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## Studies in polymer compatibility.

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STUDIES IN POLYMER COMPATIBILITY

A Dissertation Presented

By

Eugene B. Wilusz

Submitted to the Graduate School of the  
University of Massachusetts in  
partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

October 1975

Polymer Science and Engineering

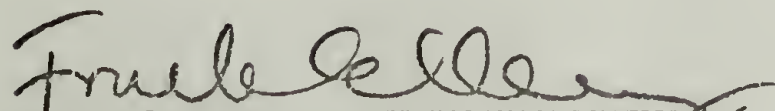
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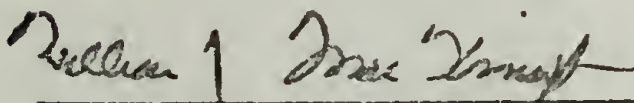
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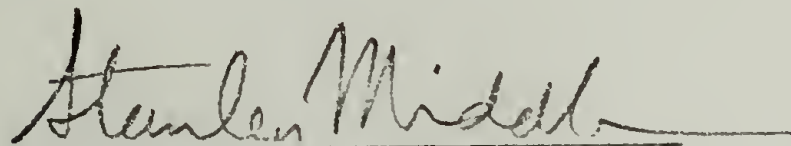
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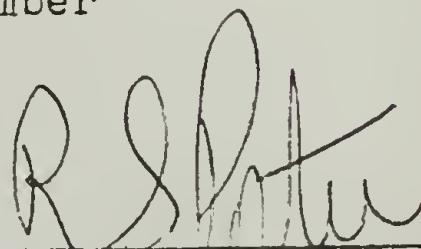
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October 1975

To my wife, Nancy, and my children,  
David and Amy Beth



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## ABSTRACT

### Studies in Polymer Compatibility

(October 1975)

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Today composite materials are increasingly replacing pure materials in many different applications because of their improved properties. One type of composite material consists of two or more polymers physically blended together to an intimate degree. Such a mixture is known as a polyblend. If such a mixture behaves like a homopolymer in characterization experiments, the polymers involved are regarded as compatible. Usually such compatibility is exhibited as a single glass transition temperature intermediate between the glass transitions of the homopolymers. Thermodynamic and kinetic difficulties encountered in mixing are responsible for the rarity of compatible polymer pairs.

One polymer of interest in compatibility work is poly- $\epsilon$ -caprolactone (PCL) because of its chain structure which has some polar as well as nonpolar character. In addition, PCL is a novel type of polyester in which the dipole moments of the ester groups along the chain reinforce one another unlike those of classical polyesters. To add information on the physical properties of PCL the

dielectric relaxation behavior of the polymer was studied over a wide range of frequency and temperature. The polymer was found to melt in the vicinity of 60°C. The main glass transition temperature was found to occur at -50 to -60°C with an activation energy of 152 kcal/mole. A sub-glass relaxation was found in the range -90 to -120°C with an activation energy of 11 kcal/mole and was attributed to short range motions involving the ester groups. The magnitudes of the relaxations were determined and found to be in general agreement with those of similar polymers.

PCL was blended with several polymers and, in general, resultant blends were found to be incompatible. Blends with greater than 90% polyethylene prepared by quenching the molten mixture into liquid nitrogen appeared to be compatible by differential scanning calorimetry.

Polyblends were also prepared of isotactic polystyrene (i-PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and were found to be compatible over the entire range of composition by differential scanning calorimetry and dynamic-mechanical measurements. It was found possible to crystallize blends of 50% or more i-PS by thermal annealing leading to a second series of blends of higher modulus. High deformation experiments indicated that the engineering properties of the polyblends were intermediate between those of the homopolymers. Finally, the experimental data were examined in the light of current theories concerning the properties of two-phase polymer systems.



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# C H A P T E R I

## INTRODUCTION

### Composite Materials

Today composite materials are increasingly replacing pure materials in many different applications. Composite materials are those consisting of two or more components. They are physically and chemically heterogeneous materials. Generally one component is said to make up the "continuous" phase while the other component makes up the "dispersed" phase. Such materials are useful because they may exhibit certain properties improved over the pure materials. They might be stronger, more attractive, more processable, or any one of a number of other ways better. In metallurgy such materials are known as alloys. In polymer science such materials might be polyblends, copolymers, or reinforced composites, all of which have their own characteristic properties. In polyblends the two or more components, both polymers, are physically mixed together. They are held together by secondary forces such as van der Waals forces, dipole interactions, or hydrogen bonding. In copolymers the two or more components are bonded to one another by covalent chemical bonds in arrangements known as random, graft, or block. Reinforced composites are polymers to which glass fibers have generally been added. This work is concerned with polyblends. The reader is referred to the text edited by Platzner<sup>1</sup> and the review article by Estes, Cooper, and Tobolsky<sup>2</sup> as good starting

points for studying the other composite polymer materials. A discussion of recent advances can be found in the book edited by Sperling.<sup>3</sup>

### Polyblends

The properties of a particular polymer can often be beneficially modified by physically mixing the polymer with other materials. Ordinary low molecular weight materials are often mixed in limited quantities into a polymer matrix. Such low molecular weight materials are commonly referred to as "plasticizers." This addition generally results in reducing the brittleness of the polymer and increasing the resistance to impact of the material.

The properties of a polymer may also be beneficially modified in special cases by mixing the polymer with another polymer. Such a mixture, as already defined, is called a "polyblend." The detailed study of polyblends has developed only in relatively recent times. Although there is a recorded preparation of a polyblend in 1912,<sup>4</sup> most of the serious early work in this field took place in the late 1940s. The first polyblend to achieve commercial status was impact-resistant polystyrene. This material was introduced in 1948 and consisted of 5 wt% of a poly(butadiene-co-styrene) rubber.<sup>5</sup> Some of the most important polyblends of today are the ABS polymers, so-called because they consist of acrylonitrile, butadiene, and styrene. Generally, styrene and acrylonitrile are copolymerized in the presence of polybutadiene producing a graft copolymer polyblend. The polybutadiene is said to contribute ductility and impact resistance while the

styrene-acrylonitrile matrix gives rigidity and strength.<sup>6</sup>

Polyblends can be of two types. The dispersed phase may be of high modulus as in the case of reinforced thermoplastics, or the dispersed phase may be low modulus as in rubber-modified, impact-resistant plastics.<sup>7</sup> There is a rapidly growing body of information currently available on the properties of polyblends. The thorough review article by Krause<sup>8</sup> is undoubtedly the best starting point for the study of these materials.

### Polymer-Polymer Compatibility

One of the more ambiguous aspects of polyblend studies today has been the use of the term "compatibility." The term has been used to convey that two polymers are somehow miscible with each other or with a common solvent. The problem arising from the use of this term is one of inconsistency.<sup>5</sup>

The use of the term "compatible" in the mixing of polymers is undoubtedly an extension of the use of the term as it applies to low molecular weight materials. When two liquids are mixed to form a product which is one phase and homogeneous, the two liquids are referred to as compatible. Such a mixture is at thermodynamic equilibrium. The determination of the compatibility of two liquids is then visual and simple. The mixing of two polymers does not lend itself to this simplicity. Polymer mixing involves not only thermodynamic considerations but kinetic factors as well.<sup>9</sup> The general use of the term "compatible" as applied to two polymers, without any further explanation, conveys little information.



A "polyblend" has been defined in one source as a physical mixture of two or more polymers.<sup>10</sup> Yu points out the impracticability of this definition and goes on to define a polyblend "as a single entity of material containing within its physical boundary at least two thoroughly mixed polymers which are not linked covalently."<sup>5</sup> It is this latter definition which will be assumed in the course of this work. It is implied here that mixing of the two species occurs to an intimate degree. The exact extent of this mixing is, however, not precisely known. The complicated nature of polymer molecules probably prevents their mixing on a monomer segment level although this level of mixing is perhaps approached in compatible pair systems.

Macknight, et al.,<sup>11</sup> have expressed this level of mixing quantitatively through the use of the parameter "s." This parameter is said to represent "the level of mixing in terms of the average normalized size of the segmental clusters in the system." If the two polymers are mixed on a level corresponding to the polymer molecules themselves, then  $s = 1$ . More intimate mixing, on a segmental level, would be the case if  $s < 1$ . On the other hand,  $s > 1$  corresponds to clustering of like polymer molecules into aggregates and, ultimately, phase separation. Polymer technologists have at times labelled two polymers as "compatible" if the blend did not exhibit "sweat out," i.e., macroscopic phase separation did not occur during some reasonable time. In this work two polymers will be considered compatible in the more rigorous sense, that is, if they mix on an intimate level with  $s < 1$ .

## Thermodynamics of the Mixing Process

In order for the mixing of two chemical species to occur, the system comprising the two species must be removed from equilibrium. The thermodynamic conditions for equilibrium in such a system consisting of two species and two phases is that the chemical potential of component 1 in phase 1,  $\mu_1^1$ , must be equal to the chemical potential of component 1 in phase 2,  $\mu_1^2$ , and similarly for component 2,  $\mu_2^1 = \mu_2^2$ . Since

$$\mu_1 \equiv \bar{G}_1 = \left( \frac{\partial G}{\partial n_1} \right)_{T,P,n_2}$$

and similarly for component 2, the same can be said for the partial molar free energy of the components, and at equilibrium  $dG = 0$  for the system. At any condition other than equilibrium  $dG \neq 0$ , since  $\mu_1^1 \neq \mu_1^2$ . Specifically,

$$dG = \mu_1^1 dn - \mu_1^2 dn$$

or 
$$dG/dn = \mu_1^1 - \mu_1^2.$$

In such a circumstance, when  $dG/dn < 0$ , there is a spontaneous transport of matter between the phases in the direction from the higher toward the lower chemical potential which will continue until equilibrium is reached.<sup>12</sup>

The free energy change for the process can also be expressed as

$$\Delta G = \Delta H - T\Delta S$$

where  $\Delta H$  is the enthalpy change for the process (or the heat of mixing),  $T$  is the absolute temperature, and  $\Delta S$  is the entropy change for the process. If the free energy change for the process is negative, mixing occurs; if positive, there is no mixing. That is, mixing can



be accomplished even in cases where the heat of mixing is unfavorable if the entropy change is sufficiently significant. The heat of mixing is generally endothermic (positive) since molecules tend to be favorably attracted to similar molecules rather than to dissimilar ones. The mixing of low molecular weight liquids occurs relatively readily because of the favorable entropy change.

Conditions for mixing a low molecular weight liquid and a polymer are more critical. In general, unfavorable heats of mixing are not significantly different from those that occur with low molecular weight materials. The effect of the entropy term is however considerably reduced since the number of individual species in the system is significantly lowered. The large number of atoms making up the polymer cannot attain as random an arrangement since they are chemically linked together. Extension of this reasoning to the case involving the mixing of two high molecular weight species leads to the conclusion that homogeneous mixing of polymers on a molecular level occurs only rarely. In general, entropy increase on mixing is not significant, often being less than  $0.005 \text{ cal/g}^\circ\text{C}$ . Superimposed on this insignificant entropy change is the difficulty of arriving at equilibrium.<sup>13</sup> It may be expected, then, that for the mixing of two polymers to occur on a monomer unit or segmental level, the heat of mixing must be small. The polymers must be almost identical in interaction. Chances for mixing are improved if the molecular weights are not high since greater randomness can be achieved. It is not surprising then that compatible, high molecular weight polymer pairs are indeed rare.<sup>9</sup> The reader is

again referred to the review by Krause<sup>8</sup> for a recent list of compatible polymer pairs.

### Quantitative Prediction of Compatibility

Several workers have tried to develop calculational techniques for predicting the compatibility (or the lack of it) of two or more polymers. A few of the more noteworthy attempts will be mentioned here.

Brodsky<sup>14</sup> suggested using the free energy of mixing to estimate the "degree of compatibility." For two polymers in the bulk phase the free energy of mixing can be determined from calculation of the heat of mixing.<sup>8,15</sup> The compatibility of the two polymers would then increase with decreasing free energy of mixing. This method seems reasonable in view of the previous discussion.

Krause<sup>8</sup> has suggested a method for predicting compatibility based on the interaction parameter  $\chi$ . In this method calculated values of  $\chi_{AB}$ , the interaction parameter between two polymers, are compared with  $(\chi_{AB})_{cr}$ , the critical point on a binary phase diagram which is the limit of compatibility. The closer the values of the two interaction parameters, then, the greater the compatibility. Reasonable success seems to be attained using this method.

Pazonyi and Dimitrov<sup>16</sup> used the difference in cohesive energy densities of the two components to predict compatibility. They concluded that if this difference is less than  $0.016 \text{ cal/cm}^3$ , mutual solution is possible regardless of the sign of the heat of mixing.

Schneier<sup>17</sup> has recently modified an approach used by Gee<sup>18</sup> which also

involves the difference in cohesive energy densities and which is apparently successful in predicting compatibility.

The importance of the theoretical aspects of this work in predicting properties of polyblends is obvious. Much remains to be done, and work will undoubtedly continue in this area.

### Preparation of Polyblends

Several methods are available for preparing blends of compatible polymers. Perhaps the most common approach is that of mechanical mixing. Such mixing can be accomplished with the aid of an extruder or a two-roll mill. In the extrusion process the melted polymers are mixed by a large rotary screw and then forced under pressure through an orifice. Most of the mixing action occurs during this ejection. It is sometimes necessary to repeat this procedure to insure thorough mixing.

The alternative to this method is the two-roll mill. One polymer is placed on a heated, rotating cylinder and melted. The polymer with which the first is to be mixed is placed on a second, similar cylinder which is however rotating at a different angular velocity. The distance between the two rolls can then be varied such that the two melts come into contact, and mixing occurs because of shearing action.

Under favorable circumstances it is possible to blend two polymers more simply, for example, by compression molding a mixture of the two powders. Whether two polymers can be mixed by compression molding or not seems to depend on the viscosity of the melt as well as the



compatibility of the two polymers. If the polymers are of high molecular weight such that sufficient pressure can be built up in the melt without the polymers flowing out of the apparatus, mixing may occur by diffusion so long as the polymers are compatible. Morozova and Krotova<sup>19</sup> found that for pairs of nonpolar polymers a diffuse interlayer of up to  $100,000 \text{ \AA}$  could be formed between two bulk polymers. They found much thinner interlayers in studying interdiffusion between a polar and a nonpolar polymer. Similar results have been obtained by Kamenskii and Voyutskii.<sup>13,20</sup> Such studies prove that substantial polymer-polymer interdiffusion does occur in favorable circumstances, and therefore mixing can be accomplished during compression molding so long as the polymer particle sizes are not too large and the two polymers are compatible.

Another possible way of getting two polymers intimately mixed is by freeze drying. That is, if two polymers can be dissolved in a common solvent in dilute solution, the solution can then be frozen, for example, by immersing it in liquid nitrogen. The solvent can then be removed from the mixture by vacuum pumping.

More sophisticated techniques are available for accomplishing this same intimate mixing. As illustrated with the ABS polymer system, one monomer can be polymerized in the presence of the other polymer. A detailed discussion of the advantages and disadvantages of each of these methods is unnecessary here. Suffice it to say that polymer systems are complicated, and trial-and-error may be necessary to establish the best method of mixing for a particular system.

## Experimental Determination of Compatibility

Many techniques are available for the study of polymer compatibility.<sup>9</sup> The selection of a technique to be used in a particular case depends on the definition of compatibility adopted and range, therefore, from the simple to the complex.

Probably the simplest technique is the solution of two polymers in a common solvent. This technique has been used, for example, by Peterson, et al.<sup>21</sup> Two polymers are considered to be "compatible" if they can be dissolved in a common solvent to form a one-phase system. Those forming a two-phase system are considered "incompatible." Such a technique is not adequate for deciding that two polymers are compatible according to the definition of compatibility adopted in this work. It can perhaps be said that this technique is a good first step in deciding whether or not two polymers are compatible. There is no guarantee that just because two polymers can be dissolved in a common solvent, they can be mixed on a segmental level in the absence of the solvent. It can, however, be concluded that two polymers are incompatible if they cannot be dissolved in a common solvent for it will certainly not be possible to mix these polymers on a segmental level in the bulk.

Having dissolved two polymers in a common solvent to form a one-phase mixture, perhaps the next logical step is to cast a film from this solution.<sup>21</sup> Such a film may or may not exhibit phase separation. If there is phase separation, clearly the polymers are incompatible. However, if there is no apparent phase separation the two polymers may



be compatible. Caution must be exercised here since mixing may or may not be at the segmental level. Optical clarity is not in itself a sufficient criterion for assuming compatibility. Transparency can arise because the indices of refraction of the two phases may be nearly equal or because the dispersed phase may be present in domains which are small relative to the wavelength of visible light.<sup>9,22,23</sup> Since light is diffracted at the interface between the two phases, the amount of visible light scattered may be small and the sample nearly transparent. The former situation is however probably rare since it calls for strict similarity of chemical species. Further investigation using more sensitive techniques is in order.

Microscopy affords the investigator probably the best and least confusing method of determining polymer compatibility. A visual inspection of the level of mixing is of obvious reliability. If distinct phases can be resolved at low magnifications, the polymers are incompatible. However, if electron microscopy reveals mixing on a segmental or nearly segmental scale, the system is clearly a compatible one. However, the resolution of the blend into two phases is generally very difficult unless one of the polymers is unsaturated and can be stained with osmium tetroxide at the double bond. For this reason the use of microscopy is strictly limited.

Many other techniques are in use. Such techniques are necessarily less direct than microscopy, yet give results of a consistently reliable nature. Generally, these techniques are concerned with the measurement of the amorphous phase glass transition temperatures. Two

polymers mixed together on a large particle size scale retain their characteristic glass transition temperatures. That is, the mixture exhibits two glass transition temperatures, each characteristic of the homopolymers. A pair of polymers mixed more intimately, but still on a coarse level, are incompatible and also exhibit two glass transitions. However, a pair of polymers which are compatible, that is, intimately mixed, behaves like a homopolymer in regard to its second-order or glass transition temperature. There is one glass transition temperature, and it occurs between the normal  $T_g$ 's for the homopolymers.<sup>24,25</sup> It is unfortunately not known as to what level of mixing is required to exhibit one  $T_g$  in the case of compatible polymer pairs. It is only known that the size of any aggregates present must be small (ca 2000Å). The elucidation of this question by the proper use of electron microscopy together with other methods discussed below is important in the study of compatibility and, indeed, in polymer science. However, any technique which is used to measure glass transition temperatures can be used to study compatibility in polymers.

The variation of the index of refraction with temperature is one such method. The index of refraction generally varies with temperature in a linear manner. However, a transition can be detected by a discontinuity in the plot. That is to say, the plot has one slope below  $T_g$  and a different slope above  $T_g$ . A homopolymer is found to exhibit one such break. Similarly, a pair of compatible polymers is found to exhibit one  $T_g$  whereas an incompatible pair shows two. Indeed, the index of refraction is not the only property of polymers which behaves

in this manner. The specific volume is a property which behaves in an analogous manner, since it is proportional to the refractive index and plots of this quantity vs. temperature will exhibit one or two  $T_g$ 's again depending on the degree of compatibility.

Another technique capable of detecting second-order transitions is calorimetry. A quick determination of second-order transitions can be made by differential scanning calorimetry. The heat capacity as a function of temperature exhibits a step-wise discontinuity at the glass transition. Again, one  $T_g$  is observed for compatible polymers and two for incompatible polymers. More precise determinations can be made by adiabatic calorimetry, but such determinations are extremely time consuming.

Dynamic-mechanical measurements are another technique capable of measuring transitions in polymers. In this method an oscillating stress is applied to a polymer film and the storage and loss moduli are measured as a function of temperature. Glass transitions are indicated by a drop in the storage modulus or a peak in the loss modulus. As before, two  $T_g$ 's indicate an incompatible system and one, a compatible system.

Dielectric techniques can be employed in the detection of the transition temperatures of polymers or polymer pairs if the polymers have significant dipoles. In this technique the real and imaginary parts of the complex dielectric constant can be measured as a function of temperature and frequency. Compatibility, or the lack of it, can then be determined in a manner analogous to that for the dynamic-mechanical technique.



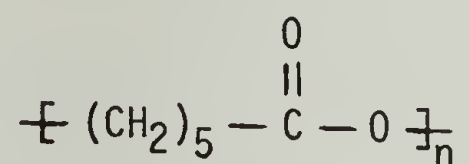
The determination of compatibility by one or more of the aforementioned techniques is by no means without some ambiguity, for there is an instance recorded in the literature where different results have been observed by different techniques applied to the same system.<sup>26</sup> In this case dynamic mechanical measurements indicated two  $T_g$ 's while differential scanning calorimetry (DSC) showed one. There is therefore evidence that the various techniques capable of detecting glass transitions differ in their sensitivity, dynamic mechanical measurements possibly being able to detect smaller phases than DSC measurements. Caution must therefore be exercised in the interpretation of results.

Given the many polymers available today and the variety of techniques at hand for studying compatibility, the compilation of a list of polymers which have been mixed in the bulk phase and the properties of these mixtures is indeed an awesome task. This task has, however, been attempted and, in fact, successfully carried out by Krause.<sup>8</sup> Since the number of compatible polymer pairs listed in the review is strictly limited, it is again emphasized that polymer systems are complicated and that compatible polymer pairs are indeed rare. Their careful study and characterization are an important aspect of polymer science.

#### Polyblends Involving Poly- $\epsilon$ -caprolactone

Recent interest has developed in polyesters prepared by ring-opening polymerization of cyclic lactones. Such polymerizations have been made possible by the development of novel catalysts,<sup>27</sup> and the

interest in these polyesters can be attributed to the uniform orientation of the ester groups in the chain imparting a sense of direction to the chain.<sup>28,29</sup> One of these polyesters is poly- $\epsilon$ -caprolactone (PCL). PCL has the structure



Further interest in this particular polyester has been generated because of claims for favorable compatibility properties of this polymer with other polymers.<sup>30,31,32</sup> The combination of polar and non-polar character together with a low melting point (60°C) make this polymer attractive for blending with other polymers.<sup>30</sup> PCL is said to beneficially modify the properties of certain commercial polymers when blended with these polymers to varying degrees. PCL is claimed to improve film gloss, anti-blocking characteristics, and clarity of polyethylene when blended with it. PCL is also said to improve the dyeability of polyolefin fibers and to lower the brittle temperature of polyvinyl chloride when it is blended with these polymers. The properties of several other polymers are also said to be improved by blending with PCL.<sup>30</sup> Such behavior is not expected in view of the fact that PCL is described as a crystalline polymer. Compatible polymers have classically been limited to amorphous materials in view of the thermodynamic and kinetic difficulties in mixing two polymers. It was this apparent compatibility and peculiar behavior of PCL which precipitated further investigation of this polymer in this work. Polyblends of PCL were therefore prepared, and



the properties of these resultant mixtures determined by differential scanning calorimetry.

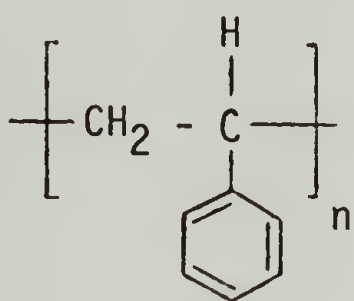
It was also of interest to determine certain physical properties of PCL itself since references to the polymer do not appear in detail in the literature. Such properties would have obvious relevance in regard to polyblends in which PCL is one of the components. Undoubtedly the lack of information concerning PCL is due to its unavailability in high molecular weights prior to recent times. In an attempt to learn more about the physical properties of PCL, dynamic-mechanical and dielectric relaxation studies were performed on the polymer, and its heat of fusion and degree of crystallinity were determined in this work. Such work is described in Chapter II and the properties of some PCL blends with other polymers are described in Chapter III.

#### Polystyrene - Poly(2,6-Dimethyl-1,4-Phenylene Oxide) Blends

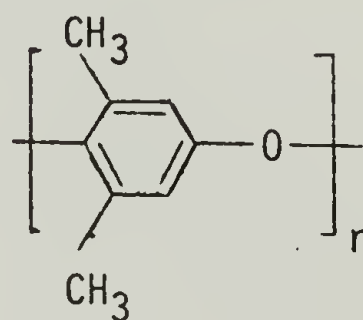
Polymer blends involving polystyrene or various substituted polystyrenes with polyphenylene oxides have also evoked interest in recent times.<sup>33</sup> The unique properties of such blends have led to their achieving commercial status as Noryl resins. Many references have appeared in the literature recently describing the properties of such blends. Largely this work results from efforts to improve the properties of polystyrene. Polystyrene has achieved wide-scale commercial application chiefly because it is inexpensive. However, polystyrene is brittle, not resistant to most organic solvents, and cannot be used at high temperatures; hence, the efforts to improve it.

Blending polystyrene with polyphenylene oxides helps to overcome these disadvantages.

