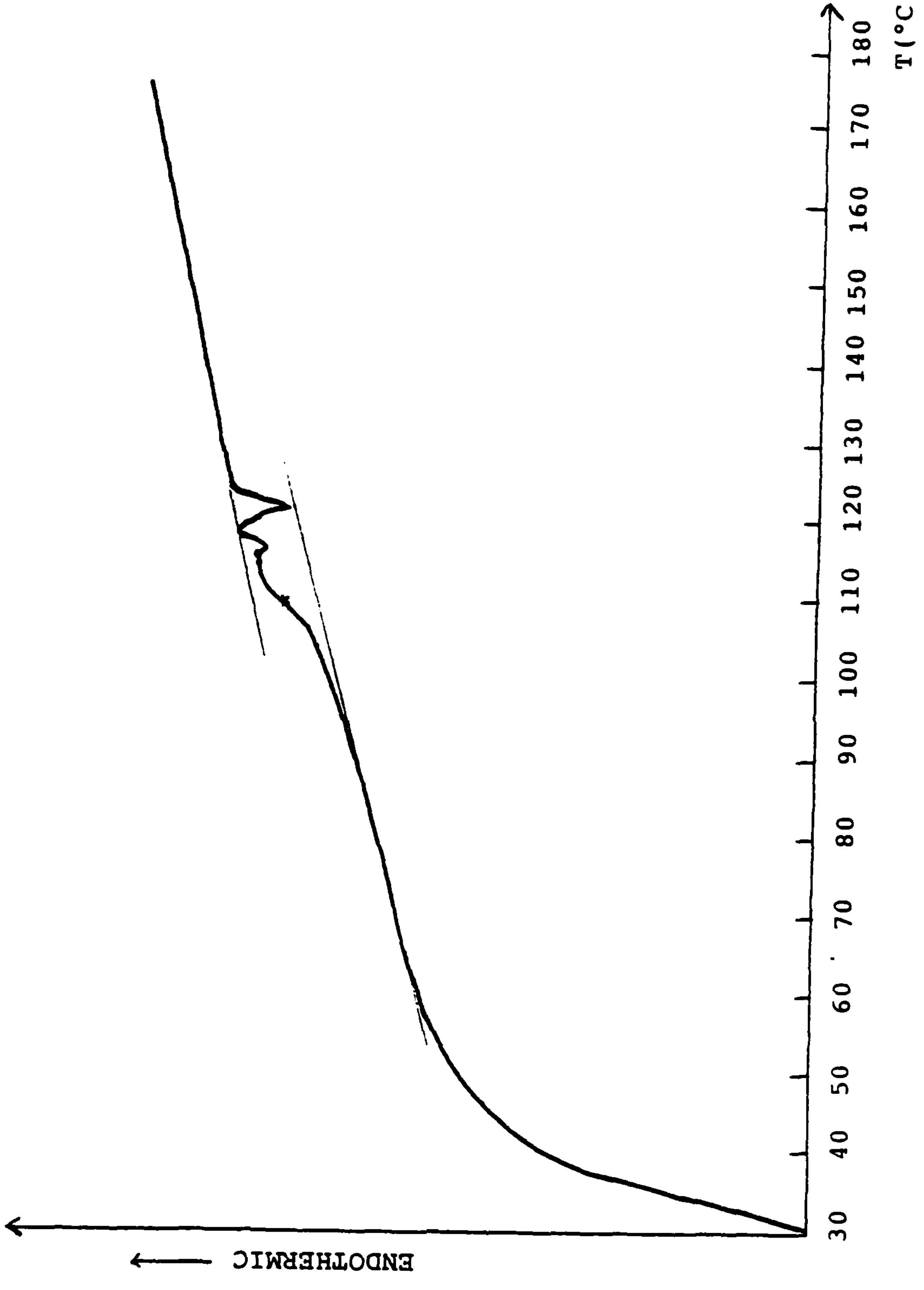
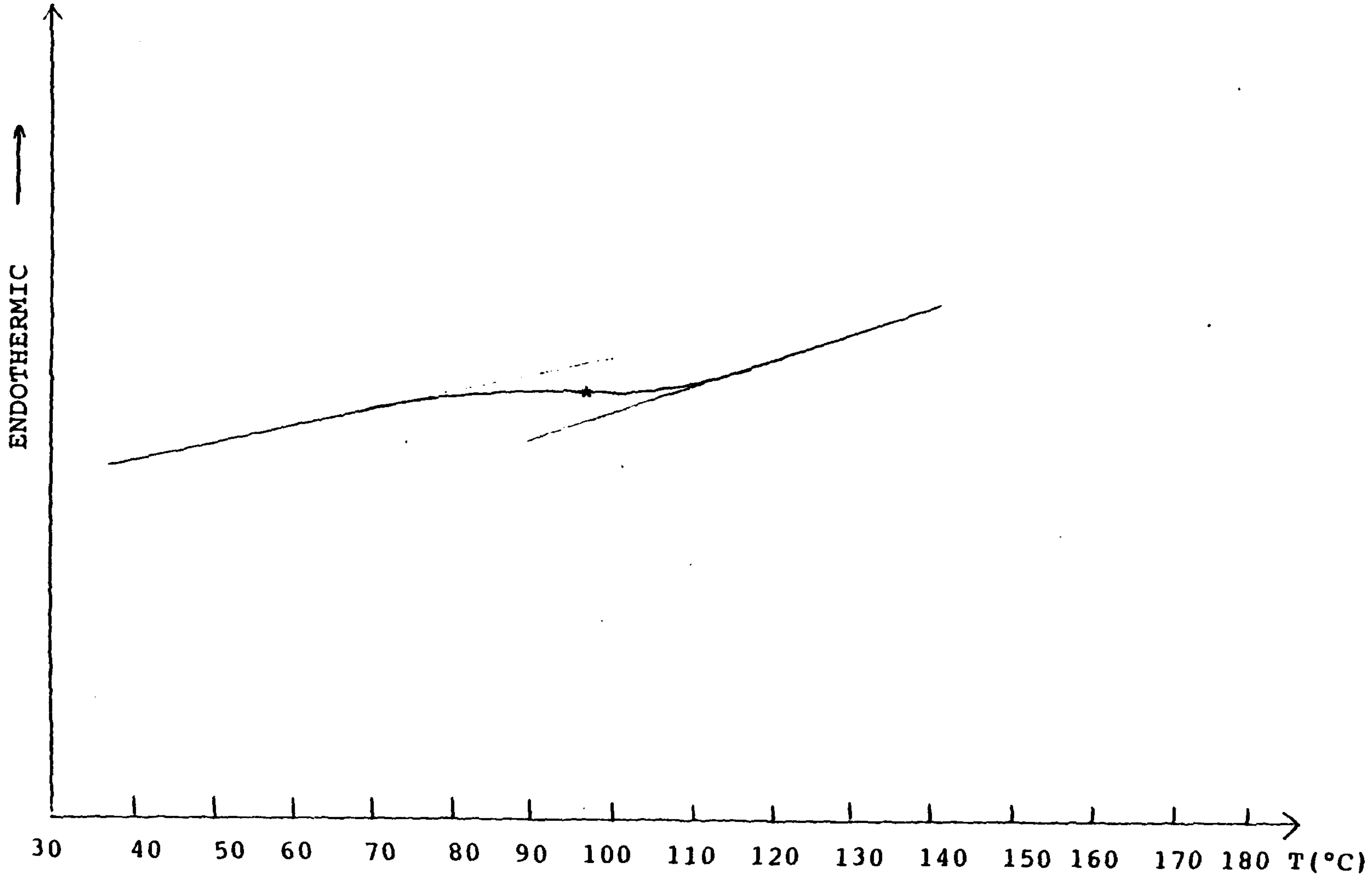