These blends commonly consist of atactic polystyrene (a-PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The structure of these two polymers is shown below



i-PS



PPO

Such blends have been found to be compatible over the entire range of composition in that only one glass transition is observed for the blends of the two polymers by differential scanning calorimetry.<sup>26</sup> Furthermore, blends of the two polymers are said to exhibit certain properties which are improved over that of the individual homopolymers, for example, tensile strength.<sup>33</sup> Some of the disadvantages of polystyrene alone are overcome by the addition of PPO. An interesting point deserving mention here is the observation that studies of these blends have indicated compatible behavior in DSC experiments while at the same time behaving incompatibly in dynamic-mechanical experiments.<sup>26</sup> This observation raises important questions about the sensitivity of various experimental techniques to the detection of polymer compatibility.

It has been found that other polymers may be substituted for atactic polystyrene and PPO in these blends. For example, poly- $\alpha$ -methylstyrene or polychlorostyrene can be substituted for the polystyrene, and halogenated polyphenylene oxides can be substituted for PPO.<sup>33</sup> Such blends invariably consist of amorphous components. The possibility of making a polyblend which contains a crystallizable component is an intriguing one which arose during the course of this work. Surely the properties of such a blend would be of interest and the study of such a blend would be of obvious academic and potential practical importance since such materials are rare.<sup>34,35</sup> For example, it might be expected that crystallization of such a polyblend under the proper conditions would add toughness to films made from the blend material. The obvious candidate for a potentially crystallizable component in such a polyblend is isotactic polystyrene (i-PS) since it is chemically identical to a-PS and differs from it only in tacticity. It was therefore a major purpose of this work to investigate polyblends of isotactic polystyrene (i-PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Among the various matters studied here are preparation of polyblends of i-PS and PPO, crystallization and melting behavior of such blends, studies of their physical properties by DSC and dynamic-mechanical experiments, and studies of their engineering properties.

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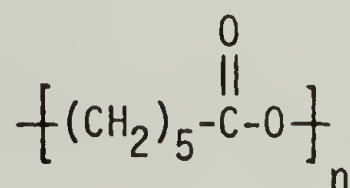
## C H A P T E R   I I

### PHYSICAL PROPERTIES OF POLY- $\epsilon$ -CAPROLACTONE

#### Introduction

Polymerization reactions involving the ring-opening of cyclic lactones to novel polyesters have been successfully carried out. Such success is attributed to the development of new catalysts.<sup>1</sup> Polyesters obtained by these novel methods are uniquely different from those obtained by classical condensation techniques involving dibasic acids and diols. In classical polyesters the dipole components of the ester groups along the chain axis cancel each other. Such is not the case in these novel polyesters where the dipole components parallel to the chain axis reinforce one another.<sup>2,3</sup> This work is concerned with one of these new polyesters — poly- $\epsilon$ -caprolactone (PCL).

PCL has the structure



This polymer is of special interest in this work since claims have been established for favorable compatibility properties of this polymer with other polymers. PCL is said to beneficially modify the properties of certain commercial polymers when blended with these polymers to varying degrees.<sup>4,5,6</sup>

The thermodynamic<sup>7,8</sup> and relaxational<sup>5</sup> properties of PCL have been determined. From these studies it is known that PCL is a crystalline polymer whose melting point is 63°C. Differential scanning calorimetry (DSC) and X-ray diffraction experiments indicate that the polymer cannot be made totally amorphous, however quenching into liquid nitrogen does decrease the degree of crystallinity by 15-20%.<sup>5</sup> The amorphous phase displays a glass transition at -64°C.<sup>8</sup> In addition a lower temperature transition has been observed in mechanical loss experiments using a torsion pendulum at about -120°C.<sup>5</sup> A definite assignment of this peak to a particular relaxation mechanism has not been made. Additionally, the crystal structure of PCL has been investigated,<sup>9,10</sup> as well as its infrared absorption<sup>11</sup> and hydrodynamic properties.<sup>12</sup> Recently the dielectric properties of PCL solutions have been reported.<sup>13,14</sup> This work seeks to add further information regarding the physical properties of PCL by means of dynamic mechanical and dielectric relaxation studies over a wide range of frequency and temperature for the purpose of further characterizing the polymer. The heat of fusion of PCL was also determined. The results of the heat of fusion study are included separately in Appendix A since this determination has already been reported by Crescenzi, et al.<sup>7</sup>

### Experimental

A sample of PCL was obtained through the courtesy of the Union Carbide Corporation. This polymer is designated PCL-700 and was used as received after it was determined that purification of the polymer



had no appreciable effects on its dielectric relaxation properties. The number average molecular weight of this polymer was 8,050 as measured by vapor phase osmometry.

Samples were prepared for measurements by compression molding into films suitable for dynamic mechanical and dielectric testing. Those samples studied were prepared by compression molding the polymer at 80°C followed by slow cooling to room temperature in the press. Samples were subsequently annealed at room temperature for a few days prior to testing.

The dynamic mechanical measurements were made using a Vibron dynamic viscoelastometer, model DDV II (Toyo Instrument Co.), at three frequencies, 3.5, 11, and 110 Hz, over the temperature range -160 to 65°C. Temperature variation was achieved in these experiments by cooling with liquid nitrogen to -160°C and then heating to the higher temperatures.

The mechanical loss tangent,  $\tan \delta$ , was read directly from the apparatus, and the complex modulus,  $E^*$ , the real component of the complex modulus,  $E'$ , and the imaginary component,  $E''$ , were calculated from the following equations:

$$E^* = \frac{L}{F} \cdot \frac{2 \times 10^9}{A \cdot DF}$$

$$E' = E^* \cos \delta$$

$$E'' = E^* \sin \delta$$

where  $A$  is the cross-sectional area of the sample in  $\text{cm}^2$ ,  $L$  is the

strain,  $DF$  is the dynamic force, and  $A$  is a factor associated with the amplitude of the force. Calculations were performed by computer, and the program used is included in Appendix C.

The dielectric measurements were made using a General Radio Capacitance Measuring Assembly (Type 1620 A) which operates on a transformer ratio-arm bridge technique.<sup>15</sup> Capacitance and  $\tan\delta_\epsilon$  or conductance were measured at frequencies of 100, 500, 1000, 5000, and 10,000 Hz over a temperature range of -140 to 65°C. Measurements below room temperature involved the use of a Balsbaugh LD-3, three terminal, dielectric cell with specially constructed 53 mm diameter, circular electrodes. Measurements were made in the sequence of descending temperature. Temperature variation was achieved by passing dry nitrogen gas through a copper coil, which was immersed in liquid nitrogen, and varying the flow rate of the gas, i.e., the higher the flow rate, the greater the cooling. Temperature stability of  $\pm 0.5^\circ\text{C}$  was achieved. Measurements above room temperature were made using a specially designed, two terminal stainless steel cell with 53 mm diameter, circular electrodes. Temperature variation was achieved by immersing the cell in an oil bath and heating the oil. Regulation of  $\pm 0.1^\circ\text{C}$  was possible. Electrodes of about 50 mm diameter were cut from aluminum sheets into circles and attached to the samples on both sides. A thin layer of silicone grease was applied to the sample to insure good contact between the sample and the electrodes. The grease did not affect the measurements. Corrections were made for d.c. conductance at high temperatures by measuring d.c. resistance in the range  $10^6 - 10^{12}$  ohms using a

General Radio Megohmmeter (Type 1862-A) and employing the correction when d.c. resistance was less than  $10^9$  ohms.

The following equations were used to calculate the dielectric constant,  $\epsilon'$ , the dielectric loss factor,  $\epsilon''$ , and the ratio  $\epsilon''/\epsilon' = \tan\delta_\epsilon$ :

$$\epsilon' = C_p/C_0$$

$$\epsilon'' = J/\omega C_0 = 1/R\omega C_0 = 1/2\pi f C_0 R$$

$$\tan\delta_\epsilon = \epsilon''/\epsilon' = J/\omega C_p = 1/2\pi f R C_p$$

where  $C_p$  is the capacitance of the cell containing a sample,  $C_0$  is the capacitance of the cell containing air,  $f$  is the frequency,  $J$  is the conductivity of the sample, and  $R$  is the resistance of the sample. Corrections were made for the use of aluminum electrodes, edge effect, high  $\tan\delta_\epsilon$  readings (greater than 0.1), and d.c. conductivity when necessary.

When using the high temperature cell (that is, above room temperature), the use of aluminum electrodes is involved. The ratio of the area of the electrode of the test cell,  $A_e$ , to the area of the aluminum electrode,  $A_{Al}$ , was the correction factor for  $\epsilon'$  and  $\epsilon''$ . Furthermore, the absence of a third electrode requires the subtraction of the edge capacitance,  $C_e$ , from the capacitance of the sample,  $C_p$ . When  $\tan\delta_\epsilon$  readings exceed 0.1, it is necessary to calculate  $\epsilon'$  from the following equation:

$$\epsilon' = \frac{C_p}{C_0} \left[ \frac{1}{1 + (\tan \delta_\epsilon)^2} \right] \frac{A_e}{A_{A1}}$$

Again, calculations were performed by computer and the program used is included in Appendix B.

## Results and Discussion

Degree of crystallinity. The degree of crystallinity of PCL was determined by DSC and X-ray diffraction techniques. DSC thermograms for both annealed and quenched PCL are shown in Figure 1. The annealed sample was kept at room temperature for a few days prior to testing. The quenched sample was cooled from the melt into liquid nitrogen just prior to the experiment. It is apparent from these thermograms that the quenched PCL has less crystallinity than the annealed PCL, but it was impossible to quench the PCL to a completely amorphous condition. Using 26.4 cal/g for the heat of fusion of PCL (as discussed in Appendix A) and the areas under the DSC melting curves, 19.8 and 14.3 cal/g for the annealed and quenched samples, respectively, degrees of crystallinity of 0.75 and 0.54 were found. Using the value of 32.3 cal/g determined by Crescenzi, et al.,<sup>7</sup> for the heat of fusion, degrees of crystallinity of 0.61 and 0.44 were found for the annealed and quenched samples, respectively.

A further observation can be made from the DSC studies. The annealed PCL displays a single, distinct melting peak, as is normally expected, while the quenched PCL displays a peak having a distinct shoulder. Such a peculiarity was also observed by Crescenzi, et al.<sup>7</sup>



Considerable controversy exists as to the molecular origin of such anomalies. It is reasonable to postulate that in this case quenching may cause the PCL to assume two different crystal forms - an imperfect type resulting from the unusually rapid crystallization and the normal, more perfect type. This explanation can perhaps be substantiated by evidence based on annealing experiments. For example, five minutes annealing at 40°C prior to further heating causes the melting peak to change shape somewhat. Fifteen minutes annealing at 40°C causes the melting peak to return almost to its normal shape. Thermograms for these experiments are shown in Figures 2 and 3 and are taken as evidence in support of the above-mentioned explanation.

Wide angle X-ray scattering curves for similar annealed and quenched PCL samples are shown in Figures 4 and 5 respectively. The X-ray scattering curve obtained here bears a distinct resemblance to that for polyethylene (see, for example, Billmeyer<sup>16</sup>). Such a result is to be expected in view of studies of the crystal structure of PCL which show that it is indeed similar to polyethylene.<sup>9,10</sup> The most prominent peak in the scattering curve corresponds to the 200 reflection. Quenching here seems to have reduced the crystalline content of the PCL by approximately the same amount as in the DSC experiments. The degree of crystallinity can be determined from these curves if the contribution of the amorphous polymer to the total scattering can be determined. This contribution is not easily evaluated, but it can be estimated as an amorphous "halo" - a curved line in the scattering curve connecting the minima and eliminating the two prominent peaks.

If the area under this halo is subtracted from the total area under the entire curve, the crystalline contribution to the scattering is determined. The ratio of this crystalline contribution to the entire area under the curve is then the degree of crystallinity. Using this technique, degrees of crystallinity of 0.73 and 0.50 were estimated for annealed and quenched PCL, respectively. In general, these estimations do not agree very closely with the theoretical estimation of Koleske and Lundberg<sup>5</sup> who predicted 0.50 for annealed PCL, and it is concluded that their estimation is probably too low. The values obtained here would seem to be the minimum possible values since a maximum amorphous halo is assumed. The results obtained here are summarized in Table I.

Dielectric properties. The results of the dielectric relaxation studies are shown in Figures 6 and 7. These plots show  $\epsilon'$  and  $\epsilon''$  vs. temperature for three frequencies, 0.10, 1.0, and 10 kHz. In most cases measurements were made for five frequencies, supplementary data being omitted from the figures for the sake of clarity. Three relaxation regions are evident as previously reported:<sup>5</sup> one in the region of 60°C, another in the region around -50 to -60°C, and still a third, a low temperature relaxation, in the region -90 to -120°C depending on the frequency. The 60°C relaxation has previously been assigned to the melting transition of the polymer,<sup>5</sup> and the -50 to -60°C relaxation has likewise been assigned to the main glass transition process.<sup>5</sup> This latter relaxation peak will be designated the  $\beta$  peak in this work. The low temperature peak will be designated the  $\gamma$  peak in accordance with usual practice.

The  $\beta$  peak. In order to help confirm the assignment of the glass transition process to the  $\beta$  peak the apparent activation energy for the process was determined from a plot of  $\log f$  vs.  $1/T$  as shown in Figure 8. The straight line obtained is indicative of Arrhenius character. There is no WLF curvature apparent. From this plot an activation energy of 152 kcal/mole was found. Such a value is consistent with a process involving relatively large scale segmental motions, and therefore the assignment of this process as the main glass transition is confirmed.

Further confirmation of this assignment can be seen from examining dielectric relaxation data for PCL which has had water added to it. Figure 9 shows dielectric relaxation data for PCL which was soaked in distilled water for 24 hours prior to measurement. Careful study of the  $\beta$  transition shows that the presence of water in the sample decreases the temperature of this transition slightly. For 10 kHz, for example, the temperature of the transition peak in the  $\epsilon''$  plot is seen to decrease from  $-53.5^\circ\text{C}$  to  $-58.0^\circ\text{C}$ . Similar effects are observed for the other frequencies studied. Water obviously acts as a "plasticizer" for this transition process, consistent with similar effects observed in other polyesters for the glass transition process (for example, polyethylene terephthalate).<sup>17</sup>

The  $\gamma$  peak. The origin of the low temperature relaxation process is of obvious interest. This relaxation process has heretofore not been assigned to a particular molecular mechanism. Such processes have in the past been attributed to a wide variety of molecular or segmental



motions.<sup>17</sup> Possibilities include such motions as the "crankshaft" mechanism for polymers containing sequences of  $\text{-CH}_2\text{-}$  groups or complicated involvement of the polymer with low molecular weight impurities such as unreacted monomer, low molecular weight polymer, solvent, or even absorbed water. Such relaxations in polyesters have even been attributed in the past to end groups.<sup>18</sup>

The activation energy for this process was determined as shown in Figure 8 and was found to be 11 kcal/mole. Again, a straight line relationship was obtained in this plot. Such a value is of the order usually observed for such low temperature relaxations. In fact, Schatzki estimated a value of about 13 kcal/mole for the crankshaft mechanism.<sup>17</sup> Some recent evidence has however tended to cast doubt on the crankshaft mechanism per se.<sup>19</sup> Furthermore, significant dielectric loss implies relaxation of a polar region of the molecule, i.e., the COO group must be involved, possibly as the end result of some type of crankshaft motion.

The effect of unreacted monomer, low molecular weight polymer, or solvent on this peak was investigated by performing dielectric relaxation experiments on purified and dried polymer. The PCL was dissolved in methyl ethyl ketone and precipitated from solution with methanol. After thorough drying in vacuo the dielectric relaxation data are essentially the same as those shown for the polymer as received in Figures 5 and 6, apparently eliminating from consideration those effects aforementioned.

The possibility that the low temperature relaxation may be related to the presence of water was next investigated (see Figure 9).



The only apparent effect of water on the low temperature peak is to cause this peak to more closely merge with the glass transition peak. The glass transition is shifted to lower temperature while the  $\gamma$  peak is shifted to higher temperature. In the 10 kHz data the low temperature loss peak is not resolvable as a distinct relaxation process. The low temperature relaxation process is thus affected by the presence of water, but it is obviously not due to the presence of water since the relaxation peak is more obvious in the dry samples. The origin of the low temperature relaxation process remains unknown as does the specific role that water plays here. Further investigation of the phenomenon could be attempted through chemical modification of the polymer. The introduction of large substituent groups onto the hydrocarbon portion of the molecule is one possibility for further looking into the crankshaft mechanism. It is perhaps a greater possibility though that the relaxation is due to small motions of the chain involving the COO groups.

The intensities of the relaxations. Further information can be obtained by considering the intensities of the relaxations - the areas under the loss peaks. These areas can be obtained from consideration of the following equation<sup>15</sup>

$$(\epsilon_R - \epsilon_U)_{T_{\max}} = \frac{2\Delta H}{\pi R} \int \epsilon'' d(1/T)$$

In this equation  $\epsilon_R$  and  $\epsilon_U$  refer to the relaxed (low frequency) and unrelaxed (high frequency) dielectric constants and  $\Delta H$  is the activation energy for the process. The intensity of the relaxation is then  $(\epsilon_R - \epsilon_U)_{T_{\max}}$ , the value of  $(\epsilon_R - \epsilon_U)$  at the temperature corresponding

to the maximum in a plot of  $\epsilon''$  vs.  $1/T$ . The latter two quantities can be evaluated from a plot of  $\epsilon''$  vs.  $1/T$  using the assumption that  $\epsilon' = (\epsilon_R - \epsilon_U) / 2$  at the temperature maximum. Such a plot is shown in Figure 10 for 0.10 kHz. From this plot it is found that for the  $\beta$  peak  $\epsilon_R = 2.879$ ,  $\epsilon_U = 2.094$ , and  $\epsilon_R - \epsilon_U = 0.785$ . For the  $\gamma$  peak  $\epsilon_R = 2.12$ ,  $\epsilon_U = 1.99$ , and  $\epsilon_R - \epsilon_U = 0.13$ . These results were found to be essentially independent of frequency. The use of a constant value for  $\Delta H$  is common practice in view of the temperature range covered. The customary WLF curvature would undoubtedly become apparent over an extended range of temperature. The results obtained here are consistent with those observed for polyesters in general. The magnitude of the peak is observed to increase with the addition of water to the polymer. Such an effect probably is indicative of the water interacting with the COO groups and helps to confirm the  $\gamma$  transition as due to limited motions involving those groups.

If it is assumed that there is a Cole-Cole distribution of relaxation times  $\tau$  in which

$$\epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_U + [(\epsilon_R - \epsilon_U) / 1 + (i\omega\tau_0)^\beta],$$

where  $\tau_0$  and  $\beta$  are empirical parameters, the values of  $\epsilon_R - \epsilon_U$  obtained can be combined with the maximum amplitude  $\epsilon''_{\max}$  to calculate  $\beta$  from

$$\tan \beta \left( \frac{\pi}{4} \right) = \frac{2 \epsilon''_{\max}}{\epsilon_R - \epsilon_U}$$

Such an analysis with  $(\epsilon_R - \epsilon_U) = 0.785$  and  $\epsilon''_{\max} = 0.0392$  yields a value for  $\beta$  of 0.13. Such a value is indicative of a broad distribution

of relaxation times as might be expected for a semicrystalline polymer.

Dynamic-mechanical experiments. The results of dynamic-mechanical experiments performed at three frequencies are shown in Figures 11 to 13. The data are in general agreement with the dielectric results discussed here and also with the torsion pendulum results of Koleske and Lundberg.<sup>5</sup> The  $\beta$  and  $\gamma$  peaks are clearly present. The  $\gamma$  peak is however of less apparent magnitude in comparison with the  $\beta$  peak than it is in the dielectric measurements. This fact lends further credence to the involvement of the dipolar ester group in the  $\gamma$  relaxation process. The temperatures at which the loss peaks occur are shifted to higher temperatures in the dynamic-mechanical experiments. Such results are the opposite of what is normally observed where the lower frequency dynamic-mechanical peaks occur at lower temperatures.<sup>20</sup> The reason for this unusual observation is not clear.

The activation energies for the relaxation processes were determined in the same manner as for the dielectric results. The activation energy plots are shown in Figure 14. Values of 36 and 6 kcal/mole were found for the  $\beta$  and  $\gamma$  processes, respectively. Such values are in general agreement with those obtained from the dielectric experiments as is usually the case.<sup>18</sup>

Comparison of PCL properties with other polymers. It is of obvious interest to examine in greater detail how the orientation of dipoles in the PCL chain might give rise to the dielectric relaxation of the polymer. Unlike polyethylene terephthalate (PET) and other polyesters prepared by condensation polymerization or step growth techniques



involving dibasic acids and dialcohols, PCL is prepared from  $\epsilon$ -caprolactone by a ring opening, chain growth mechanism. This difference in preparation leads to a fundamental difference in the structure of PCL when compared to the "conventional" polyesters as discussed in the introduction to this chapter. In PCL the components of the COO dipole moment parallel to the chain axis reinforce one another. Classically, in conventional polyesters the dipole components parallel to the chain cancel each other out. This difference is illustrated in Figure 15 for PET and PCL. The question naturally arises as to how the dielectric properties of PCL might differ from those of PET and the other conventional polyesters because of this difference.

What of the components of the dipole moments perpendicular to the chain axis? As depicted in Figure 15, these components appear to cancel each other out for both PET and PCL. It must be remembered however that there is free rotation possible about every single bond illustrated, including the carbon bond to the benzene ring,<sup>21</sup> and therefore chain conformations can be obtained with dipole reinforcement perpendicular to the chain axis. In this regard both polymers must be considered similar. In light of the difference discussed above, the dielectric properties of PET are next compared with those of PCL.

PET is by far the most widely studied polyester because of its commercial importance. It is a crystallizable polymer with a melting point of 260°C. Unlike PCL, PET can be made totally amorphous. For the crystalline polymer  $T_g$  occurs in the region of 80°C. Two relaxation peaks are observed in dielectric studies of partially crystalline



PET.<sup>18</sup> At a frequency of 100 c/s the  $\alpha$  peak occurs near 100°C, its exact location depending on the degree of crystallinity of the polymer, and the  $\beta$  peak occurs near -50°C. The  $\alpha$  peak is associated with the main glass transition process, and the  $\beta$  peak is attributed to limited motions of the polymer chain. Reddish<sup>18</sup> found that for partially crystalline PET,  $\tan \delta_\epsilon$  was about 0.02 at the  $\alpha$  peak and about 0.01 at the  $\beta$  peak at a frequency of 100 c/s.

For PCL at the same frequency,  $\tan \delta_\epsilon$  was found in this work to be approximately 0.01 for the  $\beta$  peak and about 0.009 for the  $\gamma$  peak. The low temperature loss peaks are then comparable in loss (at least in so far as the  $\tan \delta_\epsilon$  peak height is concerned), but the  $\alpha$  loss is only about one-half as great in PCL as it is in partially crystalline PET. This difference could be accounted for by two possible explanations: 1) the PET sample might be less crystalline than the PCL sample, or 2) PET may have a higher concentration of dipoles than PCL, or perhaps some combination of the two. Reddish<sup>18</sup> does not list the crystallinity of his sample. The sample is merely stated to be crystalline PET. One source<sup>22</sup> quotes the maximum crystallinity of PET as 60%. Such a degree of crystallinity is comparable to that in PCL. It is therefore likely that the difference in dielectric relaxation behavior between the two polymers can be attributed to a higher concentration of dipoles in PET. The higher concentration of dipoles in PET is due primarily to the small number of methylene groups (two) in the ethylene glycol residues which separate the terephthalic acid residues. In PCL five methylene groups separate the dipoles along the chain.

Further information can be obtained by comparing the magnitudes of the glass transition relaxation peaks of the two polymers since the magnitude of the relaxation is proportional to the number of relaxing species per unit volume. Ishida, et al.,<sup>21</sup> report a value of about 0.7 for the magnitude of the  $\beta$  relaxation of PET (independent of temperature and frequency). This value is close to that found for PCL in this work, 0.785, at a frequency of 0.10 kHz. Ishida, et al.,<sup>21</sup> give the degree of crystallinity of their sample as 0.51, similar again to that of PCL. These results would tend to support the conclusion that the  $T_g$  relaxations in PET and PCL are similar indeed. The possibility remains of a slightly stronger relaxation in PET due to a higher concentration of dipoles. For the low temperature process Ishida, et al.,<sup>21</sup> obtain 0.3 - 0.4 for the magnitude of the relaxation, somewhat higher than the 0.13 obtained for PCL in this work. Such a difference is once again consistent with the involvement of the ester dipoles in the low temperature relaxation process coupled with a greater concentration of dipoles in PET. There is no evidence at present to indicate significant additional dielectric behavior in PCL due to its unique structural difference from other polyesters.

It is instructive to further compare the dielectric results obtained here to those for ethylene-carbon monoxide copolymers. Such polymers are similar in structure to PCL except they are lacking the oxygen in the chain backbone. Such results have been reported by Phillips, et al.,<sup>23</sup> for low density polyethylene containing small amounts of carbonyl groups. Specifically, for a polymer containing

1.0 mole per cent carbonyl groups, three relaxations are observed. The  $\alpha$  peak is attributed to relaxations in the crystalline regions. The  $\beta$  peak is suggested to be due to motions in the amorphous phase. The  $\gamma$  peak was found to have an activation energy of 14.3 kcal/mole, comparable to that for PCL. It is suggested that the  $\gamma$  peak may be due to motions of a limited portion of the chain involving perhaps five carbon atoms which include the CO group. The value of  $\tan \delta_{\epsilon}$  at the  $\gamma$  peak for 10 kHz is about 0.003, considerably less than the value of 0.012 observed for PCL. Such a difference is reasonable in view of the higher concentration of ester groups in PCL, lending still further evidence for the involvement of the polar group in this relaxation.

In summary, the dielectric relaxation properties of PCL were determined over a wide range of frequency and temperature and were found to be in general agreement with the properties of similar polymers. Some enhanced dielectric activity was observed for PCL because of the added contribution of the dipole component of the ester group parallel to the chain axis.

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Table I

## Degree of Crystallinity of PCL

DSC	X-ray (Wilusz)
melting curves and heat of fusion of Wilusz	annealed - 0.73 quenched - 0.50
annealed - 0.75 quenched - 0.54	.
melting curves of Wilusz heat of fusion of Crescenzi, et al. <sup>7</sup>	.
annealed - 0.61 quenched - 0.44	.

Theoretical (Koleske and Lundberg<sup>5</sup>)

annealed - 0.50  
quenched - <0.50

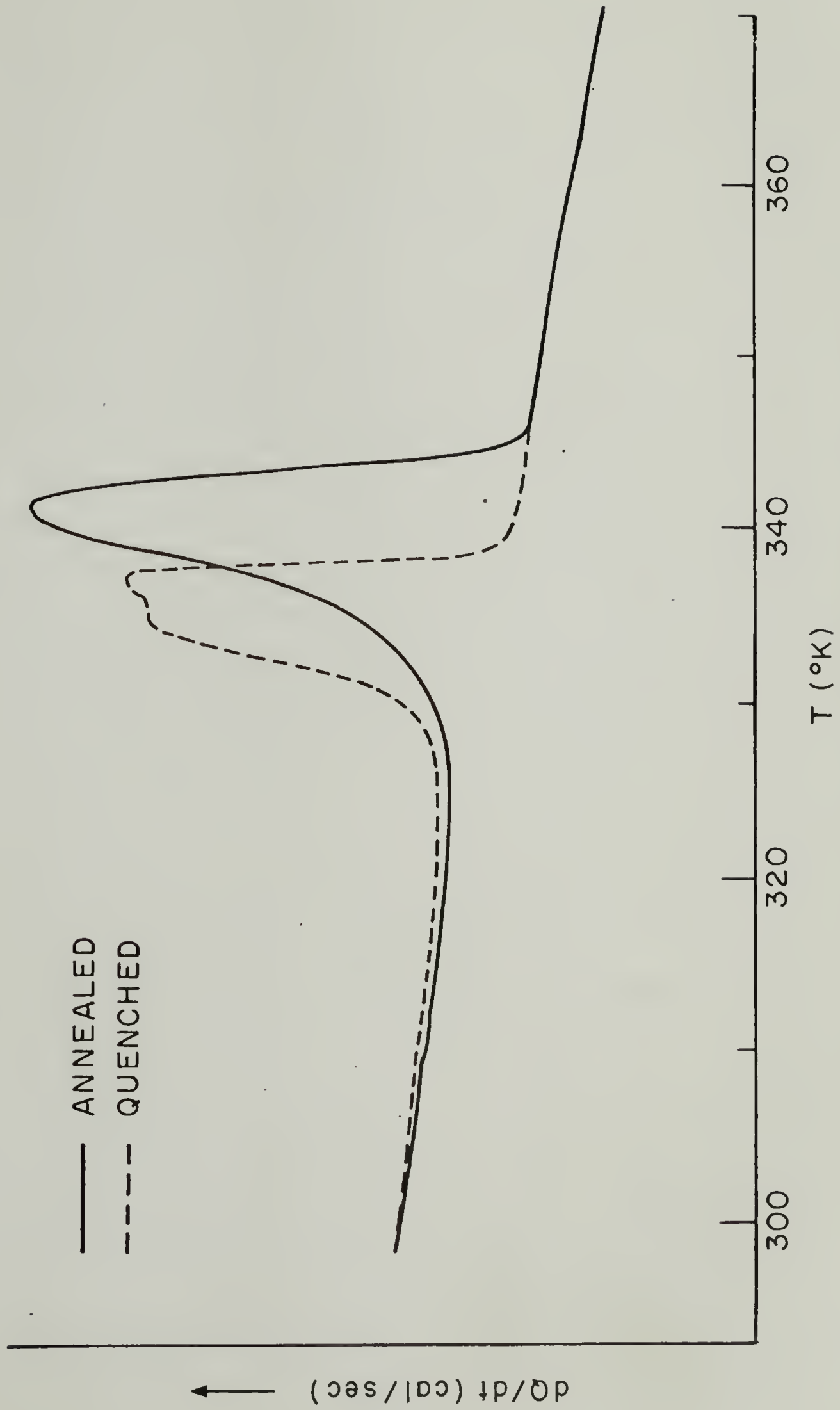


Fig. 1. DSC thermograms for annealed and quenched PCL

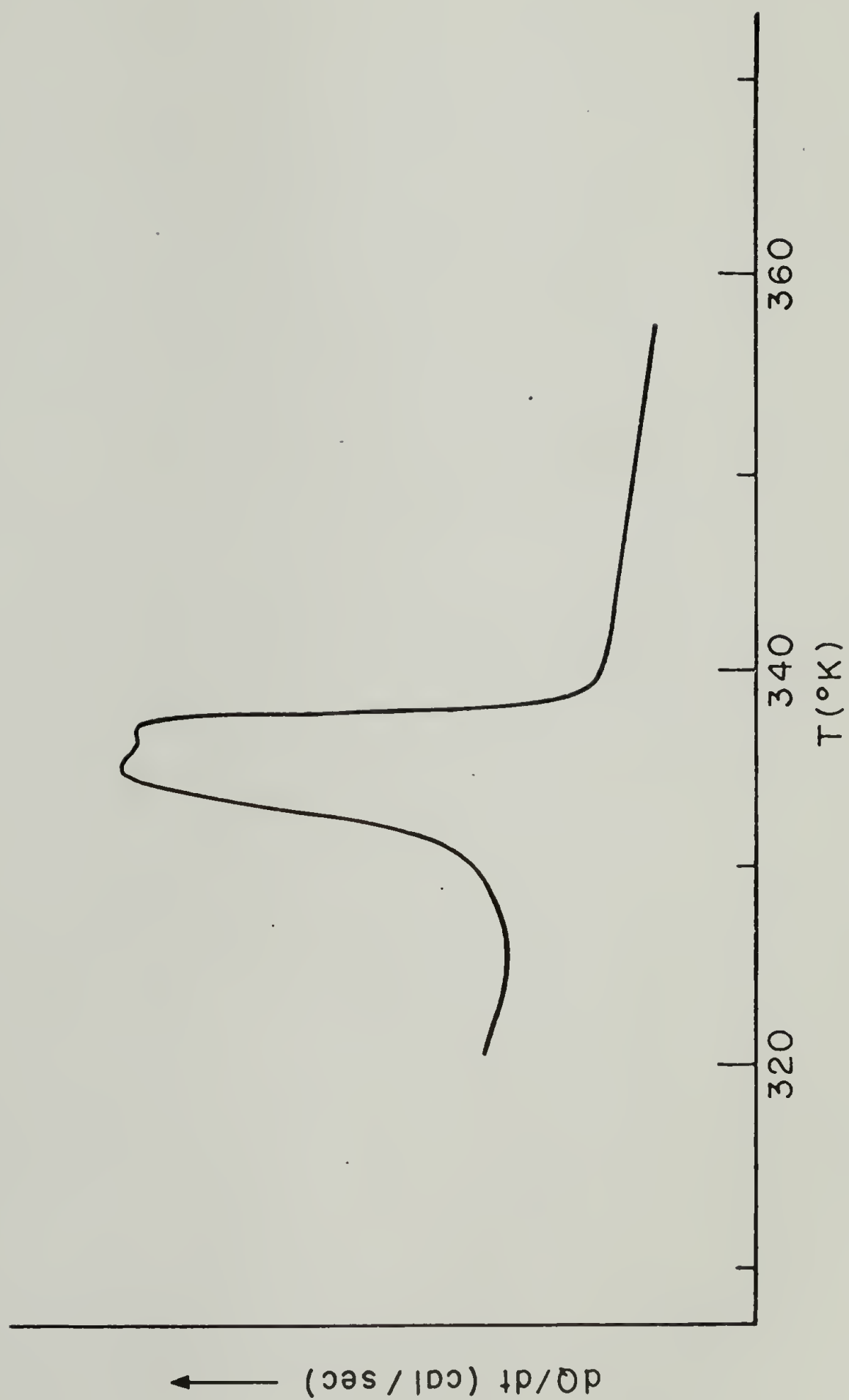


Fig. 2. DSC thermogram for PCL annealed at 40°C for 5 minutes



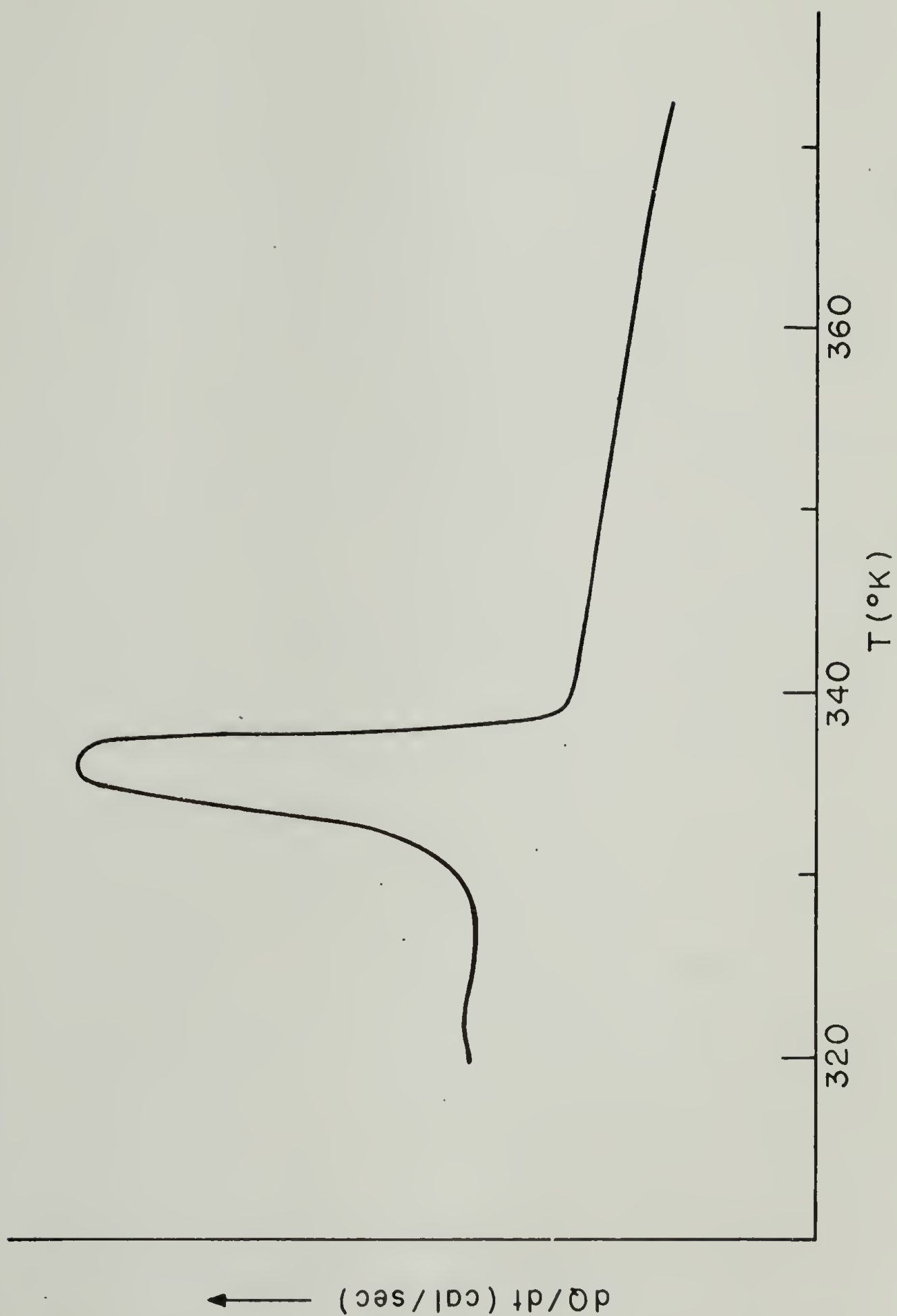


Fig. 3. DSC thermogram for PCL annealed at  $40^{\circ}\text{C}$  for 30 minutes

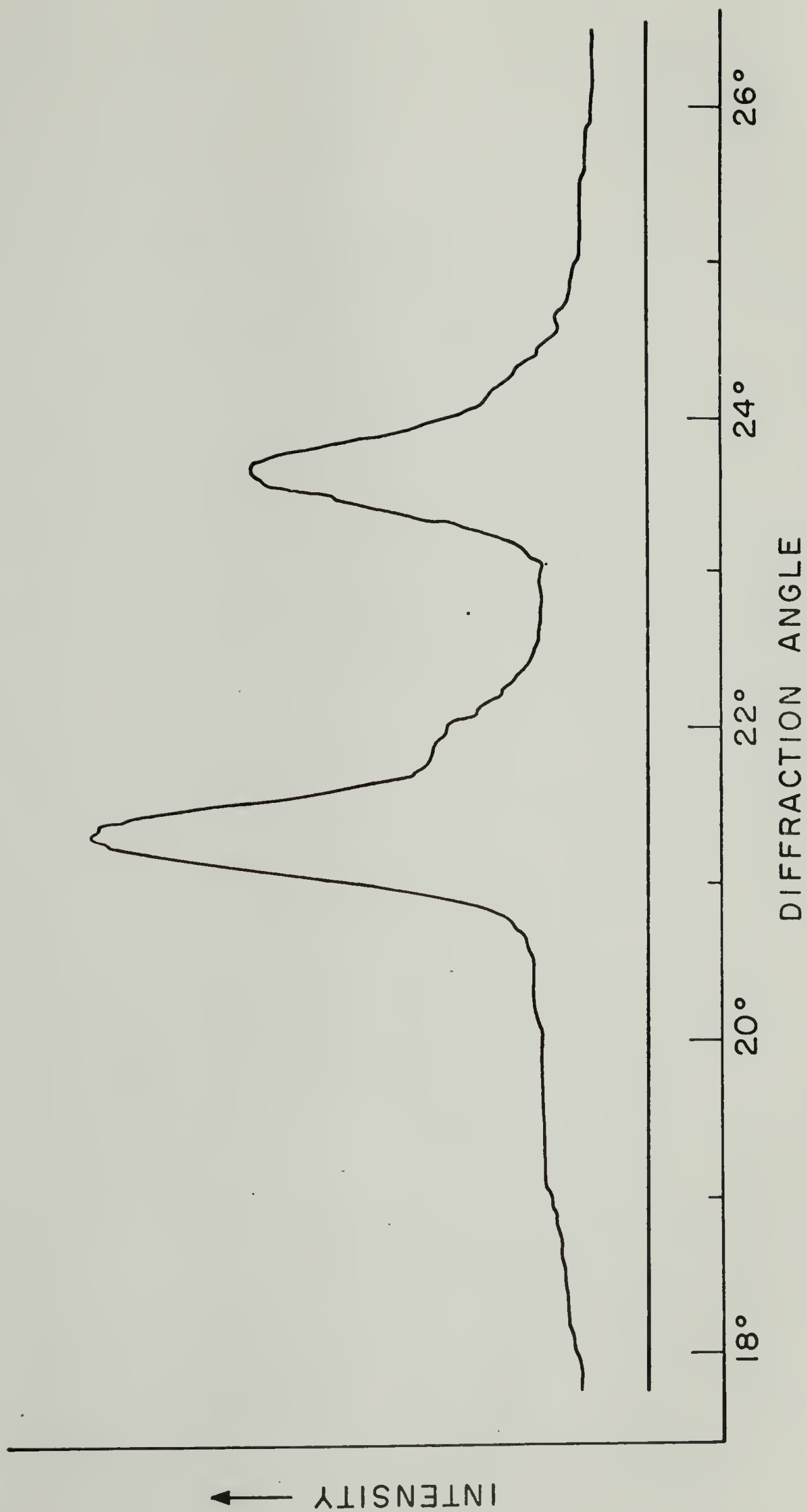


Fig. 4. X-ray scattering curve for annealed PCL

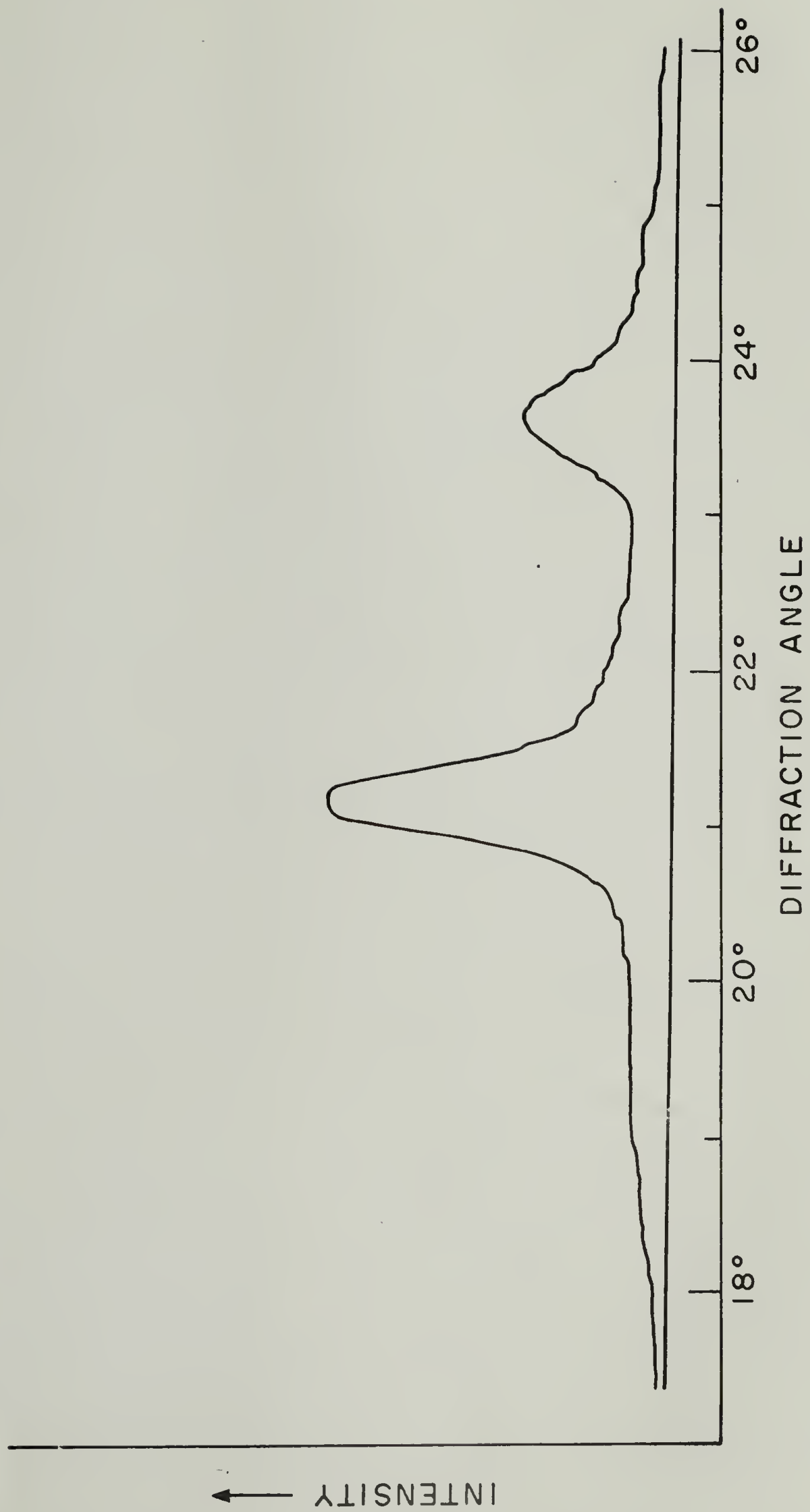


Fig. 5. X-ray scattering curve for quenched PCL

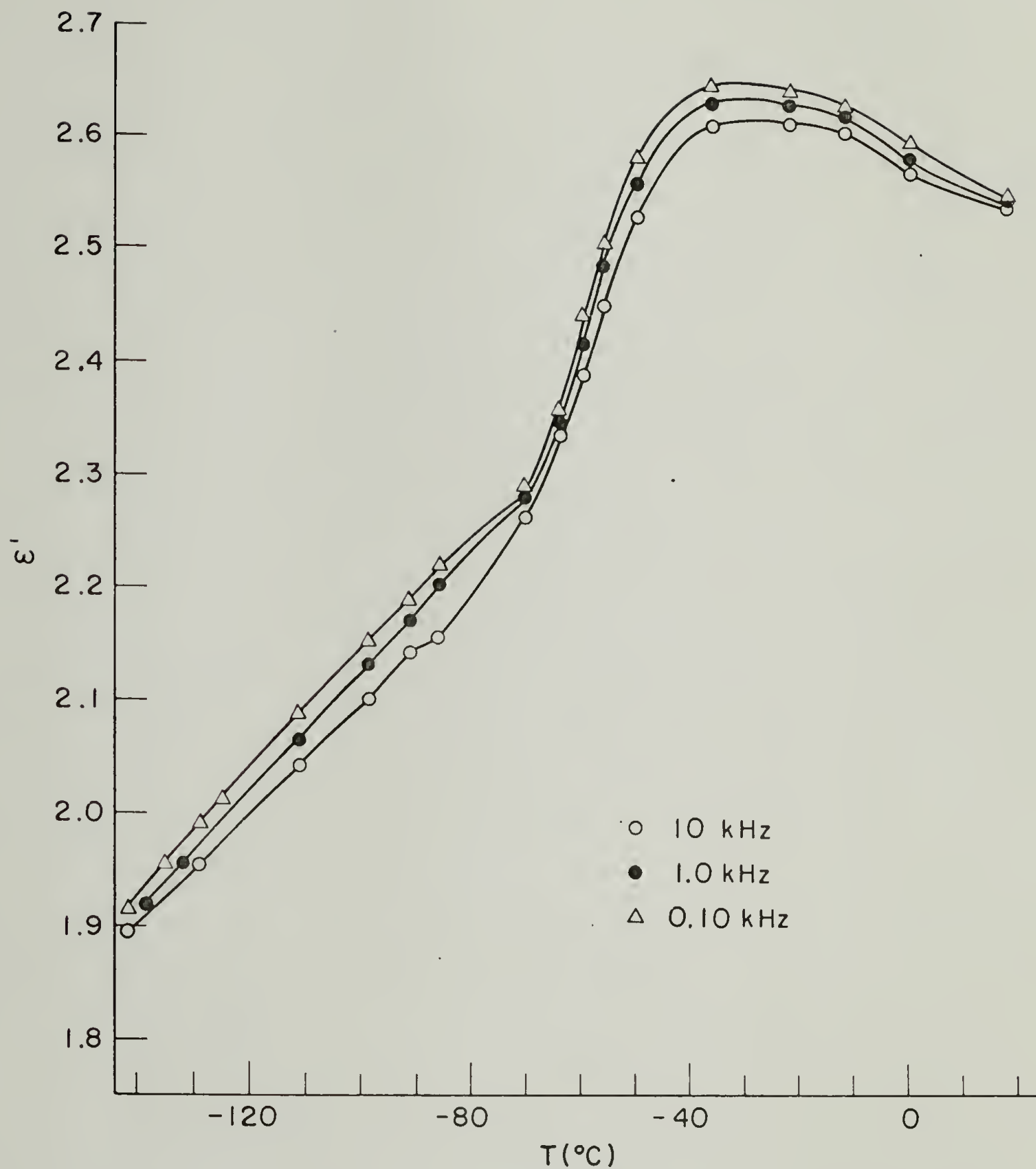


Fig. 6. Dielectric constant for PCL as a function of temperature at frequencies of 0.1, 1.0, and 10 kHz