ENDOTHERMIC
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
T(°C)

Figure 31 DSC Measurement of PMMA Sample with Cooling Rate 10°/minute


ENDOTHERMIC
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
T(°C)

experimental facilities, the cooling or heating rate can only be coarsely controlled. For more elaborate results, an improvement of the thermal control is needed. Since the heating rate is more difficult to control by our apparatus, most of our polarization measurements were taken upon cooling.

Figure 32 shows the results of cooling a diluted PMMA sample. Methyl methacrylate with 15 wt % of diocty-phthalate is polymerized, and the glass transition temperature of PMMA has been efficiently lowered. The polarization of fluorescence versus temperature for polystyrene with 15% of dimethyl phthalate dissolved in it is shown in figure 33, which has been done by Chapoy [36], by using phenyl-ß-naphthylamine, PBNA, as a fluorescent probe. The result is in quite good agreement with ours.

Polymeric glass upon heating to the temperature higher than its glass transition temperature is expected to approach its equilibrium state very quickly. By the following experiments we are able to know if the sample has attained its equilibrium state under such conditions. The sample is annealed at a certain temperature above T_g for various times and then cooled at a constant rate. If the sample is at an equilibrium state at the higher temperature, the polarization versus temperature curves

Figure 32 Polarization Versus Temperature for PMMA with 15% DOP and 10^{-5} wt% 9,10-DPA Dissolved in it, upon Cooling

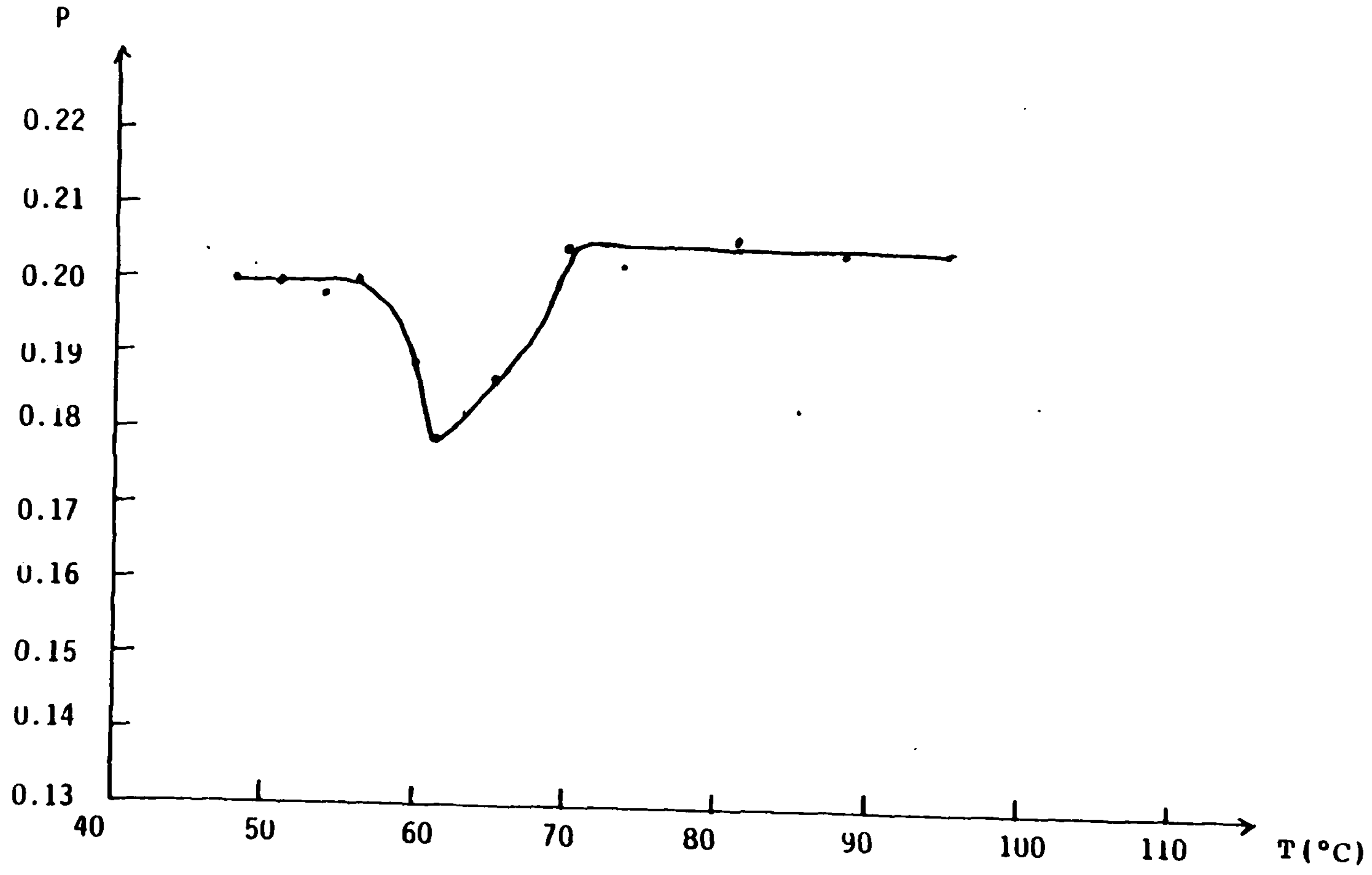
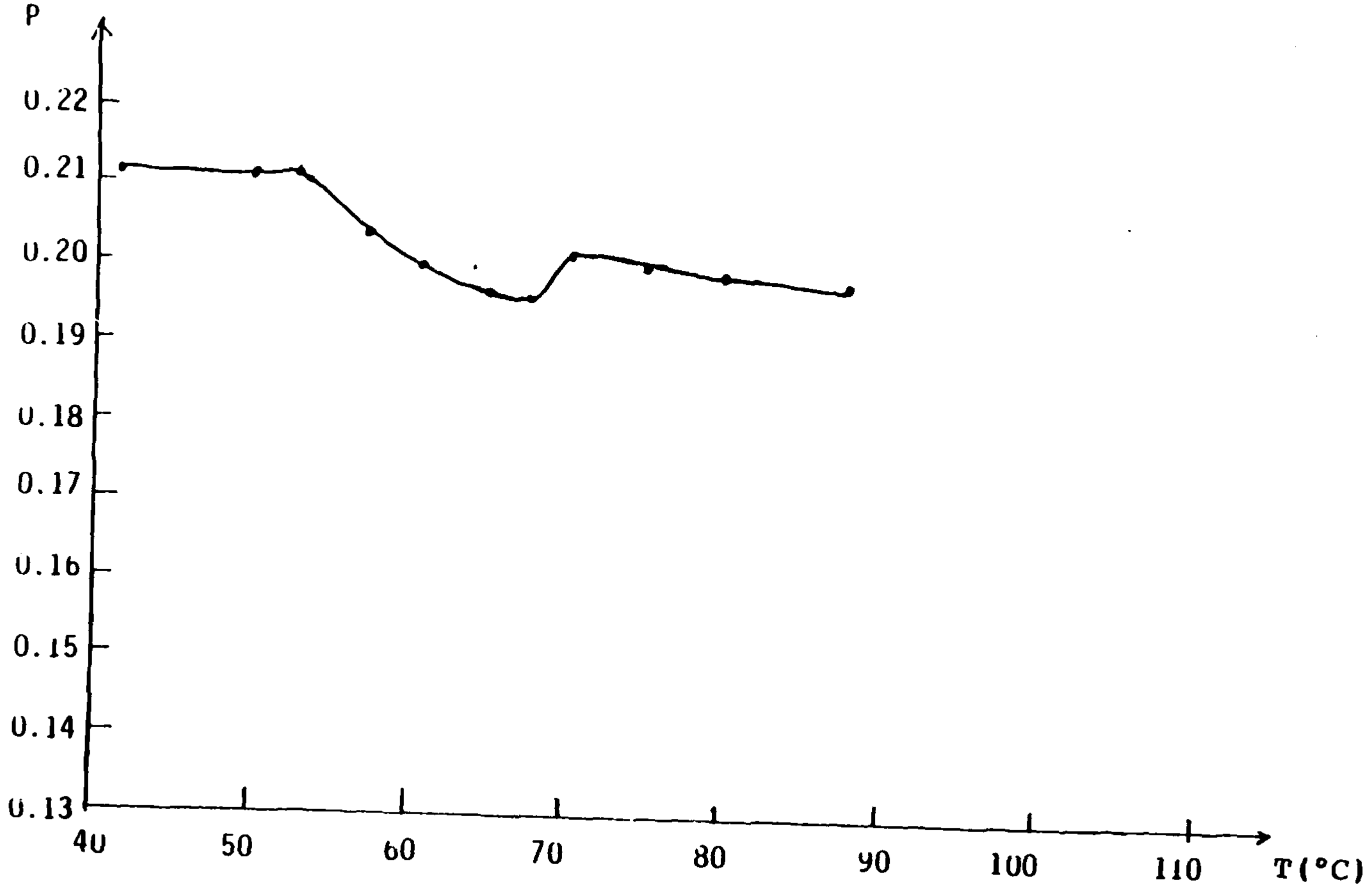