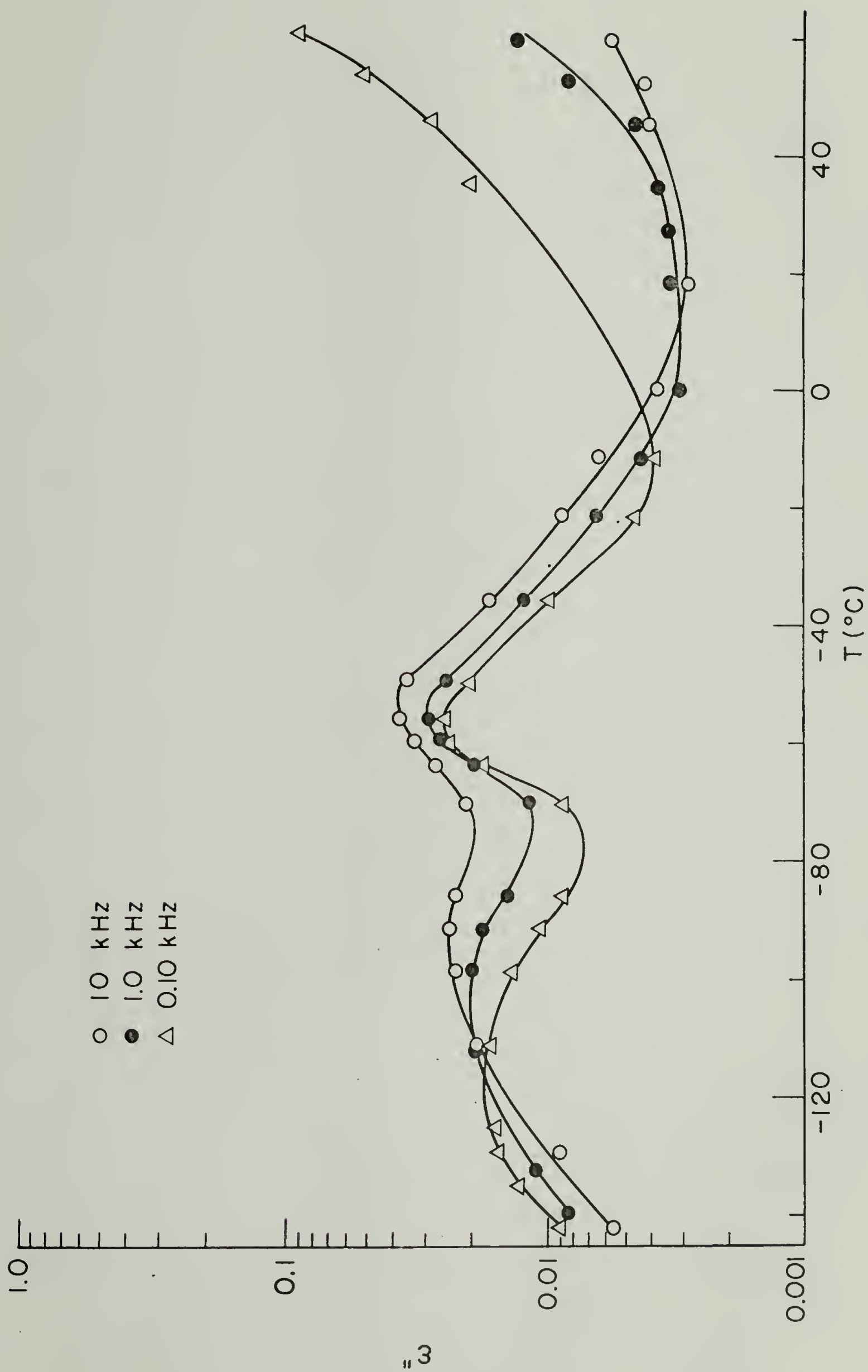


Fig. 7. Dielectric loss for PCL as a function of temperature at frequencies of 0.1, 1.0, and 10 kHz

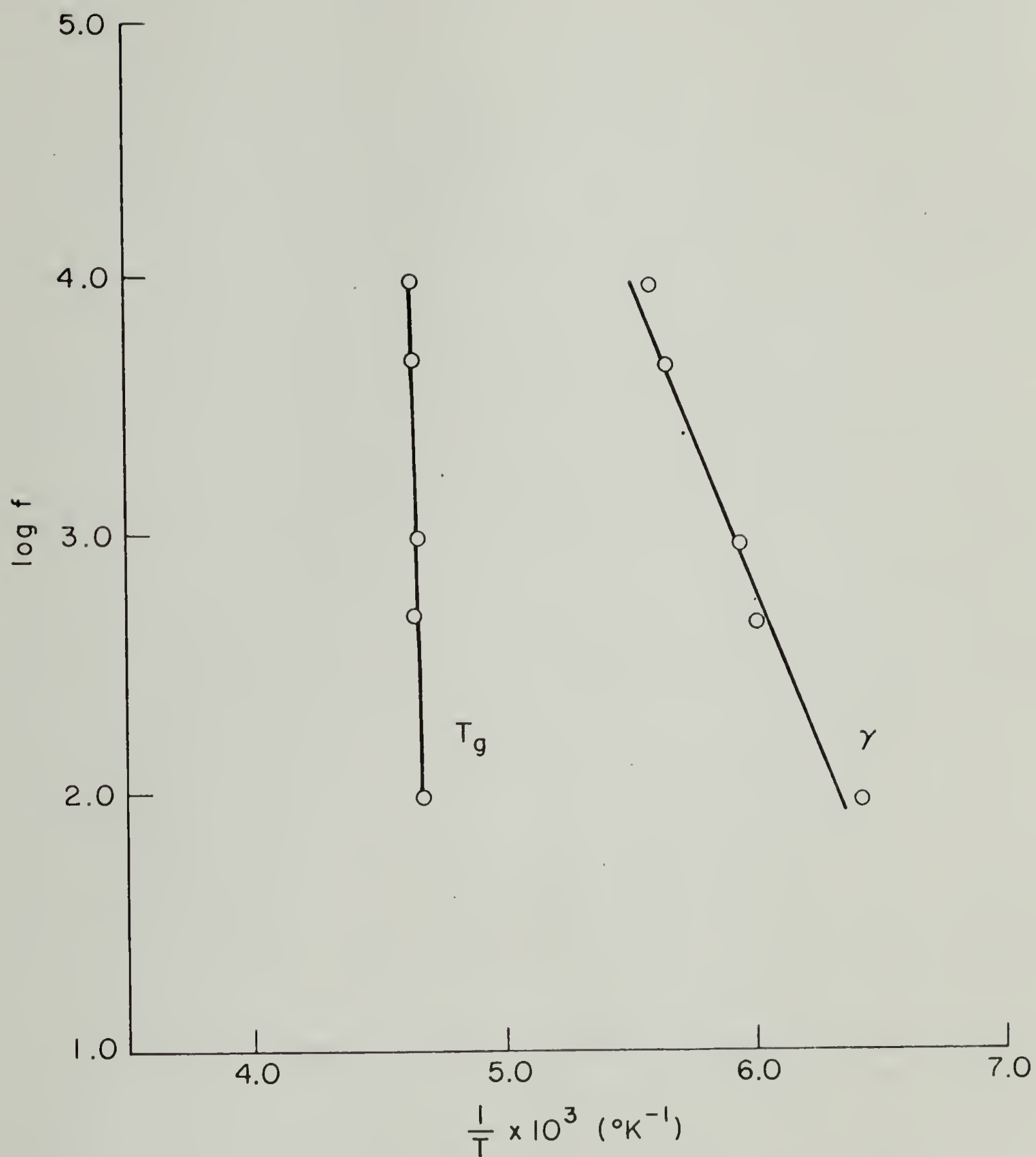


Fig. 8. Plot of  $\log f$  against  $1/T$  for the dielectric relaxation loss tangent maxima for PCL

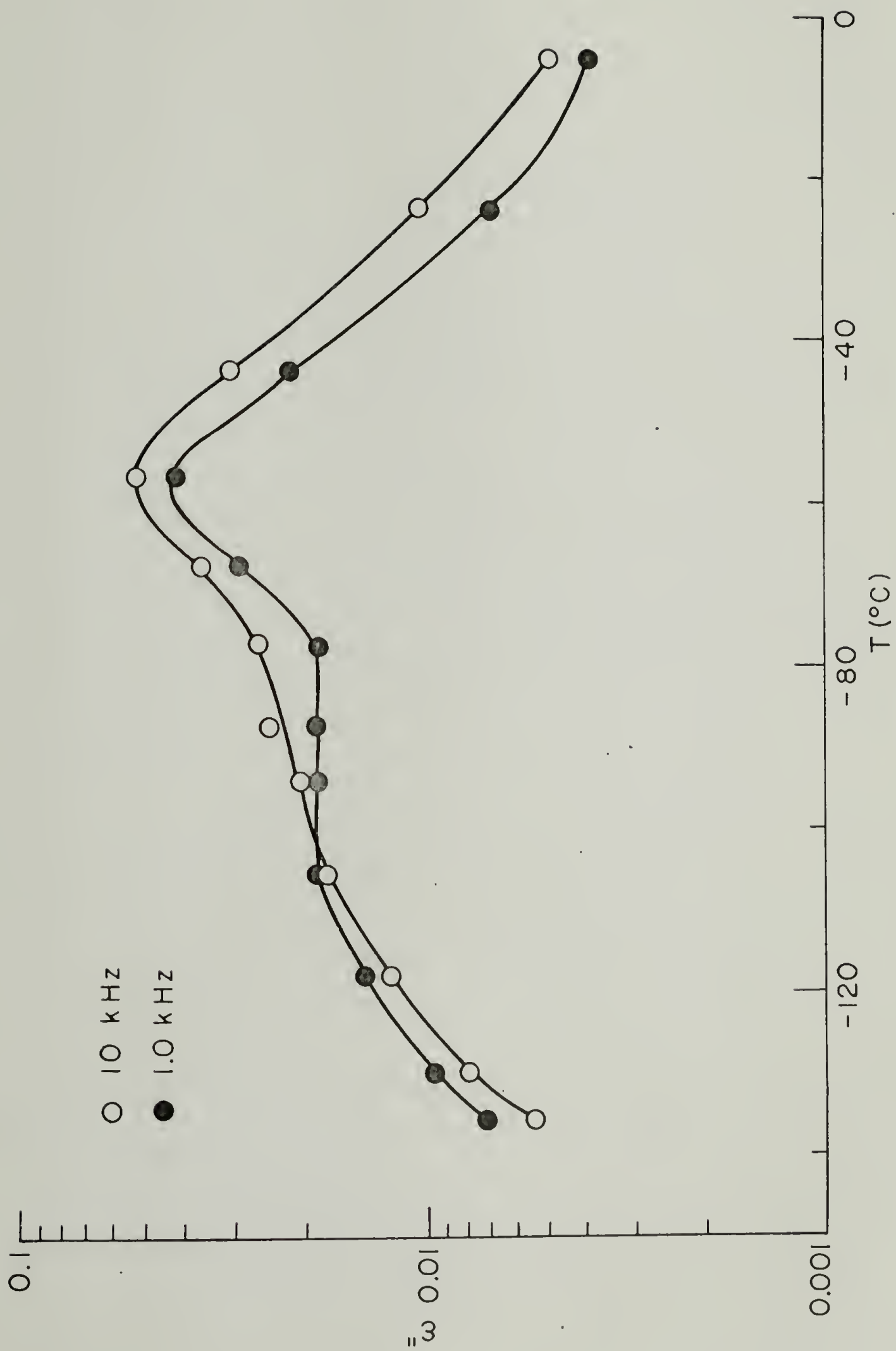


Fig. 9. Dielectric loss for water saturated PCL as a function of temperature at frequencies of 1.0 and 10 kHz

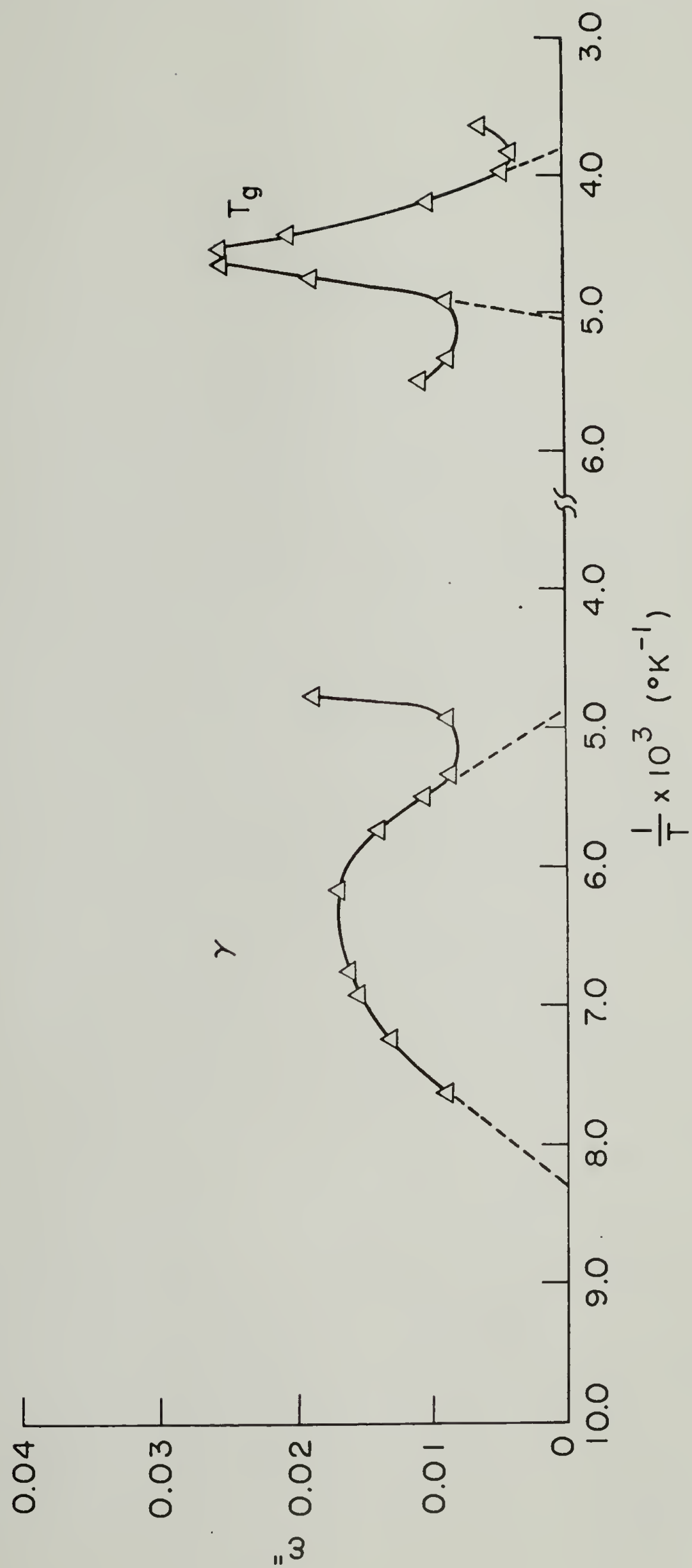


Fig. 10. Plot of dielectric loss against  $1/T$  for PCL at 0.10 kHz



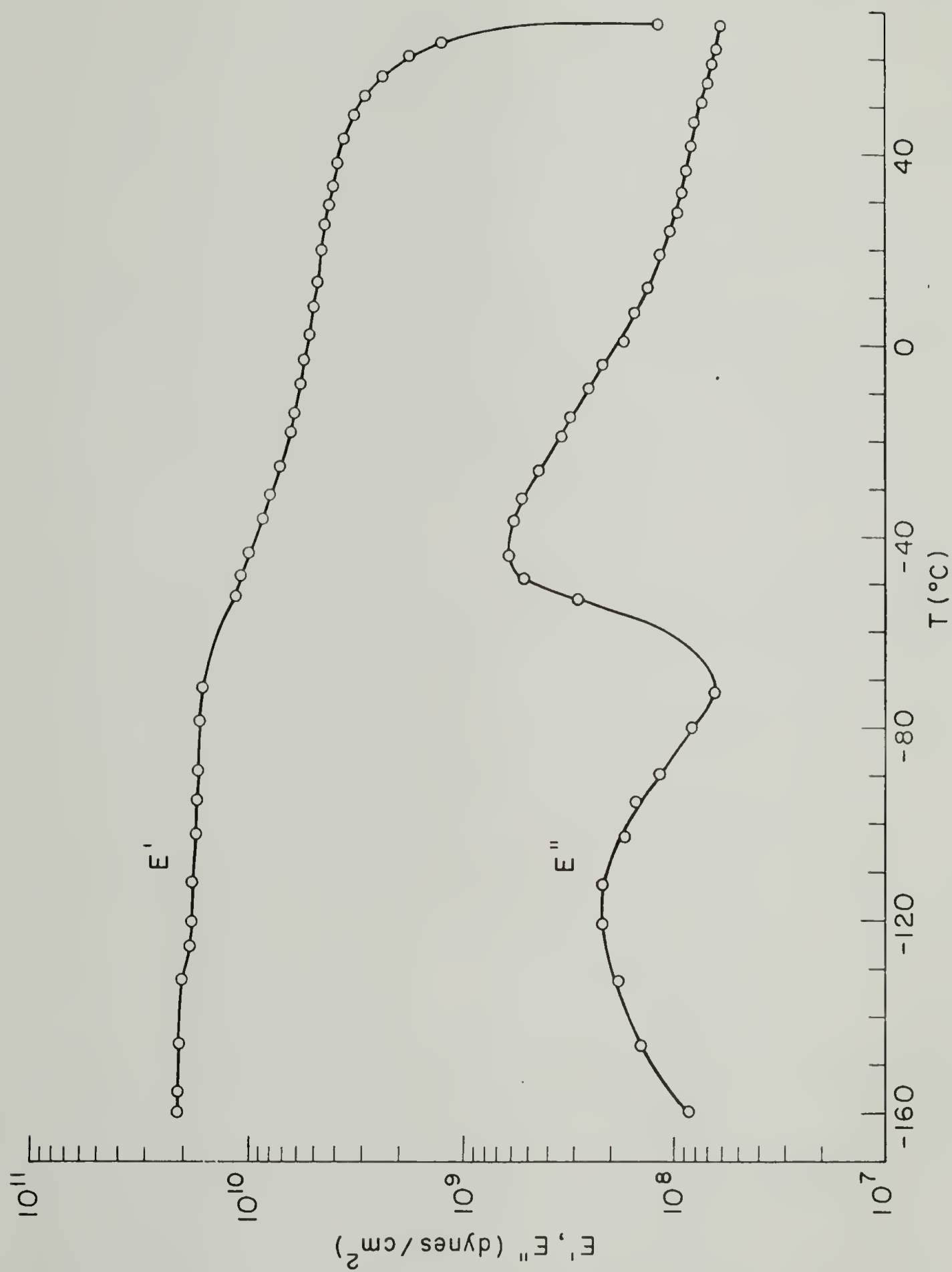


Fig. 11. Dynamic-mechanical storage and loss moduli for PCL as a function of temperature at 110 Hz

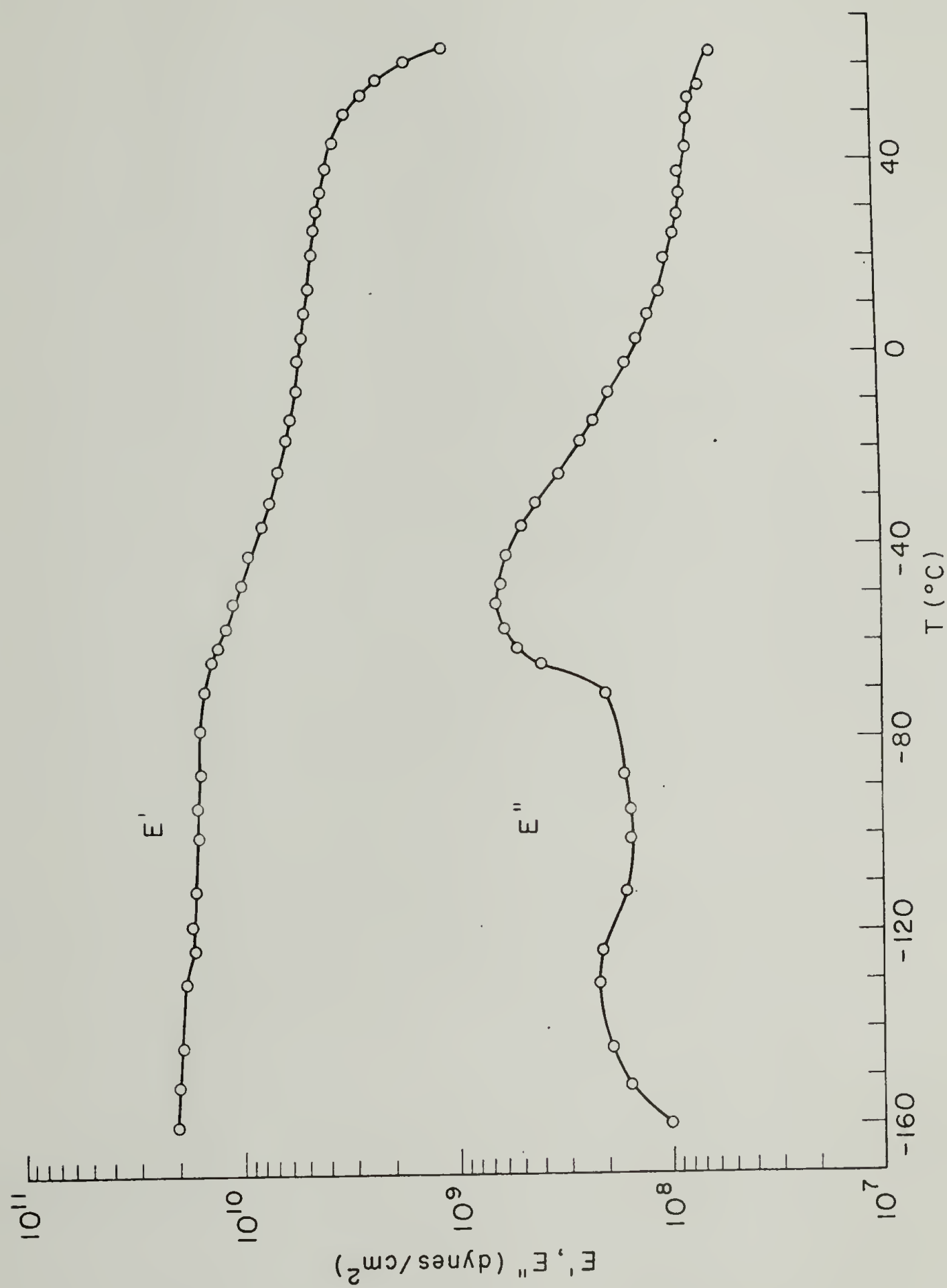


Fig. 12. Dynamic-mechanical storage and loss moduli for PCL as a function of temperature at 11 Hz

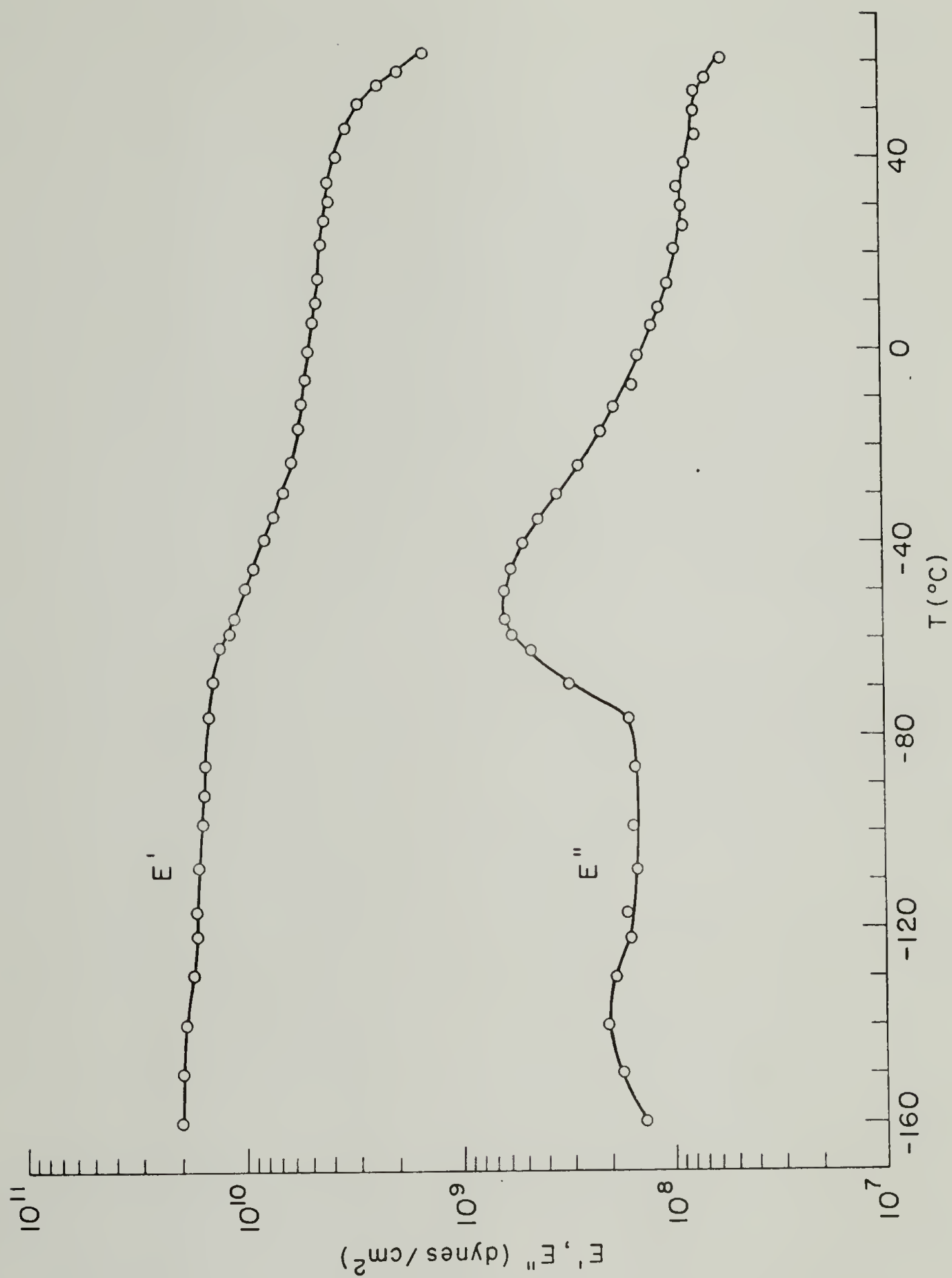


Fig. 13. Dynamic-mechanical storage and loss moduli for PCL as a function of temperature at 3.5 Hz

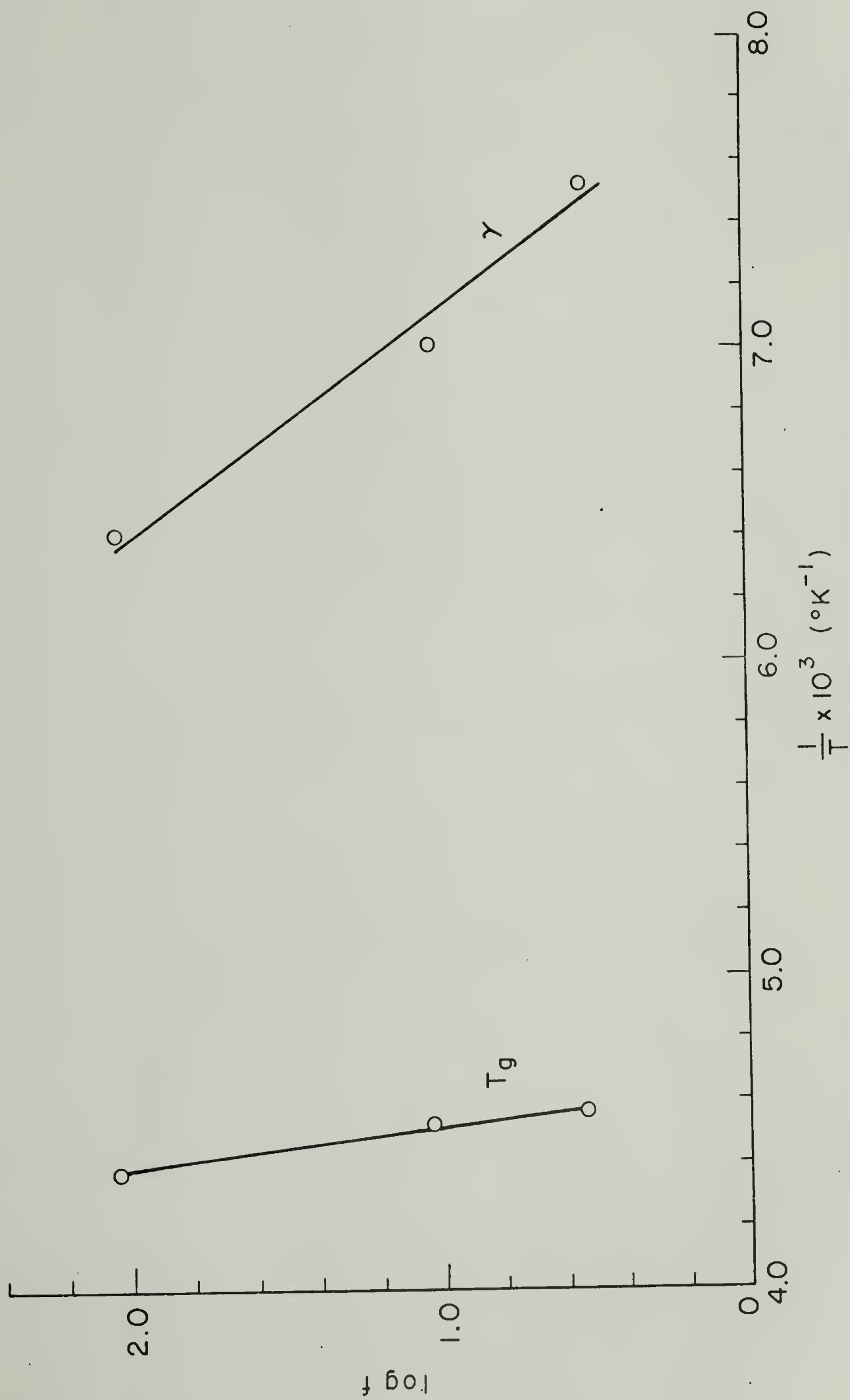
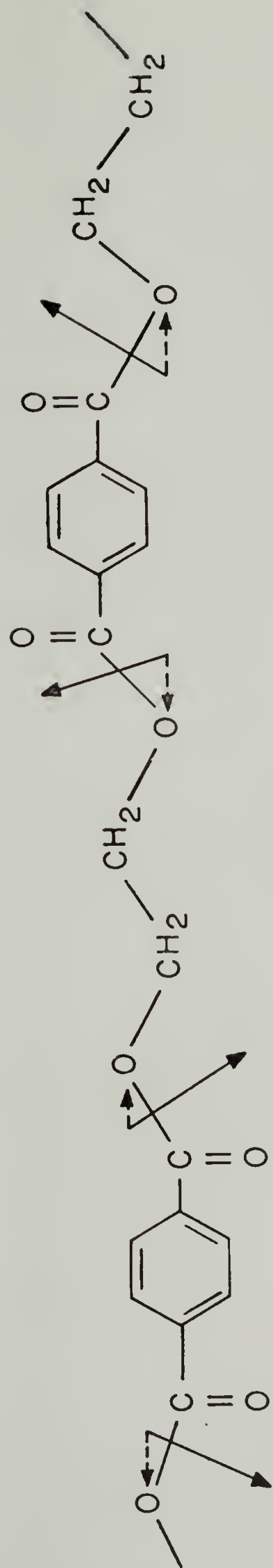
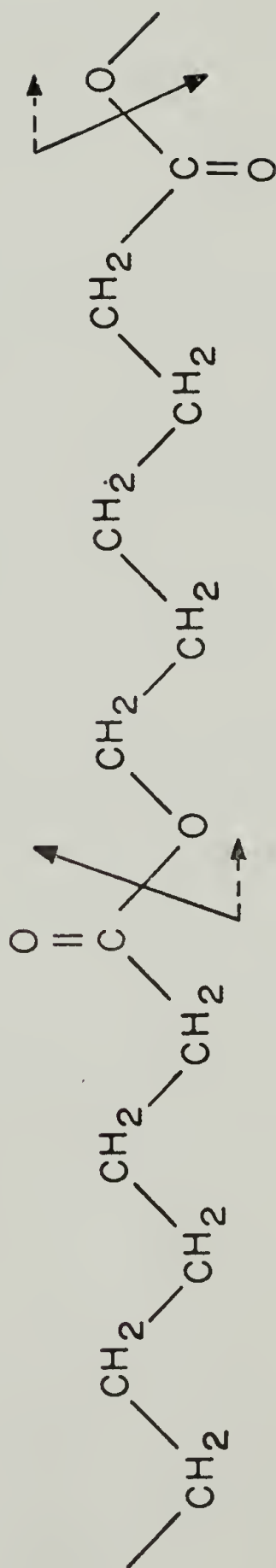


Fig. 14. Plot of  $\log f$  against  $1/T$  for the dynamic-mechanical relaxation loss maxima for PCL 55





PET : DIPOLE COMPONENTS PARALLEL TO CHAIN AXIS CANCEL



PCL : DIPOLE COMPONENTS PARALLEL TO  
CHAIN AXIS REINFORCE ONE ANOTHER

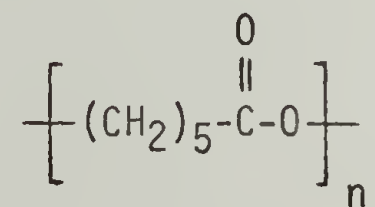
Fig. 15. Chemical structures of PET and PCL showing orientation of chain dipoles

## CHAPTER III

### POLYBLENDS INVOLVING POLY- $\epsilon$ -CAPROLACTONE

#### Introduction

As discussed in the introduction to this dissertation, claims have been made regarding favorable compatibility properties of poly- $\epsilon$ -caprolactone (PCL) with other polymers,<sup>1,2,3</sup> This compatibility with a wide range of polymers is said to be the result of a unique combination of polar and nonpolar character in the structure of PCL which is indicated as follows:



The  $-\text{CH}_2-$  groups contribute nonpolar character and render compatibility with predominantly nonpolar polymers, while the ester group contributes polarity and facilitates compatibility with polar polymers.<sup>1</sup>

PCL is found to be compatible with polyvinyl chloride (PVC) in blends containing 50% or more PVC.<sup>2</sup> This behavior is unusual for two reasons. In the first place two polymers are only rarely found to be compatible in any proportion and, secondly, two polymers found to be compatible are generally both amorphous in nature. Blends of PCL and PVC can be made in such a way as to destroy the PCL crystallinity.

It is further claimed that PCL can be mixed with a wide variety of commercial polymers and in many ways improve the properties of those

polymers.<sup>1</sup> PCL is said to improve film gloss and clarity as well as antiblocking characteristics in low density polyethylene, improve the dyeability of polypropylene fibers, and improve many properties of nitrocellulose including strength and clarity.<sup>1,3</sup> The list does not end here. Suffice it to say that these unusual claims of favorable compatibility properties precipitated investigation of PCL blends during the course of this work. Simultaneous work was being carried out on certain of the physical properties of PCL as discussed in Chapter II as well as optical microscopy and small-angle laser and X-ray scattering of PCL in our laboratory by other workers.

### Experimental

It was attempted to prepare polymer blends of PCL with other polymers by compression molding since this procedure seemed to be the simplest. That is, PCL and the polymer to be blended with it were mixed as solids and the mixture subsequently heated in the press. The temperature of molding varied, depending on the particular polymer involved in the mixture, but was always at least some degrees above the melting point of the higher melting component to insure fluidity during compression.

This procedure was first applied to PCL/PVC mixtures in an attempt to prepare blends of the two since it was known that the two polymers were compatible.<sup>2</sup> Difficulties were immediately encountered however. The major problem seemed to be the extreme fluidity of melted PCL. The viscosity of the melt was apparently not high enough to allow

sufficient pressure to be built up in the melt for interdiffusion of the two polymers to occur. The melted PCL would simply flow out of the assembly when pressure was applied. Attempts were made to blend PCL with polyvinyl acetate, polyethylene, and other polymers in the same manner, but the same problem was always encountered. It became apparent that another method of mixing was needed.

The next simplest procedure seemed to be mechanical mixing in a heated flask of some type. A round bottom flask was used in conjunction with a heating mantle and a glass stirring rod. The two polymers to be mixed were introduced to the flask as a solid mixture again and the temperature subsequently raised above the melting point of the higher melting polymer. The mixture of melts was then stirred. Again, difficulties were encountered. Only poor mixing seemed to be achieved because of the viscosities encountered. The stirrer was only able to function at slow speeds, and no mixing at all seemed to be occurring away from the center of the flask, that is, toward the walls. Therefore this method, too, was soon abandoned.

Solvent casting was also tried but results were equally discouraging. It became apparent that more sophisticated mixing techniques would be necessary to achieve the desired results. It was therefore attempted to prepare the desired polymer blends using a two-roll mill. In this procedure one of the polymers is placed onto a hot, rotating cylinder and melted. The second polymer is placed on a second, similar cylinder which is rotating however at a different angular velocity. The distance between the two cylinders is decreased until the two melts



come into contact, and mixing occurs because of shearing action. The polyblend is then easily removed by scraping with a knife. Using this technique PCL was mixed with PVC, polyethylene, polyvinyl acetate, polymonochlorostyrene, and polypropylene.

### Results and Discussion

Polypropylene and PCL were milled just above the melting point of the polypropylene. It was impossible however to achieve good mixing at this temperature since the polypropylene did not appear hot enough to form a smooth melt. Hotter temperatures could not be reached since the mill was steam heated and was operating at maximum conditions. The attempt to mix these two polymers therefore failed. Presumably, the two polymers could be mixed at a hotter temperature, perhaps by using a mill that is oil heated.

Polymonochlorostyrene (PCS) and PCL were mixed above the glass transition temperature of the PCS. The PCS used was 65% ortho and 35% para. A smooth melt of PCS was achieved here and mixing seemed to be occurring properly, however removal of the mixture from the mill revealed a product which had no mechanical integrity. It was concluded then that these two polymers were incompatible.

PCL and PVC were blended at 150°C in the composition 80% PVC and 20% PCL. The PCL used in this blend was that designated as PCL 700, which is the higher molecular weight polymer of the two types of PCL available. The other is designated as PCL 300. Generally better results were obtained with the PCL 700 throughout this work. The

PVC/PCL mixture appeared to be a successful attempt at blending upon removal from the press. A piece of the polymer sheet was then cut away and compression molded. The resulting polymer film was transparent and homogeneous, and it appeared to be more flexible than pure PVC. There was no visible evidence of PCL crystallinity, and it was concluded that at this composition these two polymers may indeed be compatible.

Blending was also carried out with PCL and polyvinyl acetate (PVA). Several mixtures were milled. These included 90%, 75%, 50%, and 25% PVA mixed with PCL 700 and 90% PVA with 10% PCL 300. A product with no mechanical integrity was obtained with PCL 300, as was generally the case. However, all of the PCL 700 mixtures seemed to be mechanically proper as the products were tough and of high quality upon removal from the mill. Films were made from the milled products and were again of good quality, homogeneous in appearance. Films of pure PVA are transparent while films of pure PCL are opaque because of substantial crystallinity. Polyblend films varied from translucent to opaque depending on the composition. The greater the PCL content, the more opaque. This appearance suggested that the two polymers were not compatible even though films were homogeneous and of good quality. The crystallinity of the PCL did not appear to be destroyed, suggesting that the two polymers mixed only in a superficial manner and not on an intimate level. The blending was however successful in producing a plasticized PVA product. Blends of 90% PVA and 75% PVA mixed with PCL 700 were significantly more flexible than pure PVA although at the expense of loss of transparency.

These blends proved interesting enough to investigate further by means of differential scanning calorimetry (DSC). Thermograms at a heating rate of 10°C/min are shown in Figures 1 and 2 for the two blends of highest PVA content. The thermograms of the polyblends are similar to those for the homopolymers. PCL crystallinity is confirmed by significant melting peaks, and the 42°C glass transition temperature of pure PVA is essentially unchanged in the blends. It is further concluded that the PCL crystallites must contain virtually no PVA since the crystalline melting point is essentially the same as for pure PCL. If the two polymers were compatible, the  $T_g$  of PVA would have been shifted toward that of PCL, i.e., toward a lower temperature, and would have decreased with increasing PCL content. Such is not the case here, and it is apparent that the two polymers are not compatible in the usual scientific sense of the word even though it may be true that the blend suffers "no obvious sweat-out or deterioration in physical properties" with time.<sup>1</sup>

The final blend to be investigated was PCL and polyethylene (PE). The same compositions were milled as was done for the PVA blends. Again, the 90% PE - 10% PCL 300 blend was of poor quality and could be easily torn. The 90% and the 75% PE compositions were the best quality blends of the four made with PCL 700. The 50% and 25% PE blends were not of good quality. The addition of PCL 700 to PE seemed to cause an effective plasticization of the PE although, once again, at a loss of transparency. Behavior in this regard seemed quite similar to the PVA blends. The loss of transparency was suggestive of PCL crystallinity.



Differential scanning calorimetry was used to further investigate the properties of these blends. Thermograms are shown in Figures 3 and 4. Figure 3 shows a thermogram which was run on the blend after it had been at room temperature for a few days. Two melting peaks are apparent in this thermogram. The high temperature peak is suggestive of PE melting while the low temperature peak is suggestive of PCL melting. This blend must then consist of a two-phase system—a predominantly PE phase containing some PCL and a predominantly PCL phase containing some PE. This is undoubtedly the case since both melting peaks are shifted to lower temperatures than for the pure materials by some 10°C or more. Such behavior is not suggestive of a compatible polymer pair.

Figure 4 however shows a thermogram run on the same sample of material used in Figure 3 only this time quenched from the melt into liquid nitrogen before the experiment. This thermogram shows only one melting peak and that at the PE temperature. There is no significant indication of PCL crystallinity which is apparently destroyed by the quenching process. The result is a one-phase system this time in which the PCL is presumably randomly distributed throughout the PE crystals. Under these conditions PE and PCL probably constitute a compatible polymer pair.

It is concluded from this work that PCL can be blended with certain other polymers to form polyblends having potentially useful properties. Most of these blends are however probably not compatible when the strict definition of thermodynamic compatibility is employed. Much work remains to be done in this area, however, before the various



properties of these polyblends are well documented. Sufficient evidence is presented here to justify continuation of work in this area. Results and conclusions of this work are summarized in Table I.

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1109-1144 (1972).

TABLE I  
Polyblends of PCL - 700

Polymer Blended with PCL	Proportion	Usable Product	Thermodynamic Compatibility with PCL
Polychlorostyrene	Various	No	No
Polyvinyl Chloride	80% PVC 20% PCL	Yes	Yes*
Polyvinyl Acetate	90% PVA 10% PCL	Yes	No
	75% PVA 25% PCL	Yes	No
	50% PVA 50% PCL	Yes	No
	25% PVA 75% PCL	Yes	No
Polyethylene (Low Density)	90% PE 10% PCL	Yes	Yes
	75% PE 25% PCL	Yes	No
	50% PE 50% PCL	No	No
	25% PE 75% PCL	No	No