P
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
40
50
60
70
80
90
100
110
T(°C)

Figure 33 Polarization Versus Temperature for Polystyrene with 15% DMP Dissolved in it, Done by L. L. Chapoy


P
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
40
50
60
70
80
90
100
110
T(°C)

at the same constant cooling rate should be the same. Figure 34 and 35 show the results. The shift in T_g is caused by the difference in the cooling rate which is dependent on the room temperature. The degree of depolarization is about the same at T_g for the same T_h.

Next, the sample is annealed at T_h long enough to attain equilibrium, and then the polarization versus temperature is measured upon air cooling. This experiment is carried out at several different T_h values; i.e. 120°C, 132°C, 146°C, and 159°C, and the results are shown in figure 36. The degree of polarization decreases at temperature T_g and below with increasing T_h. And the peak of the glass transition shifts slightly toward lower temperature for being annealed at higher T_h. This is understandable, since the average cooling rate at glass transition region is more or less affected by the annealing T_h. For example, the cooling rate at glass transition region for the sample with T_h = 150°C is lower than which with T_h = 120°C, because the excess heat between 150°C and 120°C shall warm up the surrounding air and slow down the rate of cooling. Thus, in figure 36 the higher T_h is associated with a lower T_g. However, the big difference in the degree of polarization for curves (1) to (4) might be due to the variation in molecular packing efficiency as quenched from high temperature. The same

Figure 34 Polarization Versus Temperature for PMMA-9,10-DPA Sample. The Sample is Annealed at 123°C for (O) 48 Minutes and (x) 16 Hours, and then Cooled Down

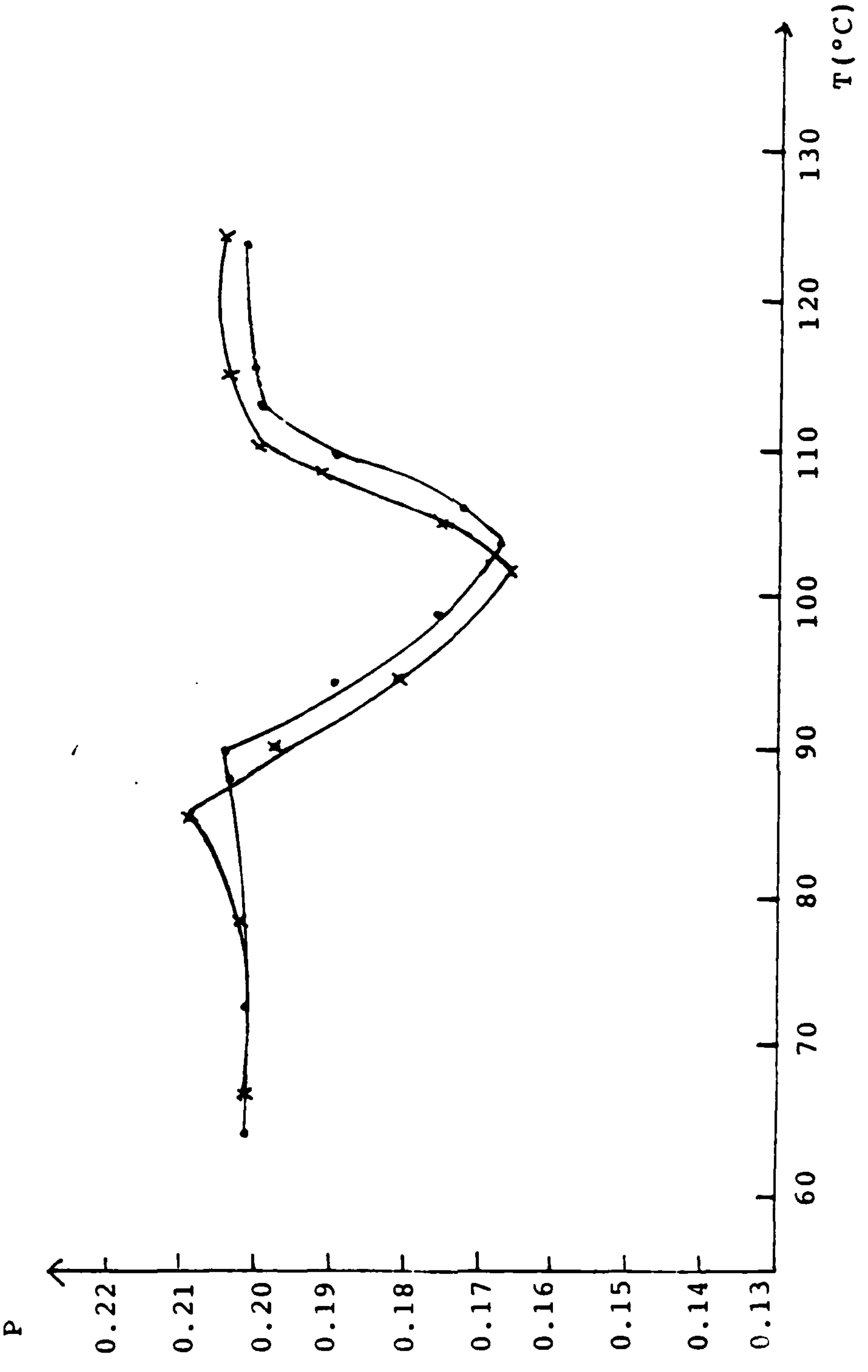

P
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
60
70
80
90
100
110
120
130
T(°C)

Figure 35 Polarization Versus Temperature for PMMA-9,10-DPA Sample. The Sample is Annealed at 146°C for (O) 2.5 Hours and (x) 3 Days, and then Cooled Down