\*According to Koleske and Lundberg

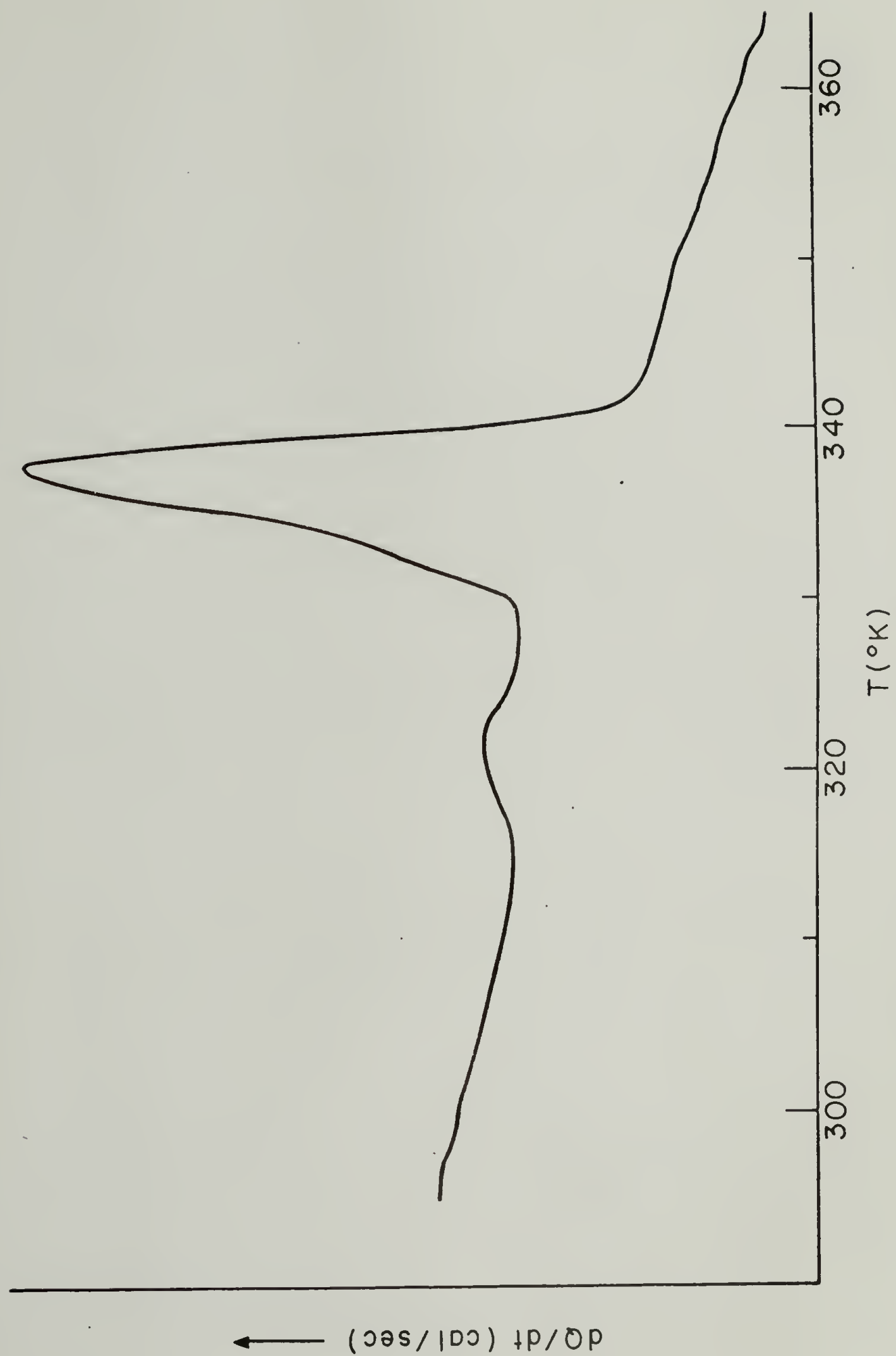


Fig. 1. DSC thermogram for polyblend of 75% polyvinyl acetate and 25% PCL



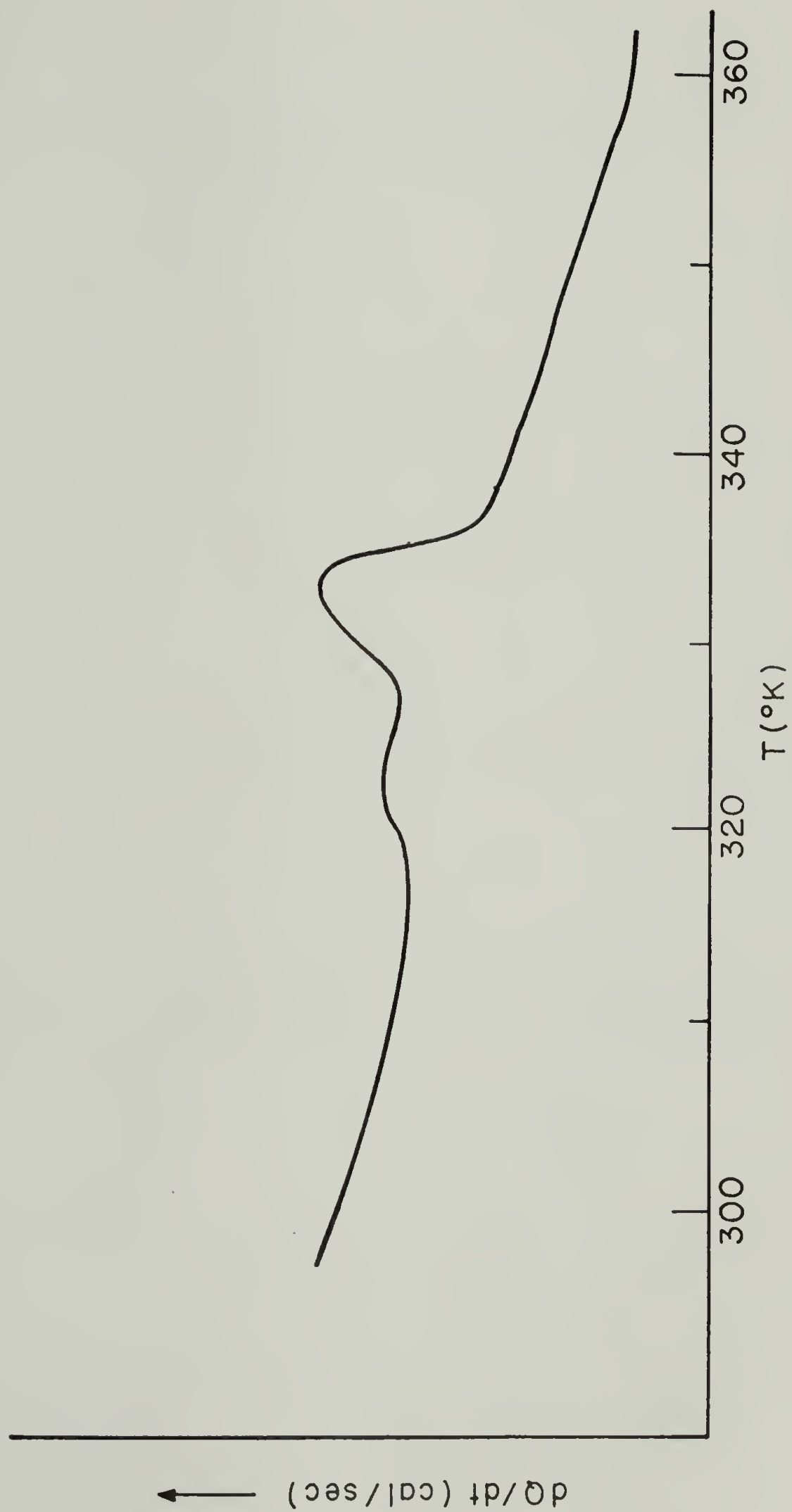


Fig. 2. DSC thermogram for polyblend of 90% polyvinyl acetate and 10% PCL

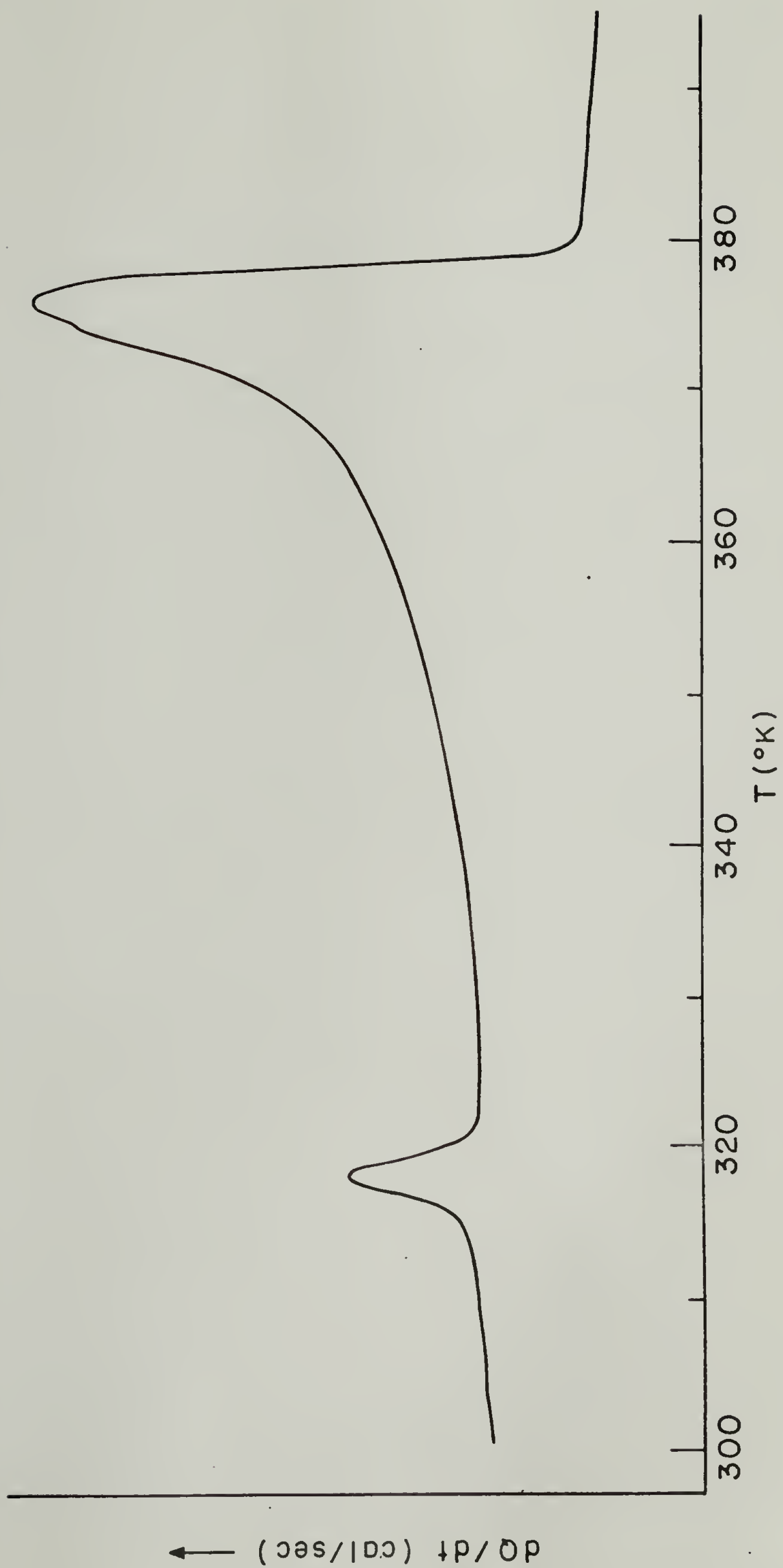


Fig. 3. DSC thermogram for annealed polyblend of 90% polyethylene and 10% PCL

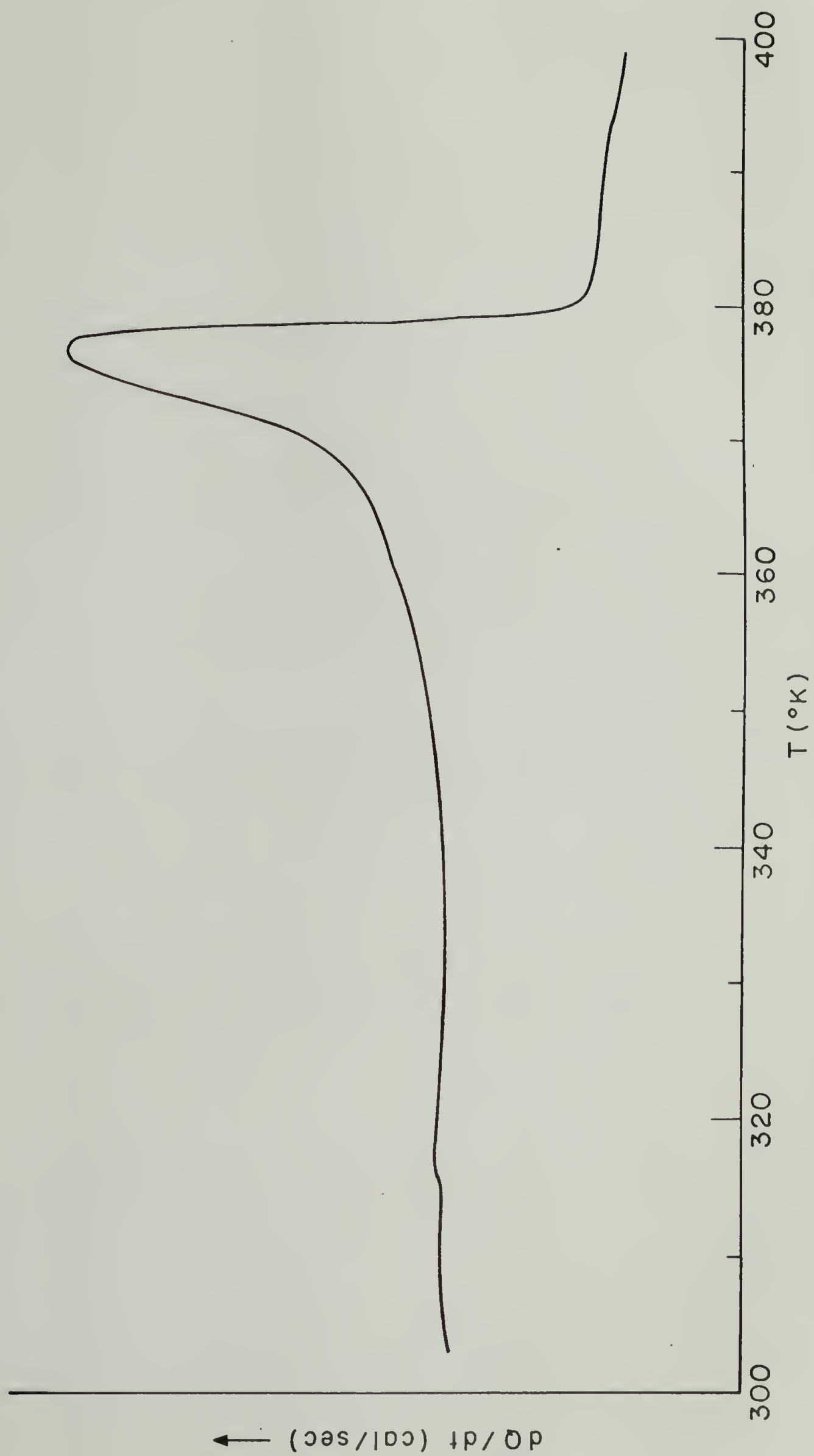


Fig. 4. DSC thermogram for quenched polyblend of 90% polyethylene and 10% PCL

C H A P T E R   I V  
PHYSICAL PROPERTIES OF THE SYSTEM  
POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)-  
ISOTACTIC POLYSTYRENE

Introduction

The mixing of two polymers in the bulk phase is a topic receiving increased attention today both for academic as well as commercial reasons. It is of course possible to favorably modify some of the properties of a polymer by blending with certain low molecular weight materials. At times it is likewise possible to favorably modify the properties of a polymer by blending in certain proportions with another polymer, although such instances are rare.<sup>1</sup> The success of such mixing is determined by the extent of polymer compatibility as well as kinetic considerations. Various techniques have been used to study the compatibility of two or more polymers in the bulk phase. These include optical transparency, mechanical integrity of the mixture, homogeneity on a microscopic level as revealed by electron microscopy, and the presence of a single glass transition temperature for the mixture intermediate between the  $T_g$ 's of the individual homopolymers.<sup>1</sup>

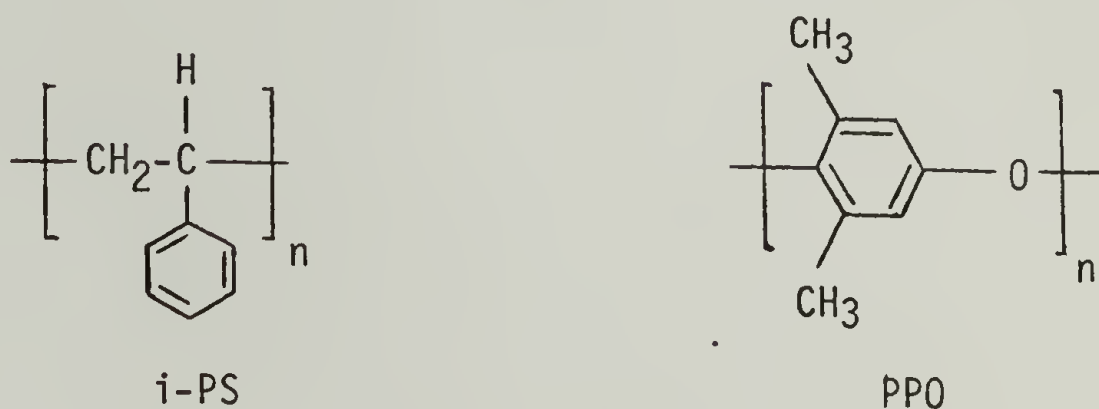
In general two polymers cannot be blended together to form a product with useful properties. Such mixtures usually have no mechanical integrity due to the enormous thermodynamic and kinetic



difficulties involved in the formation of polymer blends.<sup>1</sup> For the same reasons in compatible polymer pairs both of the components are generally amorphous. The possibility does exist however of introducing into a polymer blend a "crystallizable" component. Such a blend could at first be prepared using one of the techniques commonly in use such as milling or compression molding. However the blend would then be annealed or crystallized in some further treatment. It is reasonable to postulate that such a polyblend could have certain properties improved over those of the amorphous material. The literature contains at least two references to similar systems. Natov, et al.,<sup>2</sup> have studied such crystallization from incompatible blends, while Paul and Altimirano<sup>3</sup> have studied crystallization from a compatible blend.

It has been reported that the polymers poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and atactic polystyrene (a-PS) are a compatible pair.<sup>4,5,6</sup> These polymers are of practical as well as academic interest since they have found commercial importance as the high-temperature thermoplastic Noryl resins. As is ordinarily the case, both polymers are amorphous individually as well as in the polyblend. A special peculiarity of this system is that certain blend compositions are claimed to have tensile strengths which are significantly improved over those of either of the two homopolymers.<sup>4</sup> In this work isotactic polystyrene (i-PS) was substituted for the a-PS with the objective of seeing how the properties of the polyblend would be affected, and noting especially that i-PS is crystallizable. In particular, is it possible to crystallize the i-PS in this polyblend and thereby produce two series of

polyblends, one containing amorphous i-PS and the other containing crystalline i-PS. Such blends would be of obvious interest for their novelty as well as for the unique properties they might have. The results of such work are described here. The chemical structure of these two polymers is shown below:



### Experimental

The PPO used here was obtained from the General Electric Co. and was high molecular weight and additive free. The i-PS was obtained from the Borden Chemical Co. and had a viscosity average molecular weight of 470,000. Blends of the two polymers were prepared by compression molding mixtures of the two powders. The polymers were heated to 330°C and were maintained at that temperature for about five minutes prior to molding into films. After molding, samples were slowly cooled to room temperature in the press.

### Results and Discussion

Properties of amorphous films. Films prepared in this manner were in all cases homogeneous in appearance over the entire composition range. Films of i-PS were clear and transparent. PPO films were transparent and

somewhat yellow. Polyblend films varied in color between these two extremes. In addition, i-PS films were brittle whereas PPO films were flexible and tough. Polyblend films again varied between these two extremes in their properties. Some problem was encountered with the occasional occurrence of air bubbles in the films, but this problem was minor in nature.

Differential scanning calorimetry. The properties of these blends were first investigated by means of differential scanning calorimetry (DSC). Experiments were performed using a Perkin-Elmer DSC-1B at a heating rate of 10°C/min. Thermograms obtained indicate that 1) all of the films prepared in the above manner were amorphous in nature since they exhibited no melting endotherms, and 2) all of the films exhibited one glass transition temperature because of a single step increase in the thermal curve. The  $T_g$ 's for the polyblends are between the  $T_g$ 's for the homopolymers and vary according to the composition of the blend as shown in Figure 1. (The glass transition temperature was taken as that temperature halfway up the step increase in the thermal curve.) Such behavior is indicative of a compatible polymer pair system.<sup>1</sup> That is, sufficient intermixing of the two polymers during the molding process must cause the homopolymers to lose their identity and to form a one-phase system (at least in so far as a DSC measurement is concerned).

Dynamic-mechanical studies. In order to gain further information as to the nature of polymer-polymer interactions in this system, dynamic-mechanical experiments were performed on the polyblends. The fact that a polymer-polymer system exhibits one glass transition in a



DSC measurement does not a priori mean it will behave in the same manner in another type of experiment. Indeed, the work involving PPO and a-PS blends involved one  $T_g$  in DSC experiments while showing two in dynamic-mechanical experiments.<sup>5</sup> Measurements were carried out using a Vibron Dynamic Viscoelastometer, Model DDV II (Toyo Instrument Co.) over a temperature range -160 to 220°C at frequencies of 3.5, 11, and 110 Hz. Dynamic-mechanical data on these blends at a frequency of 11 Hz are shown in Figures 2 to 5. Blends studied included 75%, 50%, and 25% i-PS.

The dynamic-mechanical properties of pure PPO have been investigated by several workers and therefore will not be discussed here.<sup>5,7,8,9</sup> The same statement can be made for i-PS.<sup>10</sup> Dynamic-mechanical results obtained for the polyblends are in contrast to those reported by Stolting, et al.,<sup>5</sup> for the a-PS/PPO system where single loss peaks appear with shoulders, apparently indicating a merging of two transition peaks and only partial intermixing at some level detectable in such an experiment. In the i-PS/PPO results reported here, the glass transitions appear to occur as single processes indicated by a clear, single loss peak. The reasons for the difference in behavior of these two very similar systems are not readily apparent.

A further observation can be made here regarding the mechanical loss peaks. As is generally the case, the glass transition peak is broadened in comparison with those of the homopolymers. This broadening is also observed in the a-PS/PPO work as well as in DSC measurements and can, in effect, be attributed to a merging of the two  $T_g$ 's for the

individual homopolymers into one for the polyblend.<sup>5</sup> A similar broadening effect has been observed to occur in crystalline samples of isotactic polystyrene and polyethylene terephthalate in comparison to amorphous samples of the same polymers.<sup>10</sup> In these cases the broadening was attributed to restrictions imposed by the crystallites on the amorphous phase. It is possible that the width of the temperature range over which the glass transition process occurs can be used as a measure of the level of mixing in an amorphous polymer blend system, a broad range indicating only relatively coarse mixing, and a narrow one indicating thorough mixing. It can perhaps be concluded at this point that the i-PS and PPO are well mixed enough in the polyblend to exhibit only one  $T_g$ , but since the range over which the transition occurs is relatively broad, mixing cannot be on a strictly segmental level. Aggregates of some size must still be present but must be less than ca. 2000Å in diameter since the films involved are transparent and homogeneous in appearance. Such aggregates could potentially be investigated by electron microscopy.

The results obtained for the a-PS/PPO system allowed a model of this system to be devised where a-PS appeared to be the continuous phase in blends of 50% a-PS or more due to the fact that it is the component which becomes fluid first.<sup>5</sup> The PPO made up the continuous phase in the 75% PPO blend because of the quantity involved. Nothing is observed in this work to contradict this model and perhaps the same model could be assumed to hold true in the i-PS/PPO system except that a greater degree of mixing probably occurs in the latter.



The conclusion that the degree of mixing achieved in this system appears to be greater than that observed in the a-PS/PP0 system is based on two points. First, the  $E''$  loss peaks observed in this work are not as wide as those in the a-PS/PP0 work. Second, the shoulder in the  $E''$  measurements which consistently appeared below the main loss peak in the a-PS/PP0 work was much less obvious in this work and, indeed, was only apparent in the 50/50 polyblend. Mixing in the 50/50 polyblend does not seem to be as good as in the other blends.

Such mixing as occurs in this system must do so by means of interdiffusion of the two polymers, since there is no mechanical mixing involved. In the case of compatible polymers such interdiffusion can occur even to the extent of  $100,000\text{\AA}$  in a short period of time.<sup>11</sup> Such intermixing as occurs must obey the customary laws of diffusion which dictate that

$$\overline{x^2} = 2Dt$$

where  $\overline{x^2}$  is the mean square displacement in the x direction, D is the diffusion constant, and t is the time allowed for diffusion.<sup>12</sup> Using this relationship it is possible to estimate an "effective" diffusion constant for this system. If it is assumed that diffusion occurs completely through the smaller PP0 particles and only partially through the larger ones, x can be estimated at perhaps  $0.5\mu$ . Such a displacement is approximately one-half the diameter of the smallest PP0 particles. (The PP0 particles used in this work were found to vary in size from about  $1\mu$  to about  $1\text{mm}$  as measured under the light microscope.) Allowing for 20 minutes of maximum diffusion at a temperature

over 50°C above the  $T_g$  of PPO, the i-PS becoming fluid much sooner, a diffusion constant,  $D = 10^{-12}$  cm<sup>2</sup>/sec, is calculated for this system. Such a diffusion constant compares with those listed by Letz for generally incompatible polymers. It may therefore be the case that diffusion occurs to an even greater extent, perhaps  $x = 5\mu$ , in which case  $D = 10^{-10}$  cm<sup>2</sup>/sec. At this point diffusion is occurring to the extent of 50,000Å, a value of the same order as discussed above for compatible polymers, perhaps leaving some PPO aggregated in the final product in domains of around 100Å diameter or less.

Crystallization of the polyblends. It is well known that i-PS can be crystallized by suitable annealing techniques. It was therefore decided to attempt to crystallize the i-PS in these polyblends and to study the effect of crystallization on the properties of these blends. The amorphous polyblends were subsequently annealed at temperatures above the glass transition of the blend for a period of 24 hours. The results of this crystallization procedure are indicated in Figure 6. It was found possible to crystallize all of the polyblends which contained 50% i-PS or more. Crystallization was most successful at annealing temperatures midway between the glass transition for the blend and the crystalline melting point. Heats of fusion resulting from the melting of these crystals as measured by DSC varied from 8.0 cal/g for i-PS to 2.4 cal/g polyblend for the 50/50 polyblend (or 4.8 cal/g i-PS). It must therefore be possible for units of i-PS to be mobile enough above the glass transition of the blend to allow a substantial number of i-PS segments to cluster together into a crystal. That such

segmental motions must occur is apparent since the presence of only a single glass transition temperature in the blends refutes the possibility of large aggregates of i-PS being present prior to annealing.

Some representative melting curves are shown in Figures 7-9. A common occurrence seemed to be the appearance of double and triple melting peaks. It was not possible to reach any definite conclusions about the cause of these multiple melting peaks. Such peaks can be due to incomplete crystallization and it seems likely that is also the explanation here.

A further observation can be made by looking at the melting temperature of these crystals as shown in Figure 10. As the PPO content of the blends is increased, the melting point of the crystals is lowered. Such behavior is indicative of imperfections or lack of size in the crystals. Such imperfections or incomplete crystallization could possibly be due to kinetic reasons, i.e., it may take longer than 24 hours to attain complete crystallization. This possibility was refuted by annealing the blends for longer periods of time with essentially no change in results. It must then be concluded that further crystallization is not possible, and the lack of size or imperfections in the crystals are caused by the presence of the PPO. Assuming a model then of a system containing an amorphous phase and a crystalline phase both of which contain i-PS and PPO, it is possible to estimate the quantity  $v_u/v_l$ . This quantity is the ratio of the specific volume of the polymer repeat unit to that of the diluent which appears in the well known theory of Flory.<sup>13</sup> In the ordinary case of low molecular weight diluents this



quantity is on the order of 1.0. It is of interest to note what value would effectively be predicted for this quantity in the case of two polymers. This quantity can be determined from Flory's equation

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(v_u/v_1)(v_1 - x_1 v_1^2)$$

in which  $T_m$  and  $T_m^0$  are the melting points of diluted and undiluted polymer, respectively,  $R$  is the gas constant,  $\Delta H_u$  is the heat of fusion per repeat unit,  $v_1$  is the volume fraction of diluent, and  $x_1$  is the interaction parameter. From a plot of  $(1/T_m - 1/T_m^0)/v_1$  vs.  $v_1/T_m$  the quantity  $v_u/v_1$  can be determined from the intercept. This method is difficult to apply because of a lack of sufficient data points as shown in Figure 11. An alternative method is to obtain the desired quantity from the initial slope of a plot of  $1/T_m$  vs.  $v_1$ . This plot is shown in Figure 12. From this plot it was found that  $v_u/v_1 = 0.27$ , indicative of the fact that the polymer repeat units of i-PS occupy a lesser volume than the "diluent" PPO. It can be concluded from this plot also that the interaction parameter,  $x_1$ , is high in magnitude since the graph shows significant curvature. High values of  $x_1$  are classically indicative of a lack of mixing,<sup>14</sup> and this is taken as evidence that mixing in this system cannot be on a near segmental level but aggregates of some size must be present.

Dynamic-mechanical studies of crystallized blends. In order to add further information about this polymer-polymer system, dynamic-mechanical measurements were also performed on the crystallized polyblends. The results of these experiments are shown in Figures 13-15.



Several observations are worthy of discussion here. For i-PS results agree rather well with those reported previously.<sup>10</sup> Glass transition loss peaks of roughly the same magnitude are observed for both crystallized and amorphous i-PS samples. The glass transition temperature (as taken from the maximum in the loss peak) was slightly higher for the crystallized sample, 115°C, as opposed to 109°C. It had previously been reported that the temperature of maximum loss is independent of the degree of crystallinity in polystyrene.<sup>10</sup> There would seem to be some question about this in view of the results obtained here.

A comparison of the magnitude of the storage modulus,  $E'$ , below the main glass transition temperature for the various polyblends studied is shown in Table I. In all cases studied the crystallized polyblend exhibited a higher value of  $E'$  than did the amorphous blend of the same composition. Such behavior is consistent with greater stiffness and rigidity in the crystallized materials. The value of  $E'$  decreased as the amount of the crystalline component (i-PS) decreased. In the case of the amorphous blends  $E'$  was found to pass through a minimum at intermediate compositions.

Again, only one  $T_g$  is observed in all cases. Loss peaks for both crystalline and amorphous blends of the same composition are roughly of the same magnitude although the peaks for the crystalline materials are wider. Furthermore, the temperature of the  $E''$  peak is shifted to higher values for the crystalline materials than for the amorphous. Both of these effects have been observed previously in dynamic-mechanical studies of polymers and have been attributed to the crystallites imposing

restrictions on the amorphous phase.<sup>10</sup> The same explanation apparently holds here. If it is assumed that the two amorphous polymers intermix well enough to form a one-phase system (at least in so far as DSC and dynamic-mechanical experiments are concerned), then the crystallization process removes i-PS from the amorphous phase and forms a two-phase system.. This two-phase system must then consist of a crystalline i-PS phase possibly containing some trapped PP0 and an amorphous phase which retains some i-PS. The removal of i-PS from the amorphous phase necessarily causes the  $T_g$  to shift toward the value for pure PP0. However, the fact that the  $T_g$  remains substantially below that for pure PP0 and that there is still only one  $T_g$  indicates compatibility in the amorphous phase.