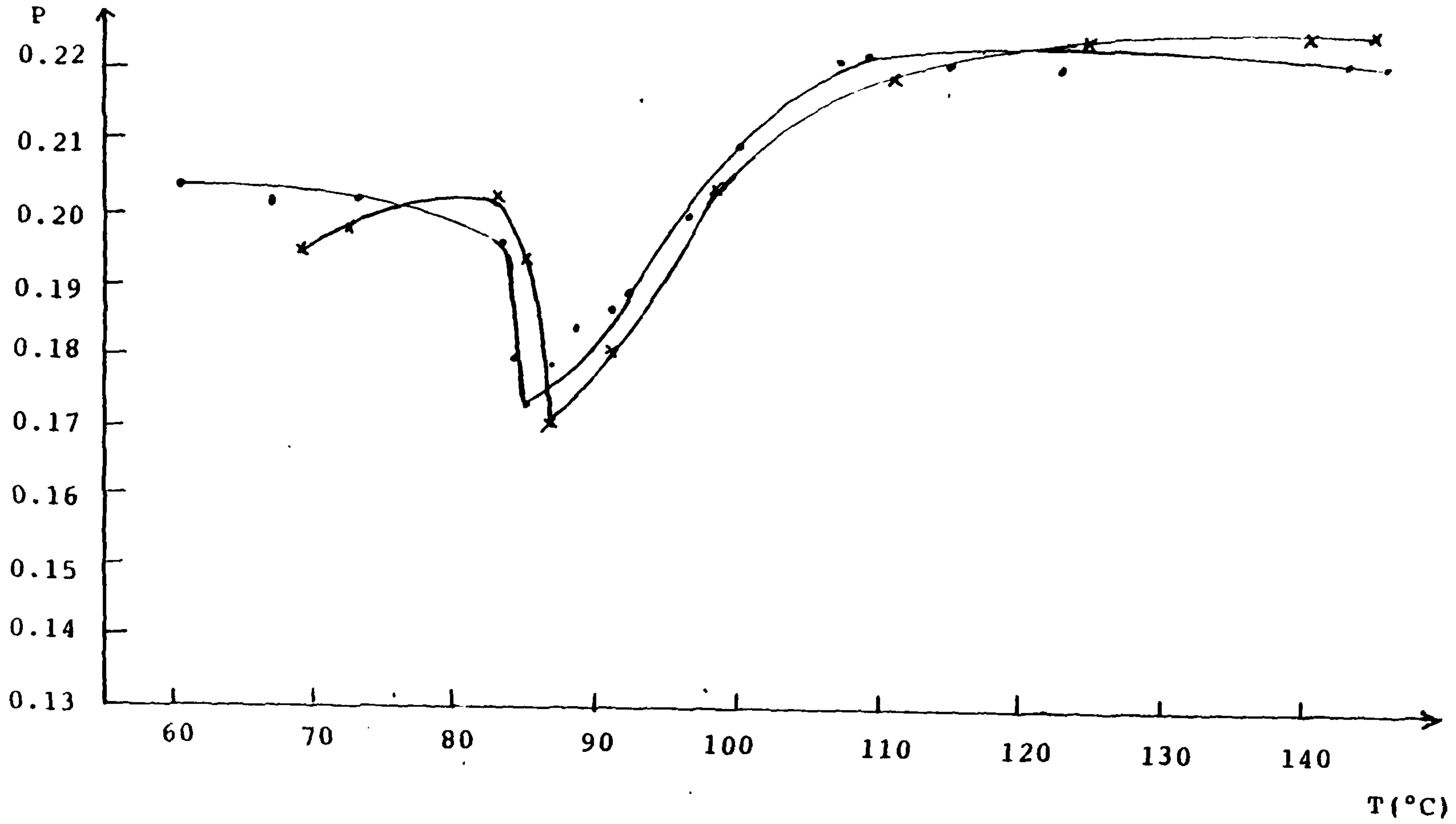
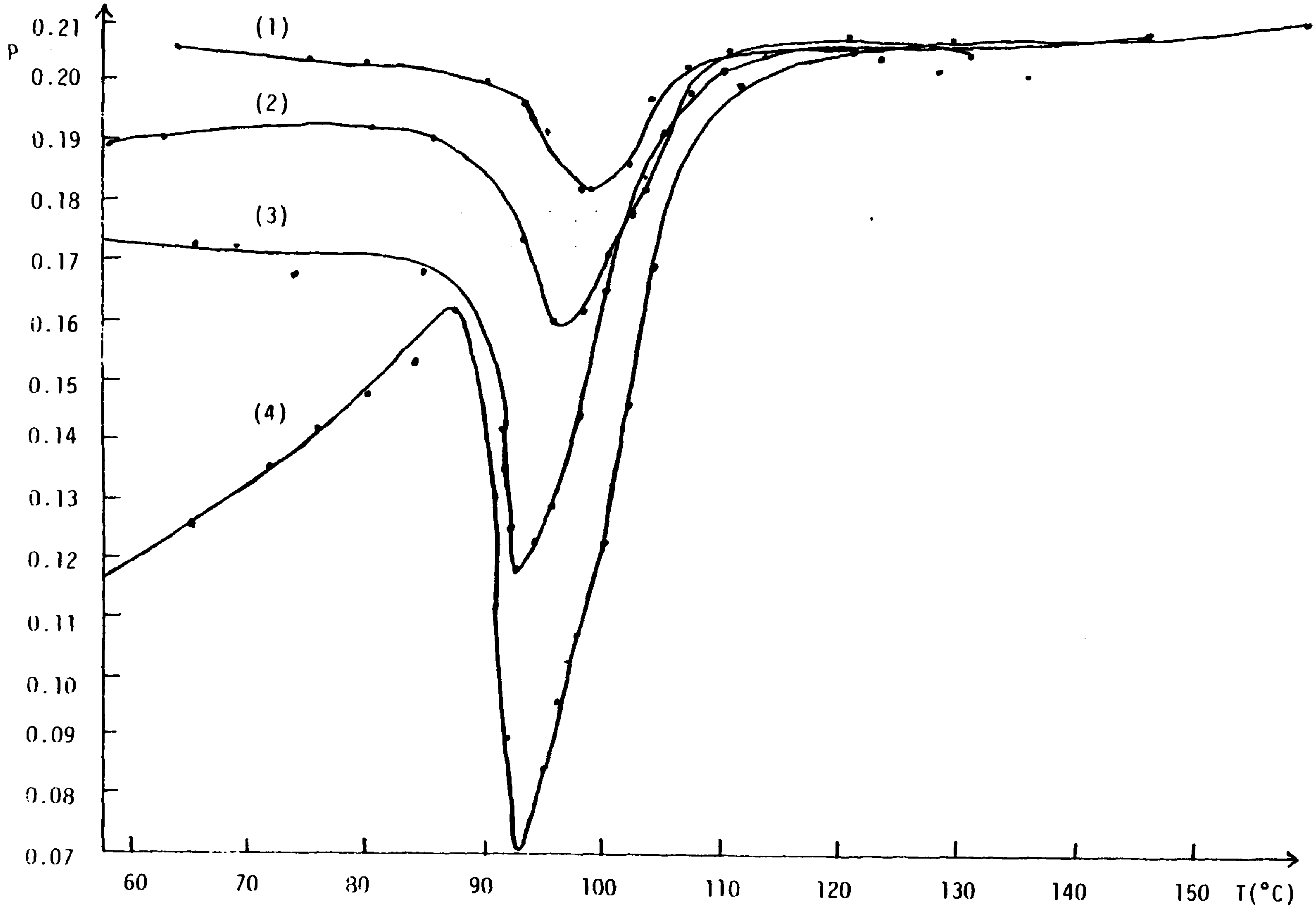

P
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
60
70
80
90
100
110
120
130
140
T(°C)

Figure 36 Polarization Versus Temperature for PMMA-9,10-DPA Sample. The Sample is Annealed at (1) 120°C, (2) 132°C, (3) 146°C, and (4) 159°C, and then Cooled Down



P
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
(1)
(2)
(3)
(4)
60
70
80
90
100
110
120
130
140
150
T(°C)

experiment is done with a different molecular probe; i.e., PMMA doped with 10^{-5} wt% of 9-VA. And a similar result is obtained in figure 37. However, this phenomenon is imperceptible for diluted polymer, see figure 38.

Isothermal annealing experiments are carried out at a temperature $T_{g,1}$, which is, for instance, 92°C in figure 36 when T_h = 150°C. The mobility of probe at that temperature is large, and relaxation of the polymeric molecule toward its lower energy state is expected to occur. However, the sample is annealed at $T_{g,1}$ for over 17 hours and the degree of polarization is still the same, i.e. 0.07. Various $T_{g,1}$'s and annealing time are tried, no obvious change in degree of polarization is observed. Apparently, the microviscosity within polymer matrix is not affected by the isothermal annealing at $T_{g,1}$ in this case. This might be due to that the fluorescence lifetime of the dye does not match the relaxation frequencies of polymers, or the size of the dye is not suitable, or some other reasons.

Figure 37 Polarization Versus Temperature for PMMA with 10^{-5}% of 9-VA in it. The Sample is Annealed at (1) 108°C, (2) 126°C, (3) 130°C, and (4) 150°C, and then Cooled Down

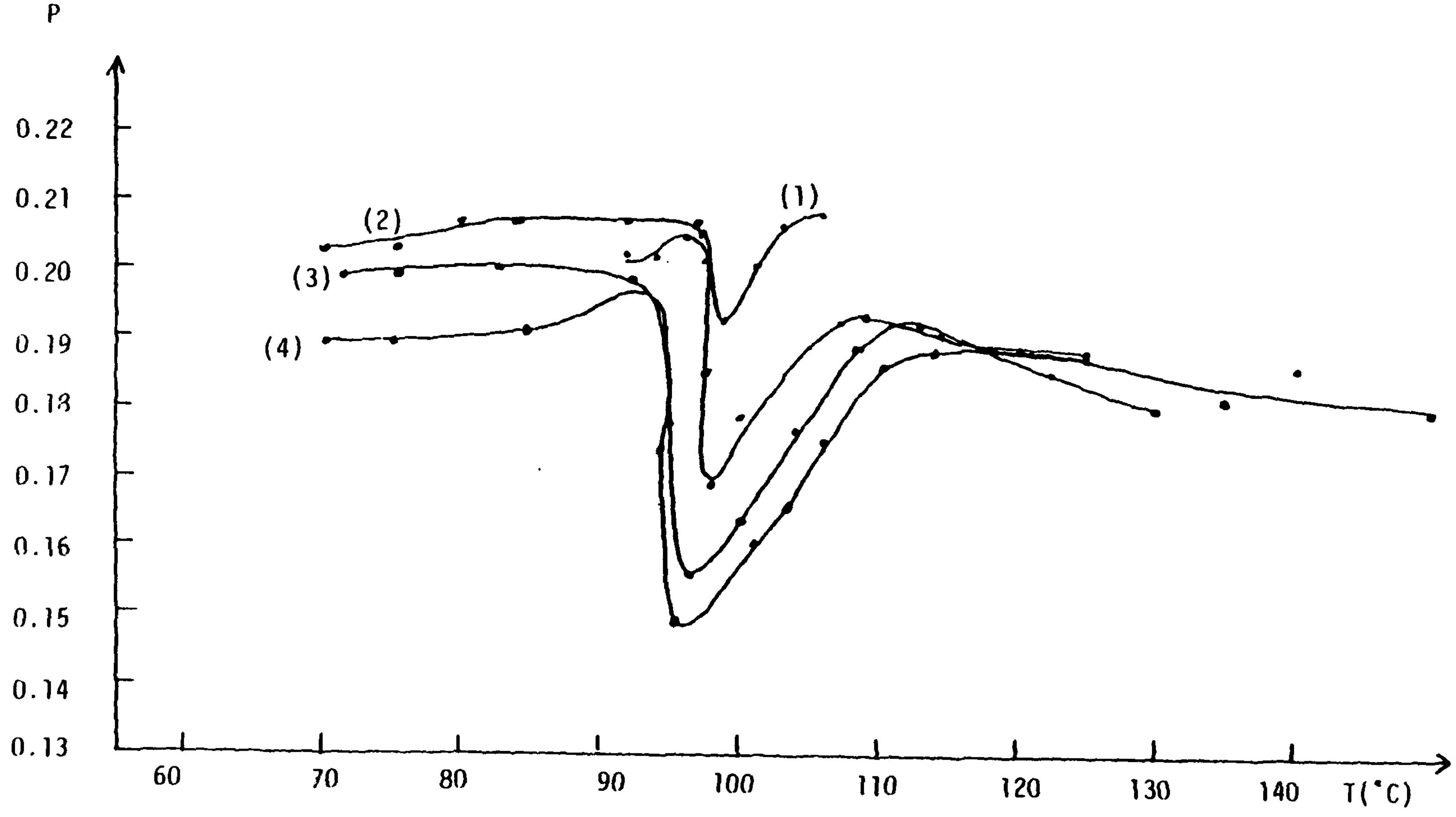
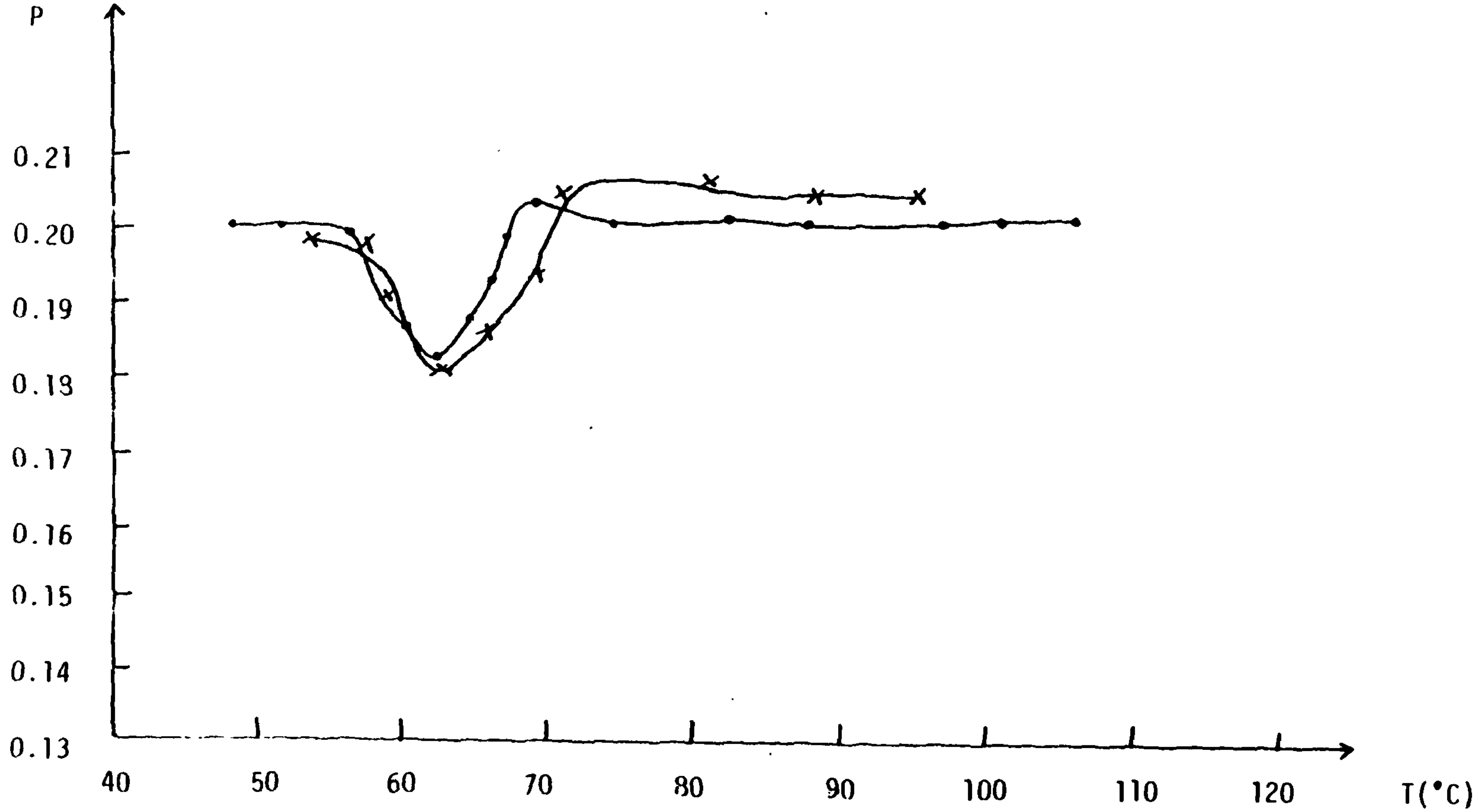

P
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
60
70
80
90
100
110
120
130
140
T(°C)
(1)
(2)
(3)
(4)

Figure 38 Polarization Versus Temperature for PMMA with 15% of DOP and 10^{-5} wt% of 9,10-DPA Dissolved in it. The Sample is Annealed at (x) 100°C for 38 Hours and (O) 113°C for 3 Hours, and then Cooled Down


P
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
40
50
60
70
80
90
100
110
120
T(°C)

CHAPTER 4

DISCUSSION

§4.1 Fluorescence Depolarization Measurement

The quantum efficiency of most fluorescent molecules decreases with increasing temperature because the increased frequency of collisions at elevated temperature improves the probability of deactivation by vibrational decay. The fluorescent molecule has a natural radiative lifetime, τ_o. However, nonradiative processes involving the excited state will reduce this to the observed radiative lifetime, τ, as the quantum efficiency is reduced:

$$\tau = \Phi\tau_o \qquad (4\text{-}1)$$

where Φ is the quantum efficiency for fluorescence ($\Phi \leq 1$).