Since the glass transition process is due to segmental motions in the amorphous phase, it is possible to estimate the composition of the amorphous phase from Figure 1. The glass transition temperatures obtained from  $E''$  loss peaks are shown in Table II. In the case of the 75% i-PS/25% PP0 blend, crystallization changed the glass transition temperature from 115 to 123°C. From Figure 2 the composition of the amorphous phase is found to be  $w_1 = 0.67$ , where  $w_1$  is the weight fraction of PP0. Therefore,  $w_2 = 0.33$ , weight fraction of i-PS. This in turn means that the composition of the crystalline phase must be significantly changed such that  $w_1 > 0.25$  and  $w_2 < 0.75$  for this phase.

For the 50/50 blend crystallization had no effect on  $T_g$ . Such a result was expected in view of the fact that no crystallization was detectable in the dynamic-mechanical experiments and, at best, was difficult to observe even in DSC measurements.

High deformation properties of the polyblends. The unique behavior of this polymer-polymer system prompted an investigation of the engineering properties of the blends. It had already been claimed that in the a-PS/PP0 system certain blends had improved tensile strengths even over that of either of the two homopolymers. Therefore an investigation was undertaken of the tensile strengths, per cent elongations at break, and Young's moduli of the blends as a function of composition. All of the above properties were measured on an Instron at 25°C.

Figure 16 shows the tensile strength of the polyblends as a function of composition. For the amorphous blends the tensile strength is found to vary in a continuous manner from a low value just under  $2.8 \times 10^8$  dynes/cm<sup>2</sup> for pure i-PS to a high of  $5.9 \times 10^8$  dynes/cm<sup>2</sup> for pure PP0. There is no evidence of a maximum in the curve as is claimed in the a-PS/PP0 system.<sup>2</sup> A plateau seems to be reached from about  $w_1 = 0.85$  to 1.00 weight fraction PP0 in the blend. It is clear that the addition of PP0 to i-PS significantly improves the tensile strength of i-PS in a more or less linear manner. The addition of i-PS to PP0 however seems to have little effect on the strength of PP0 until 15 - 20% i-PS is reached. Such behavior is further evidence for the compatible nature of this polymer-polymer system. In polymer systems in general the tensile strength of both component polymers tends to decrease as the other component is blended with it. The difference in behavior between the a-PS/PP0 system and the i-PS/PP0 system is not readily apparent. The lower curve in Figure 16 shows the tensile strength vs. composition results for the i-PS/PP0 system in which the i-PS component



has been crystallized by thermal annealing. The data include pure i-PS, 75% i-PS/25% PPO, and 50% i-PS/50% PPO. The results are similar to that obtained for the amorphous blends, but displaced to values of lower tensile strengths. Pure i-PS has a tensile strength of just under  $10^8$  dynes/cm<sup>2</sup>, and this value is increased in a more or less linear manner as PPO is added up to the 50/50 composition blend which has a tensile strength of just over  $2 \times 10^8$  dynes/cm<sup>2</sup>.

Figure 17 shows the results for per cent elongation at break as a function of composition. For the amorphous blends it was found that PPO could be extended about 8% whereas pure i-PS could only be extended about 2%. Polyblends could be stretched to extensions between these two limits and were found to vary in a continuous manner. The lower curve in Figure 17 shows similar results for those polyblends which had been crystallized. Crystallization was found to lower the per cent elongation at break about 1% throughout the composition range 50% i-PS/50% PPO to 100% i-PS.

Figure 18 shows Young's modulus as a function of composition for the samples studied. For the amorphous polymers the modulus was found to decrease continuously from a value of about  $2.3 \times 10^{10}$  dynes/cm<sup>2</sup> for pure i-PS to  $1.7 \times 10^{10}$  dynes/cm<sup>2</sup> for pure PPO. Crystallinity was found to have no appreciable effect on the moduli of these polyblends.

Comparison of experimental data with current theories. The dynamic-mechanical data obtained here are next examined in the light of current theories concerning the prediction of the elastic moduli of two-phase systems. Specifically, it is of interest in this case to examine



the properties of a two-phase system consisting of small, rigid particles interdispersed in a polymer matrix. Such a model can be applied here since the crystallites of i-PS can be considered as interdispersed in an amorphous polymer matrix of i-PS and PPO, much like small spheres or beads would be, so long as the concentration of i-PS is not too high. In the case of high concentrations of i-PS, phase inversion would be expected to occur, and the system would then consist of less rigid, amorphous particles dispersed in a rigid, crystalline matrix.

Classically, the theories due to Kerner<sup>15</sup> and van der Poel<sup>16</sup> for the prediction of the modulus of a two-phase composite from the moduli of the components have been used.<sup>16</sup> These theories have mainly been used for the case of reinforcement of a rubbery matrix by incorporation of isotropic rigid particles. Two-phase systems consisting of a rigid matrix with dispersed rubbery particles have not received as extensive study despite their importance in the plastics industry as impact materials and despite the fact that the Kerner and van der Poel theories can be adjusted to this morphology. Extensive reviews of these theories and others have been compiled by Hashin<sup>18</sup> and Nielsen.<sup>19</sup>

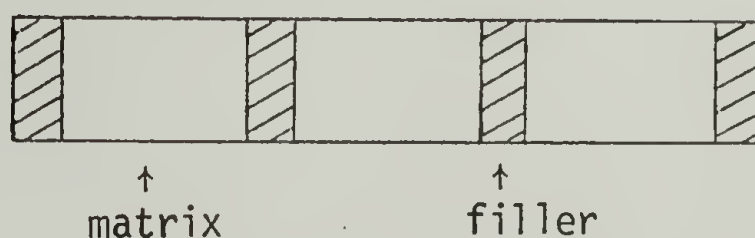
Kerner's approach was used here to analyze the i-PS/PPO data. Although derived for the shear modulus, Kerner's equation can be applied to Young's modulus for isotropic elastic materials where Young's modulus is proportional to the shear modulus. In this form Kerner's equation is

$$E = E_1 \frac{v_2 E_2 / [(7-5v_1)E_1 + (8-10v_1)E_2] + v_1 / 15(1-v_1)}{v_2 E_1 / [(7-5v_1)E_1 + (8-10v_1)E_2] + v_1 / 15(1-v_1)}$$

where  $E$ ,  $E_1$ , and  $E_2$  are the Young's moduli of the blend, the continuous

phase, and the dispersed phase, respectively,  $v_1$  and  $v_2$  are the volume fractions of the continuous and dispersed phases, and  $\nu_1$  is Poisson's ratio for the continuous phase. Assuming the crystalline phase to be pure i-PS and estimating the composition of the amorphous phase from the measured glass transition temperatures of the blends, the volume fractions of the dispersed and continuous phases can be estimated. Finally assuming Poisson's ratio to be 0.5, the modulus of the blend can be calculated. Calculations from Kerner's equation are compared with experimental data in Figure 19. Agreement with experimental data is seen to be best at low filler concentrations where the assumptions made are probably most reasonable.

It is also instructive to examine the high deformation results in the light of current theory. The literature contains few theories for explaining the high deformation properties of two-phase polymer systems. One of the simpler theories involving such a system is that due to Nielsen,<sup>20</sup> who considers a model where the filler particles are attached to the polymer matrix in a series arrangement as depicted below.



Perfect adhesion is assumed between the two phases. Such an assumption is not unreasonable in the case under consideration here since the two phases are chemically linked together by tie molecules. This analysis also neglects shear effects around the filler particles, triaxial

stresses in the polymer, and effects due to Poisson's ratio. If the further assumption is made that the polymer breaks at the same elongation in the filled system as the bulk unfilled polymer does, then the elongation to break of the filled system relative to the unfilled polymer is

$$\epsilon_B(\text{filled})/\epsilon_B(\text{unfilled}) = 1 - \phi_F$$

where the elongations to break are those measured in a tensile stress-strain test ( $\Delta L/L_0$ ) and  $\phi_F$  is the volume fraction of filler. Analogous to theories of the modulus, the size of the filler particles does not enter into the equation.

Experimental results for the i-PS/PP0 system are compared with Nielsen's theoretical prediction in Figure 20. Agreement is quite satisfactory, lending credence to the model.

Nielsen has furthermore combined this simple model with theoretical equations for the modulus of filled systems containing spherical particles due to Kerner<sup>14</sup> and Eilers and Van Dijck<sup>21</sup> for the purpose of predicting the relative tensile and impact strengths of these systems. Both combinations predict a minimum in the relative tensile strength vs. volume fraction of filler curve. In fact, both predict drastic decreases in the tensile strength with only small amounts of filler. At high filler concentrations the Eilers-Van Dijck modification predicts tensile strengths greater than that of the unfilled polymer. Such behavior is not observed in the i-PS/PP0 system. The addition of crystallites (filler) to the system is found to have a continuously

detrimental effect on the tensile strength in line with Nielsen's prediction for lack of adhesion between the phases. The exact cause of these weaknesses in the system remains uncertain, perhaps originating within the crystals themselves since there is evidence to indicate the crystals are small and not perfect.

In summary, it was found possible to prepare a series of polymer blends involving the two polymers isotactic polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide). Such blends were found to result in useful polymer film products, and differential scanning calorimetry as well as dynamic-mechanical experiments confirmed the compatibility of these two polymers. It was further found possible to crystallize the isotactic polystyrene in these polyblends by thermal annealing, resulting in a second series of polyblend films. Engineering properties of these films were studied and found in general to be intermediate in nature between those of the homopolymers.



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TABLE I  
Storage Modulus ( $E'$ ) of i-PS/PP0 Polyblends from Dynamic  
Mechanical Measurements at 25°C (dynes/cm<sup>2</sup>)

Composition	Amorphous	Crystalline
100% i-PS	$1.00 \times 10^{10}$	$1.60 \times 10^{10}$
75% i-PS/25% PP0	$0.75 \times 10^{10}$	$1.15 \times 10^{10}$
50% i-PS/50% PP0	$0.60 \times 10^{10}$	$0.75 \times 10^{10}$
25% i-PS/75% PP0	$1.00 \times 10^{10}$	
100% PP0*	$1.50 \times 10^{10}$	

\*According to Stolting, et al.<sup>5</sup>

TABLE II

Glass Transition Temperatures of i-PS/PP0 Polyblends (°C)

Composition	Amorphous	Crystalline
100% i-PS	109	115
75% i-PS/25% PP0	115	123
50% i-PS/50% PP0	149	—
25% i-PS/75% PP0	173	—
100% PP0*	220	—

\*According to Stolting, et al.<sup>5</sup>



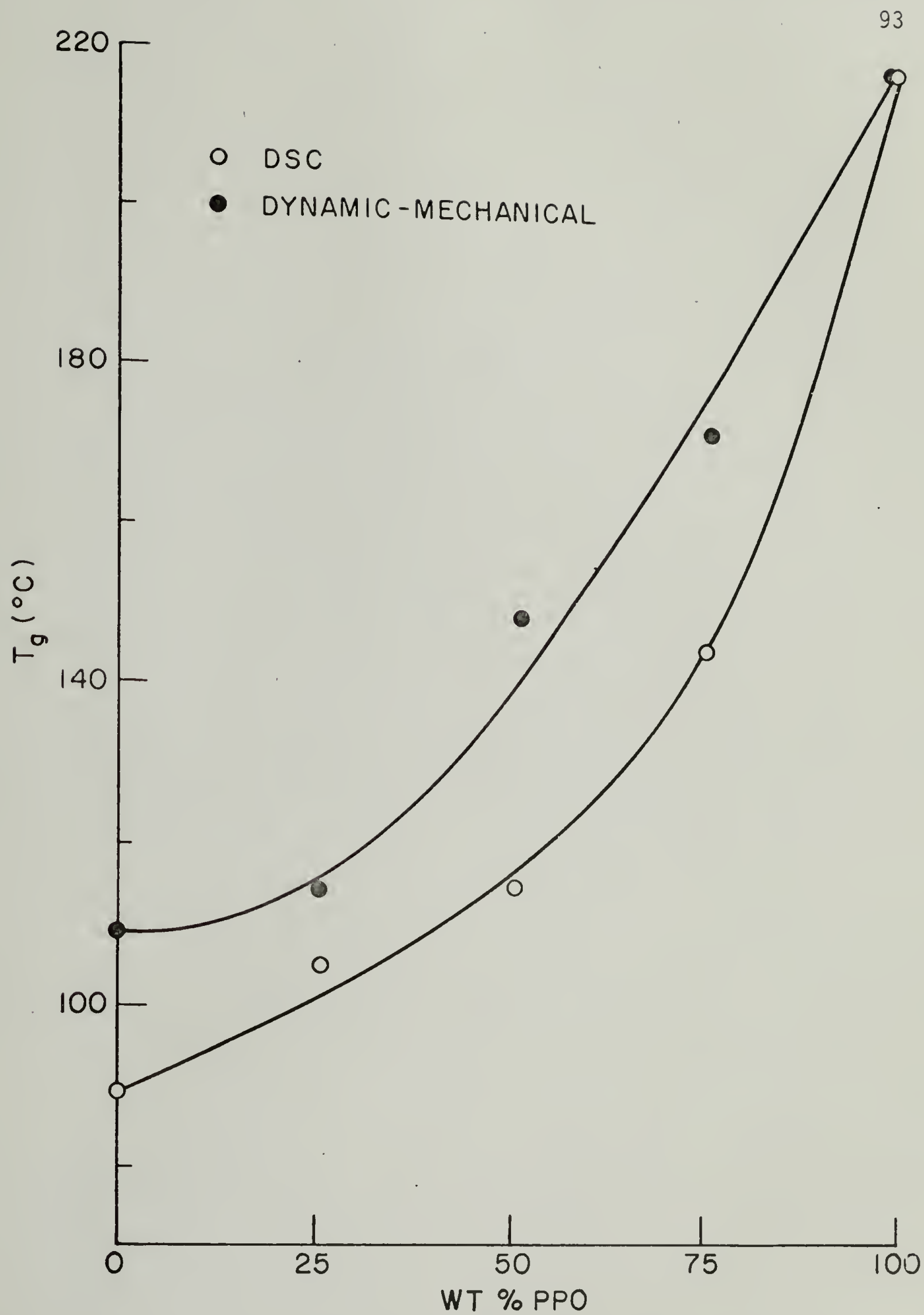


Fig. 1. Glass transition temperature as a function of composition for i-PS/PP0 polyblends

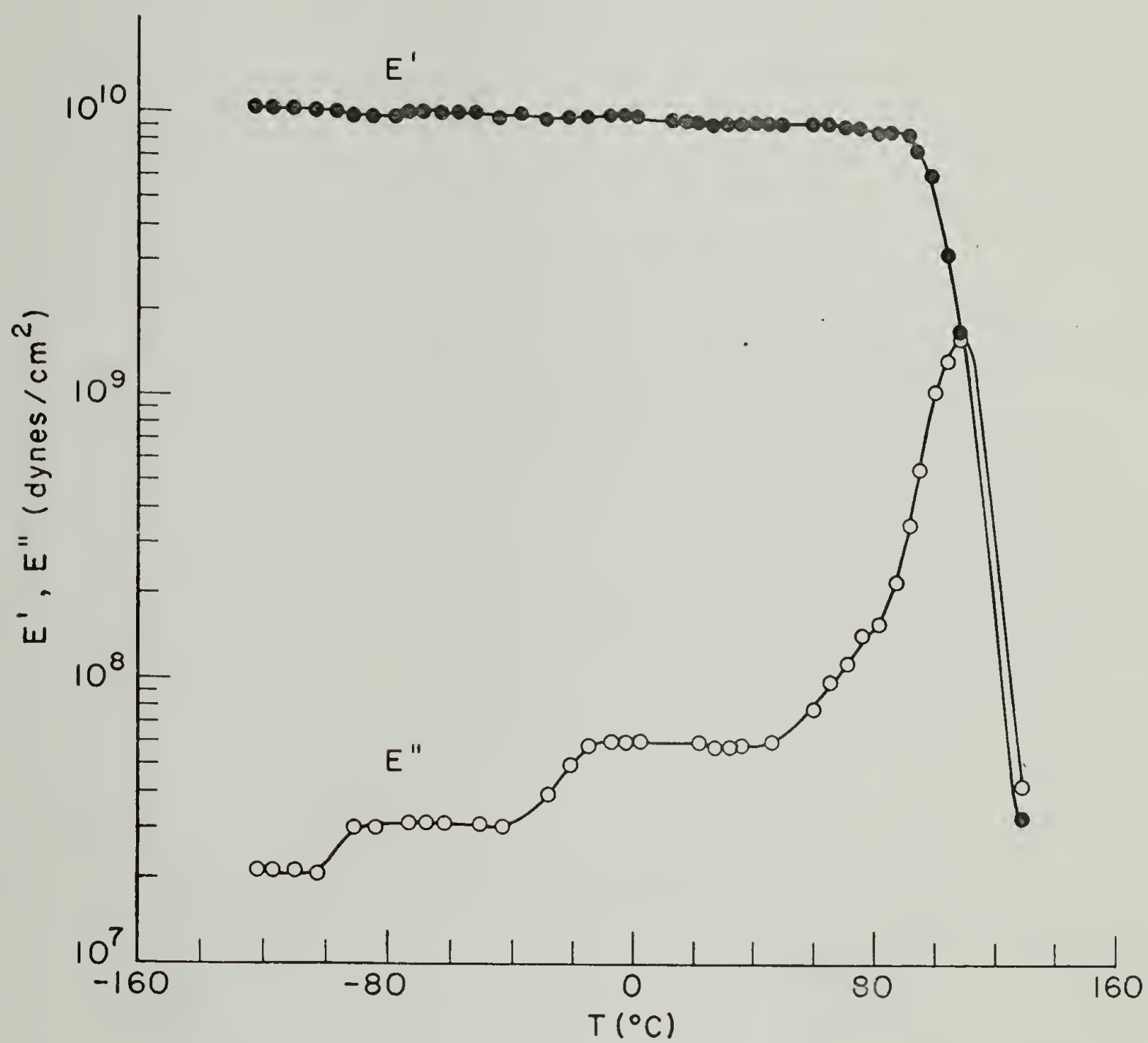


Fig. 2. Dynamic-mechanical storage and loss moduli for i-PS as a function of temperature at 11 Hz

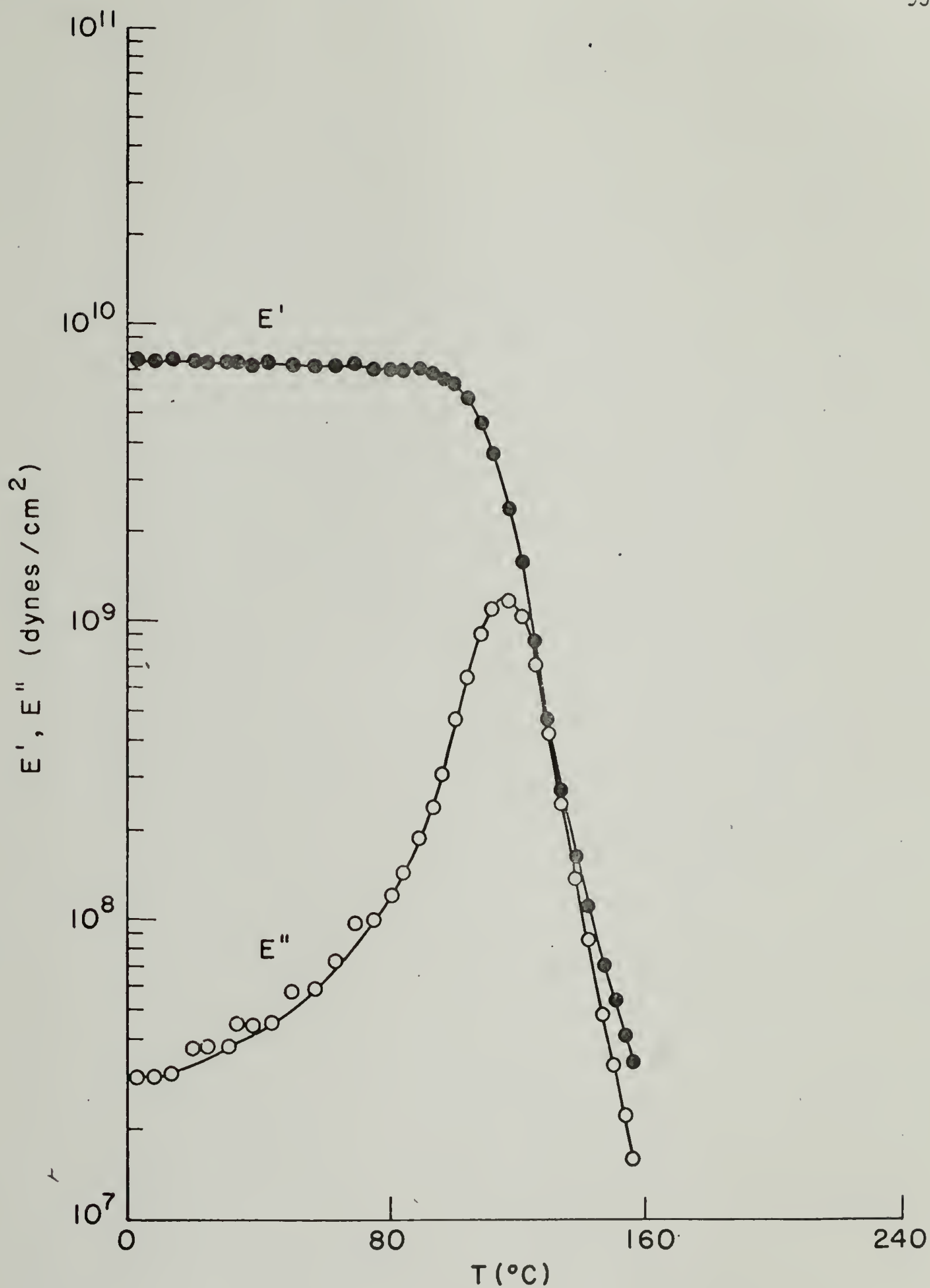


Fig. 3. Dynamic-mechanical storage and loss moduli for polyblend of 75% i-PS and 25% PPO as a function of temperature at 11 Hz

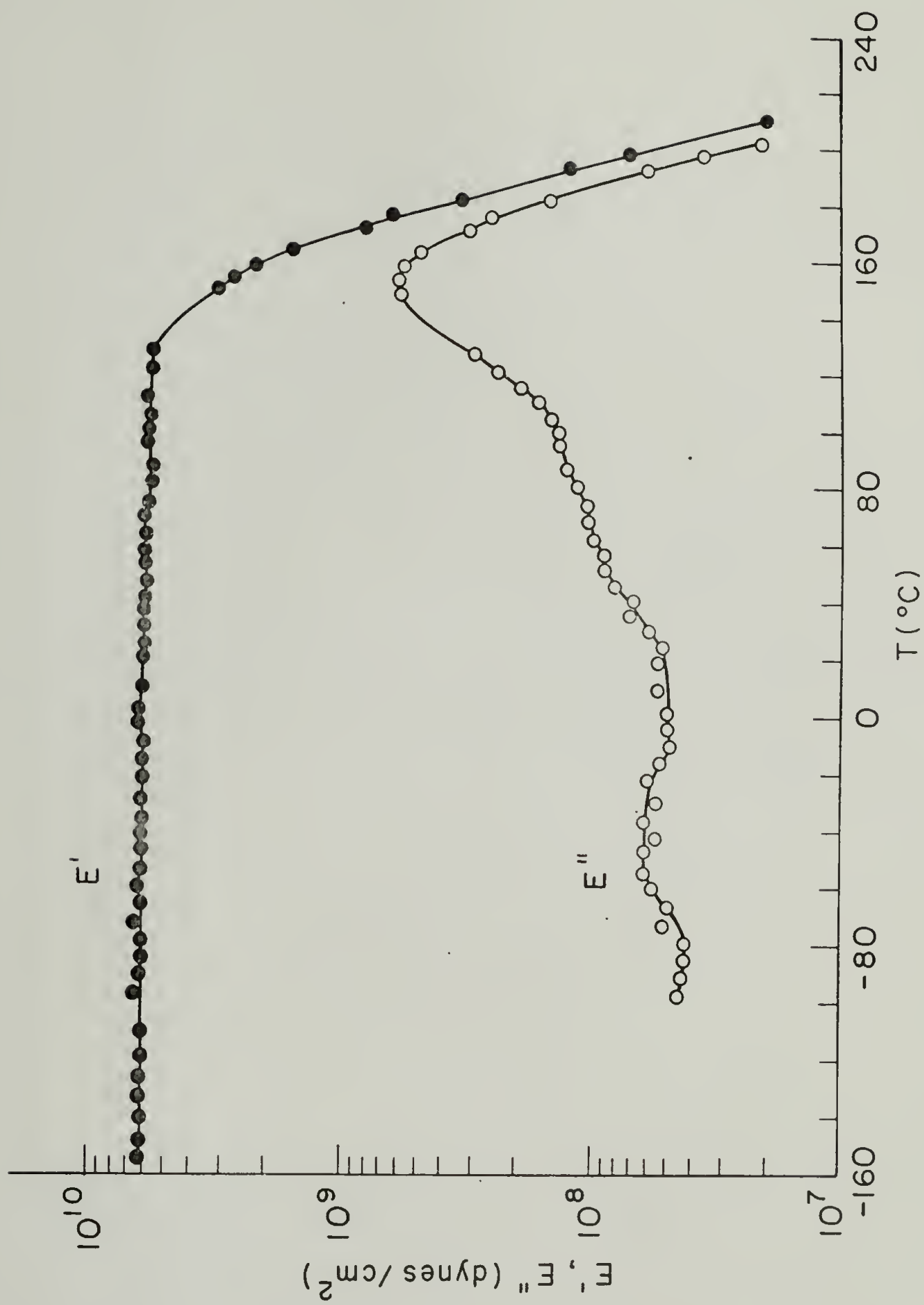


Fig. 4. Dynamic-mechanical storage and loss moduli for polyblend of 50% i-PS and 50% PP0 as a function of temperature at 11 Hz