In performing these experiments it was found that at higher temperature the quantum efficiency of the fluorescent molecule decreased slightly as the temperature was increased; an example is given later in this section. This results in an apparent value of P which becomes greater than it should be with increasing T if Φ remained constant, i.e. τ remained constant. Thus ρ/τ does not appear to decrease with temperarure as strongly as it should since τ is also decreasing.

If a radiationless process competing with radiation is temperature dependent, at T_1 and T_2 one would have:

$$\tau(T_1) = \Phi(T_1)\ \tau_o \tag{4-2}$$

$$\tau(T_2) = \Phi(T_2)\ \tau_o \tag{4-3}$$

and

$$[\tau(T_2)] \ / \ [\tau(T_1)] = [\Phi(T_2)] \ / \ [\Phi(T_1)] \tag{4-4}$$

when $\Phi(T_2) \ / \ \Phi(T_1)$ is the relative quantum efficiency as a function of temperature alone.

$$[\Phi(T_2)] \ / \ [\Phi(T_1)] = [I_f(T_2)] \ / \ [I_f(T_1)] \tag{4-5}$$

where $I_f(T)$ is a measure of intensity of fluorescence; eq. (4-5) is true with the assumption that the intensity of exciting light is constant, and the molar extinction coefficient of the dye is independent of temperature.

In order to calculate quantum efficiency, the intensity of light source is monitored by a power meter.

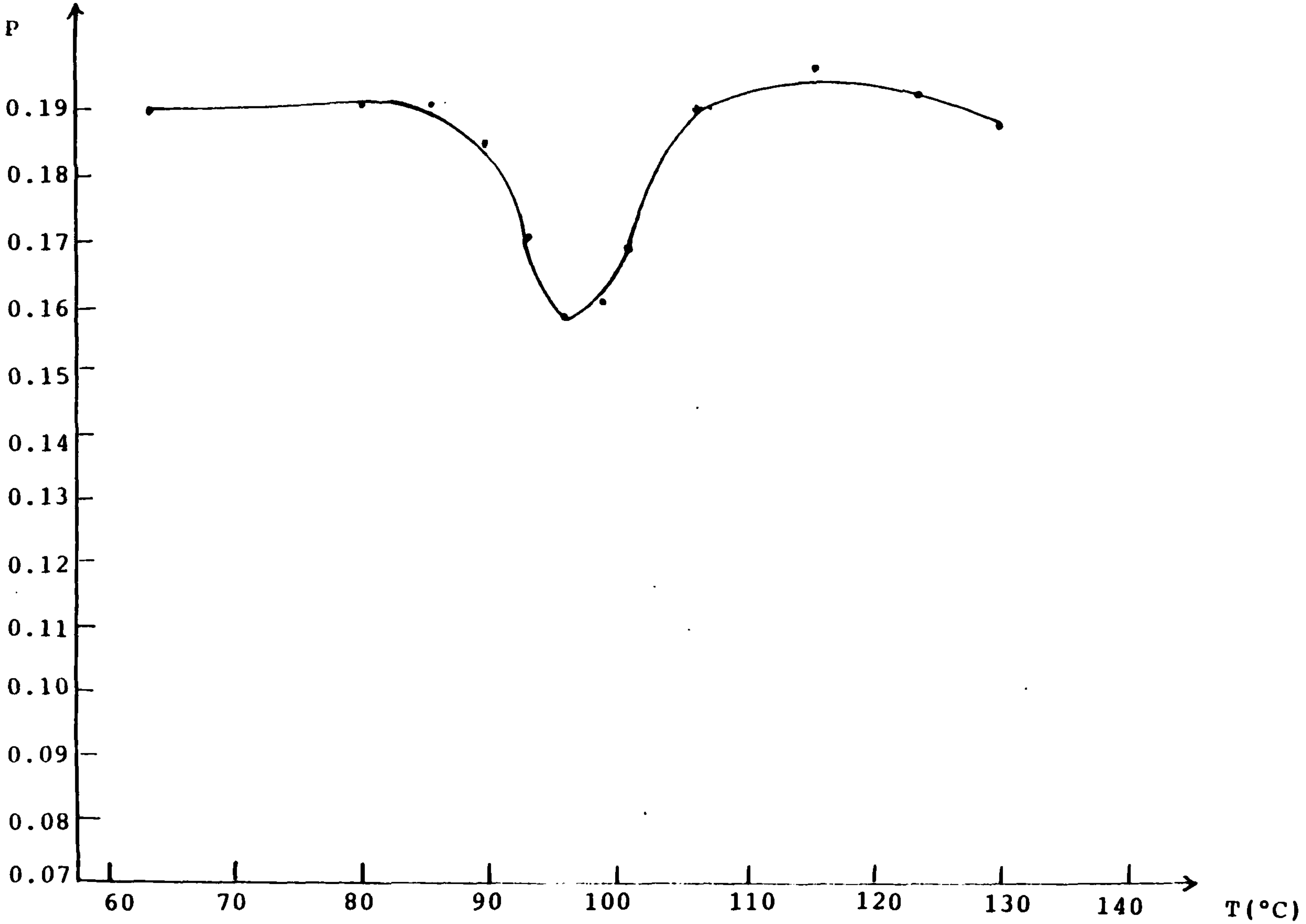
In this case the intensity, and hence lifetimes have been normalized to 50°C. The normalized results for data from curve 2 in figure 36 (T_h=132°C) are shown in figure 39. The normalized P values have obviously changed only at T>120°C, P decreases with increasing temperature. At 115°C the unnormalized P is only about 4% larger than the normalized P, while at 130°C the difference between these two values is about 10% of normalized P. In this research, we are more interested in the variation of P at the glass transition region, within this temperature range, the fluorescence lifetime changes very slightly. For simplicity of the treatments, the data shown in this work are not normalized.

§4.2 Microviscosity of Polymers

Our results in these experiments are quite interesting. The molecular probe within the polymeric matrix is found most mobile in the glass transition temperature range, while the rotational motion of the probe is comparably restrained at temperature above or below this region. This suggests that the microscopic viscosity of polymeric systems originates from a very different mechanism than that of the macroscopic viscosity.

Two interpretations of this result are to be

Figure 39 Normalized Polarization Versus Temperature for Sample PMMA Containing 10^{-5} wt% of 9,10-DPA with T_h=132°C


P
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
60
70
80
90
100
110
120
130
140
T(°C)

discussed in the following sections; One is from the view point of a medium mobility effect, and the other one is from a consideration of hole free volume.

§4.2.1 Effect of Medium Mobility toward Probe

In our results, at temperatures higher than the glass transition region, the segments are bouncing around very rapidly, even though the fractional free volume at these temperatures is much larger than the fractional free volume below T_g, the measured polarization values are quite close. Accordingly, the bouncing rate of segments must be comparable to the fluorescence lifetime of the probe at high temperature. Thus, the rotating probe is about equally impeded by the bouncing segments at temperature range AB, in figure 28, as by the frozen holes at temperature range DE.

As the polymer is cooled down from the temperature above T_g to close to T_g (range BC in figure 28), the jumping frequency q, which is by far the most temperature-sensitive quantity, decreases with T more rapidly than the decreasing of free volume, due to thermal contraction, within this temperature range. Therefore, the observed polarization decreases with T in this temperature range.

At temperature T_g and below (the CD range in figure

28 the jumping frequency of segments is small and about to cease, and the contraction of the holes with decreasing temperature has a more profound influence upon the probe. Thus, the degree of polarization increases to a temperature where the contraction of the holes is too slow to be observed, due to decreasing segmental mobility.

The mechanisms of thermal expansion below T_g and the relocation of segments above T_g are manifested by the foregoing description. And the formation of a downward convex curvature at glass transition in the polarization temperature plot is speculated to relate to the activation energy needed for polymer segments to jump. At T_g the energy needed to do work against surroundings so as to expand the volume available for segments to jump is biggest. This leads to a speculation that the net excess volume which excludes the volume required for molecular jumping and actually occupied volume is the largest at T_g for polymers. Since at that temperature the long range molecular motion has not yet occurred while the volume is expanded to an extent close to the critical volume V^*.

The activation energy is expected to decrease with increasing plasticization. The work needed becomes smaller by adding plasticizer, the volume expanded is accordingly small. The results seem to be in good agreement with this hypothesis, however, more evidence is needed to make such a conclusion. The volume we probed here is quite different from free volume defined in section 2.3, since the effect of segmental mobility towards probe is also counted.

§4.2.2 Redistribution of Hole Free Volume

Kishimoto et al. [44] had speculated that diffusion in polymeric systems with small penetrants is accompanied with a localized cooperation of the vibrations of a few monomer units on the polymer chain and, hence, is independent of the average free volume in the system. A similar point of view is taken by Frisch [45] who indicates that the minimum void volume needed for the movement of very small penetrant molecules is less than the average void volume of the system, and by movement of the solvent molecules into preexisting cavities the diffusion of the penetrants occurs. Frisch et al. [46] extended this basic idea and derived a modified free volume theory valid for the diffusion of small molecules in polymers.

However, Vrentan [47] pointed out that the free volume available for molecular transport or hole free volume in pure polystyrene is about 3.5% of the volume of the polymer at 150°C, which is 50°C above the glass transition temperature of undiluted polystyrene. And the minimum free volume required for the displacement of a hydrogen molecule (as estimated using the molar volume of liquid hydrogen at 0°K) is more than two times the average hole free volume associated with each polymeric jumping unit. The movement of a water molecule requires more than three times this average free volume. Apparently, 9,10-DPA is much larger than hydrogen or water, and the free volume within polymer matrix required to accomodate 9,10-DPA should be even bigger. Hence, it would appear that a significant redistribution of the free volume in the system must take place even if molecules as small as hydrogen and water are to undergo movement within the polymer.

The average hole free volume per polymeric jumping unit can be increased by raising the temperature of the system. And as the polymer is cooled down to the freezing-in temperature, the segmental jumping of polymer molecules decreases, the hole containing the probe contracts with decreasing temperature. As shown in figure 36 and 37, the hole size for probe at T_g increased with annealing temperature, T_h. A smaller hole free volume can be regenerated by heating the larger hole free volume to temperature above freezing-in temperature. For example, in figure 36, the hole free volume of 9,10-DPA at temperature T_g and below with T_h = 146°C is larger than that with T_h = 132°C, however, if the polymer is cooled from 146°C down to room temperature, and then reheated to 132°C the smaller hole free volume at T_g is reproducable. When the polymer is annealed at T_h = 159°C, the redistribution of free volume would allow the probe to rotate very freely at T_g (P=0.07). However, thermal degradation might have happened at such a high annealing temperature that the results no longer reproducable as reheated from room temperature to a lower T_h, i.e. 132°C.

The plasticized polymer is more liquid like, and the holes within it is less localized as the holes within a rubbery polymer. Therefore, the hole free volume at T_g is less effected by annealing T_h in figure 38.

§4.3 Conclusion

From above remarks we can conclude that the medium mobility effect toward the probe and the temperature-dependent redistribution of free volume lead to a completely different mechanism for the glass transition compared with macroscopic observation. Since the average void volume of a polymeric system is too small to accomodate a rotating fluorescent dye, the bouncing of the neighboring polymer segments at temperature higher than T_g will impede the rotational motion of the dye. However, this jumping motion of polymer segments allows a redistribution of the hole free volume which is then frozen into polymer matrix below temperature T_g. The more segmental jumps evoked, i.e. by higher T_h, the better the probe is accomodated, this is elucidated by the lower degree of polarization at T_g. And, the size of the hole created by redistribution of free volume should be dependent on the size of the probe and the flexibility of the polymer chains. This thesis gives some information about how a molecular probe behaves in a polymeric enviornment over a wide temperature range from a fundamental aspect. It provides a possible explanation for the difference between the observed hole free volume of rotating probe and the expected average free volume as described in free volume theory.

The difficulty in applying free-volume theory to glass transition is that it does not take account of the molecular interaction in the system, and as the probe used is too bulky compared to the average void volume in polymer system a temperature-dependent redistribution of free volume occurs. All of these factors play an important role in the fluorescence depolarization studies of glass transition phenomena.

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