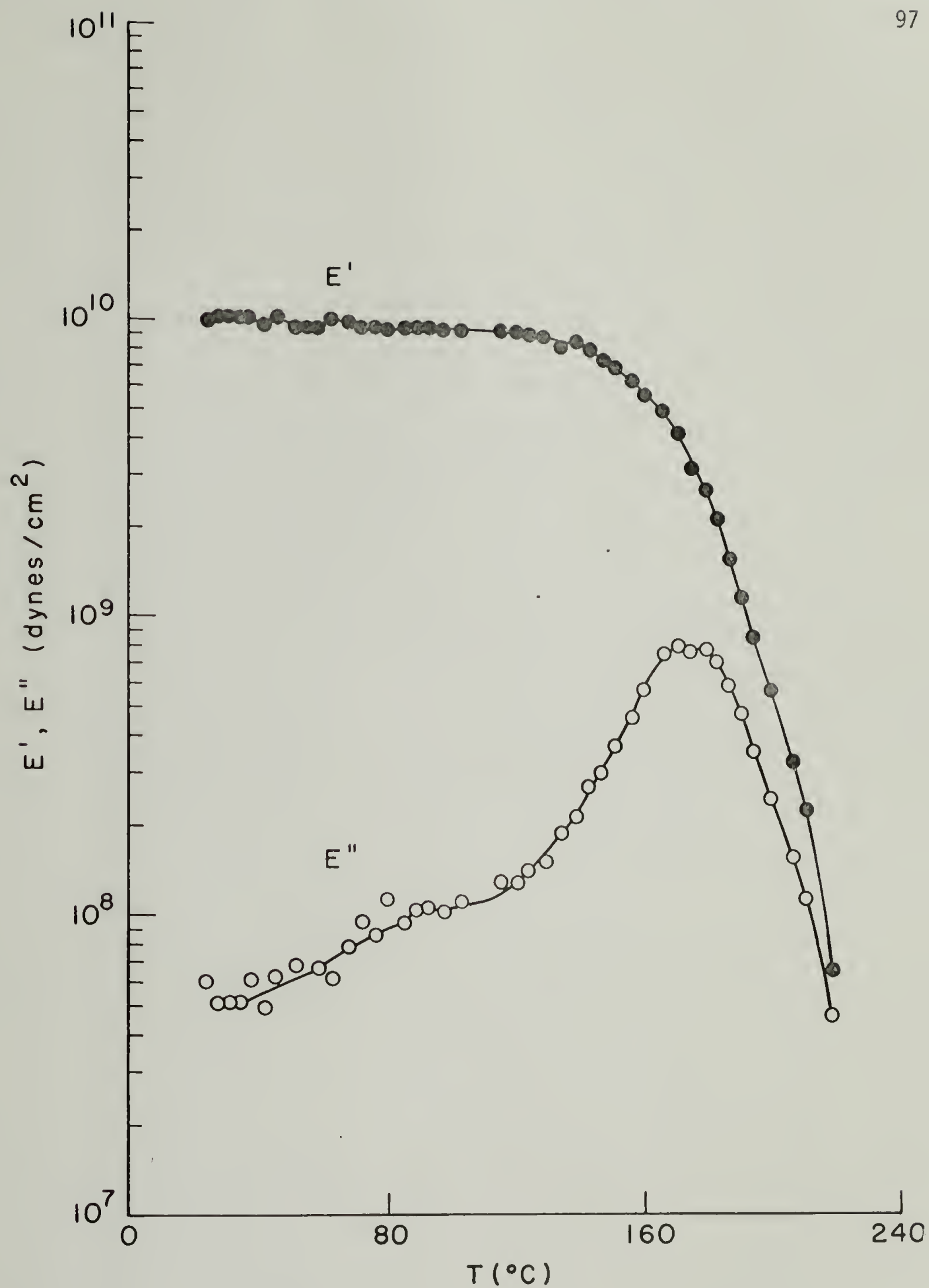


Fig. 5. Dynamic-mechanical storage and loss moduli for polyblend of 25% i-PS and 75% PPO as a function of temperature at 11 Hz

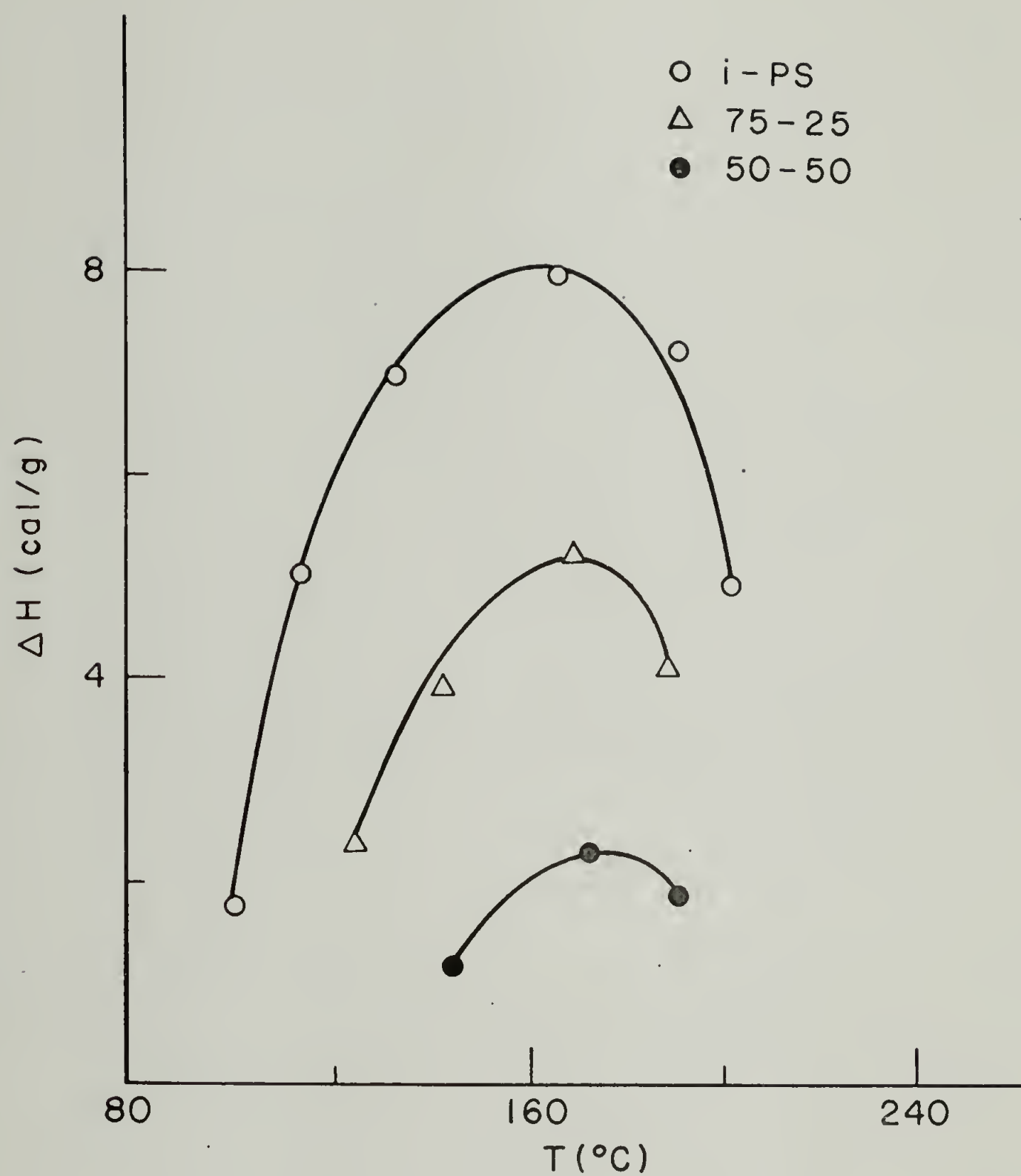


Fig. 6. Enthalpy of fusion as a function of annealing temperature for i-PS and polyblends of i-PS and PPO

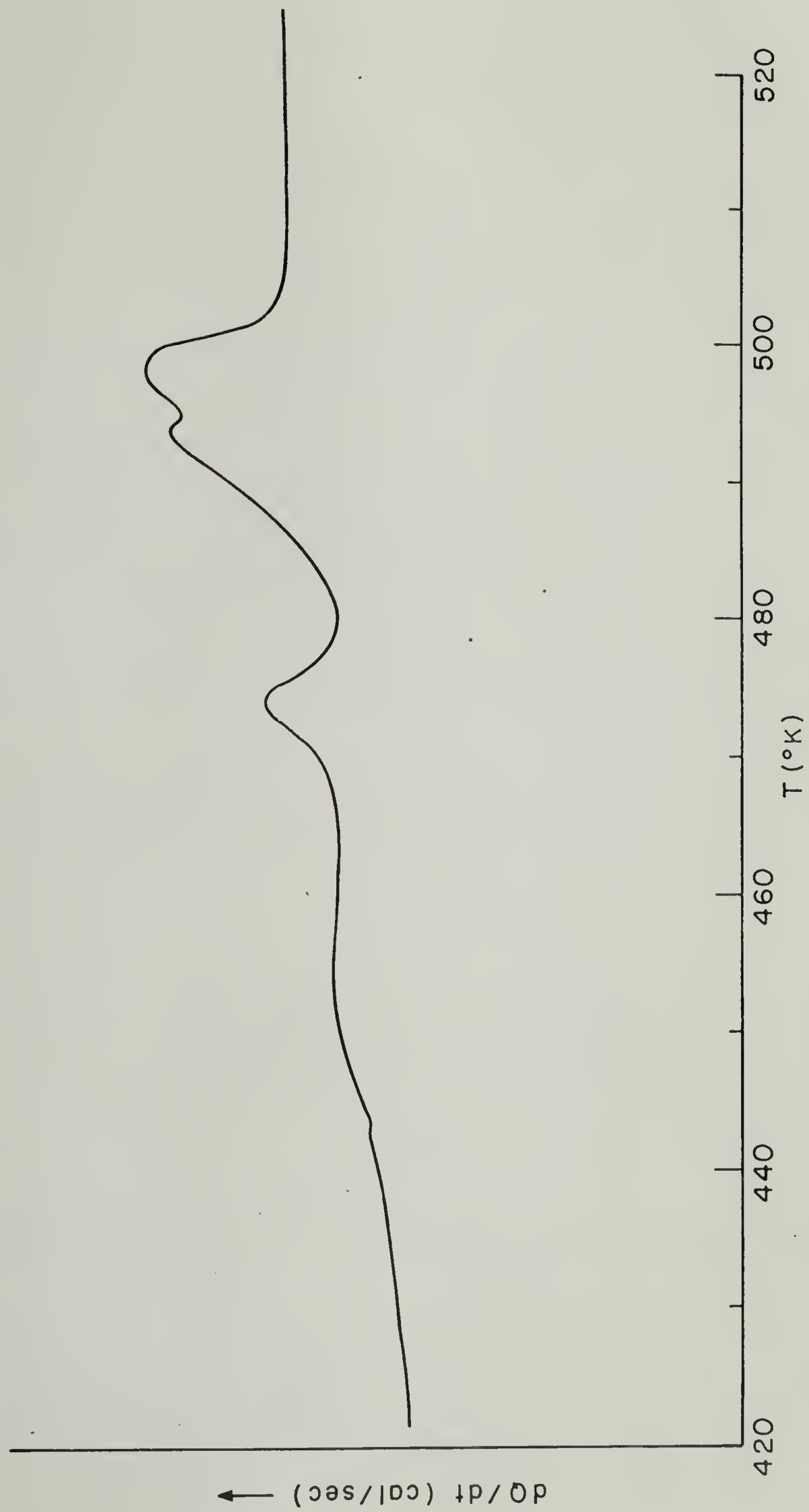


Fig. 7. DSC thermogram for polyblend of 75% i-PS and 25% PPO annealed at 146°C for 24 hours

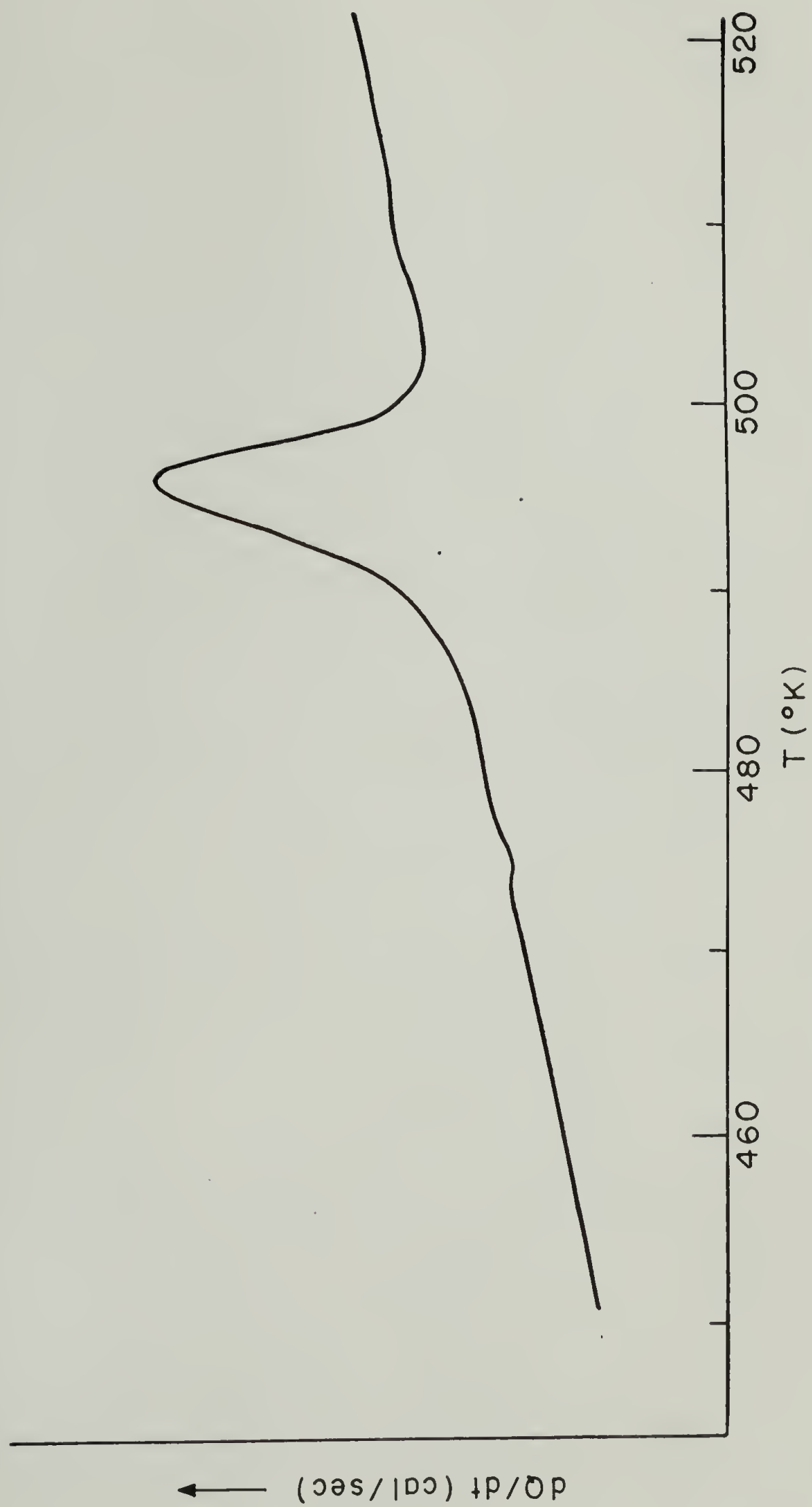


Fig. 8. DSC thermogram for polyblend of 75% i-PS and 25% PP0 annealed at 193°C for 24 hours



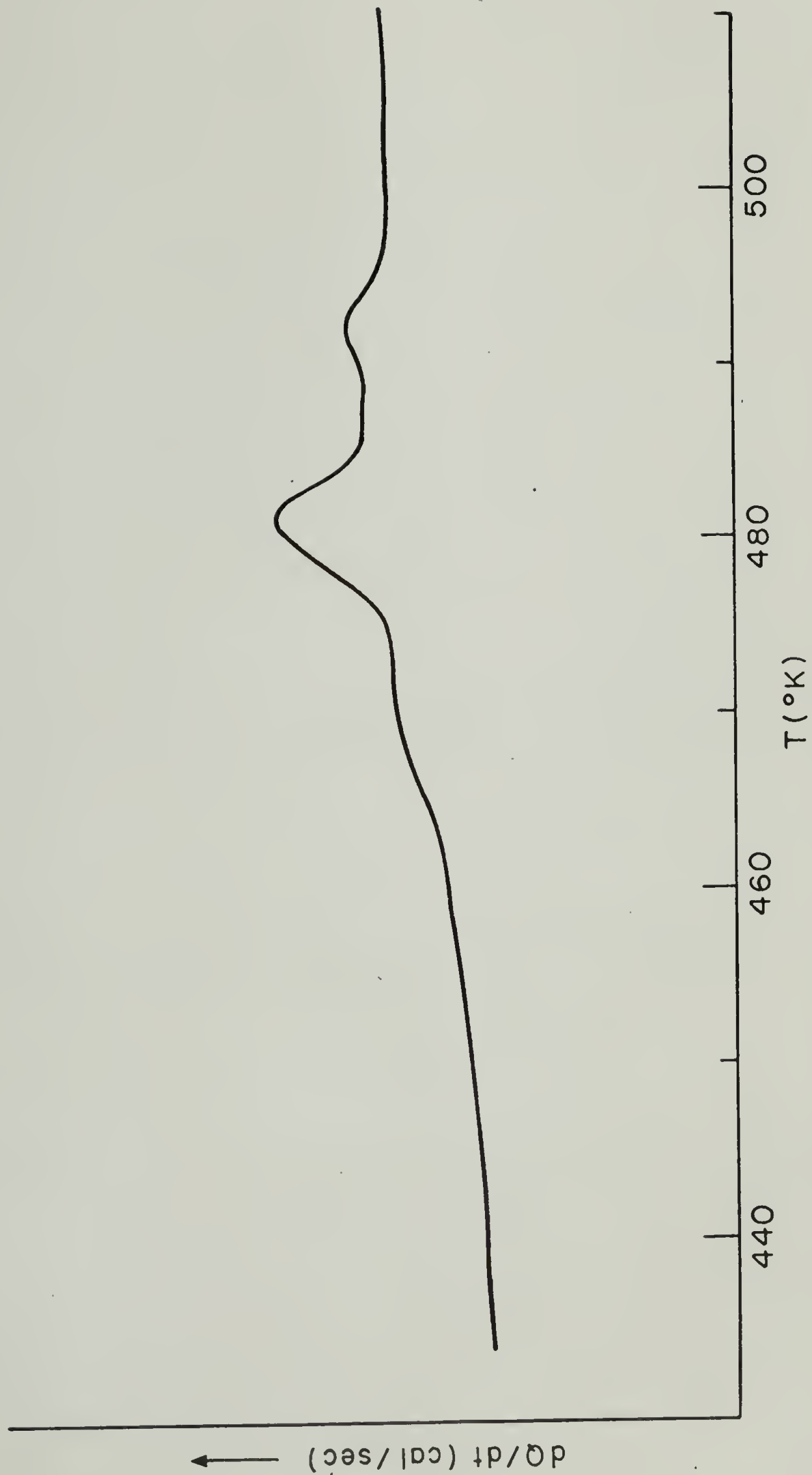


Fig. 9. DSC thermogram for polyblend of 50% i-PS and 50% PPO annealed at 164°C for 24 hours

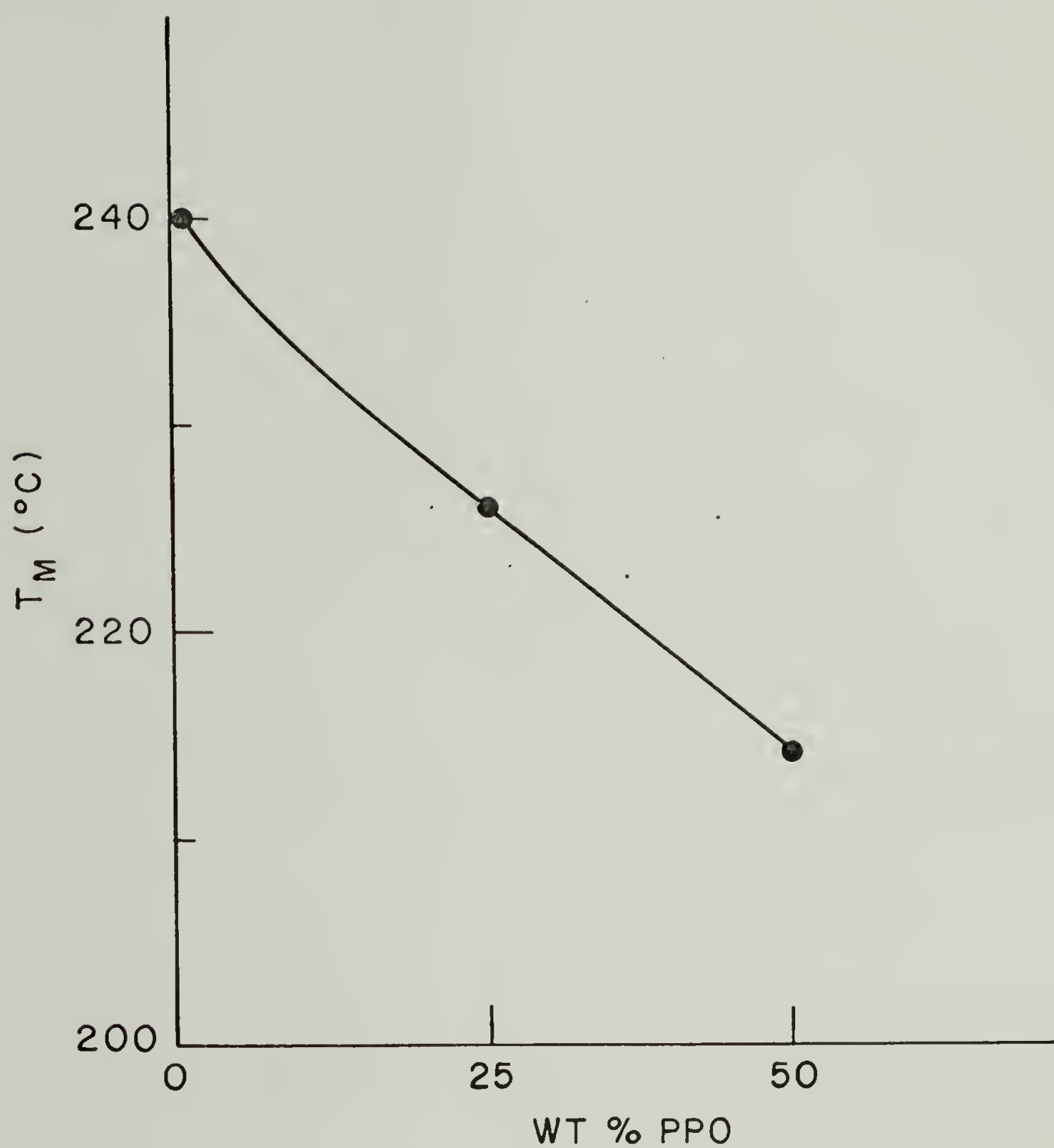


Fig. 10. Melting temperature as a function of composition for crystallized i-PS/PPO polyblends

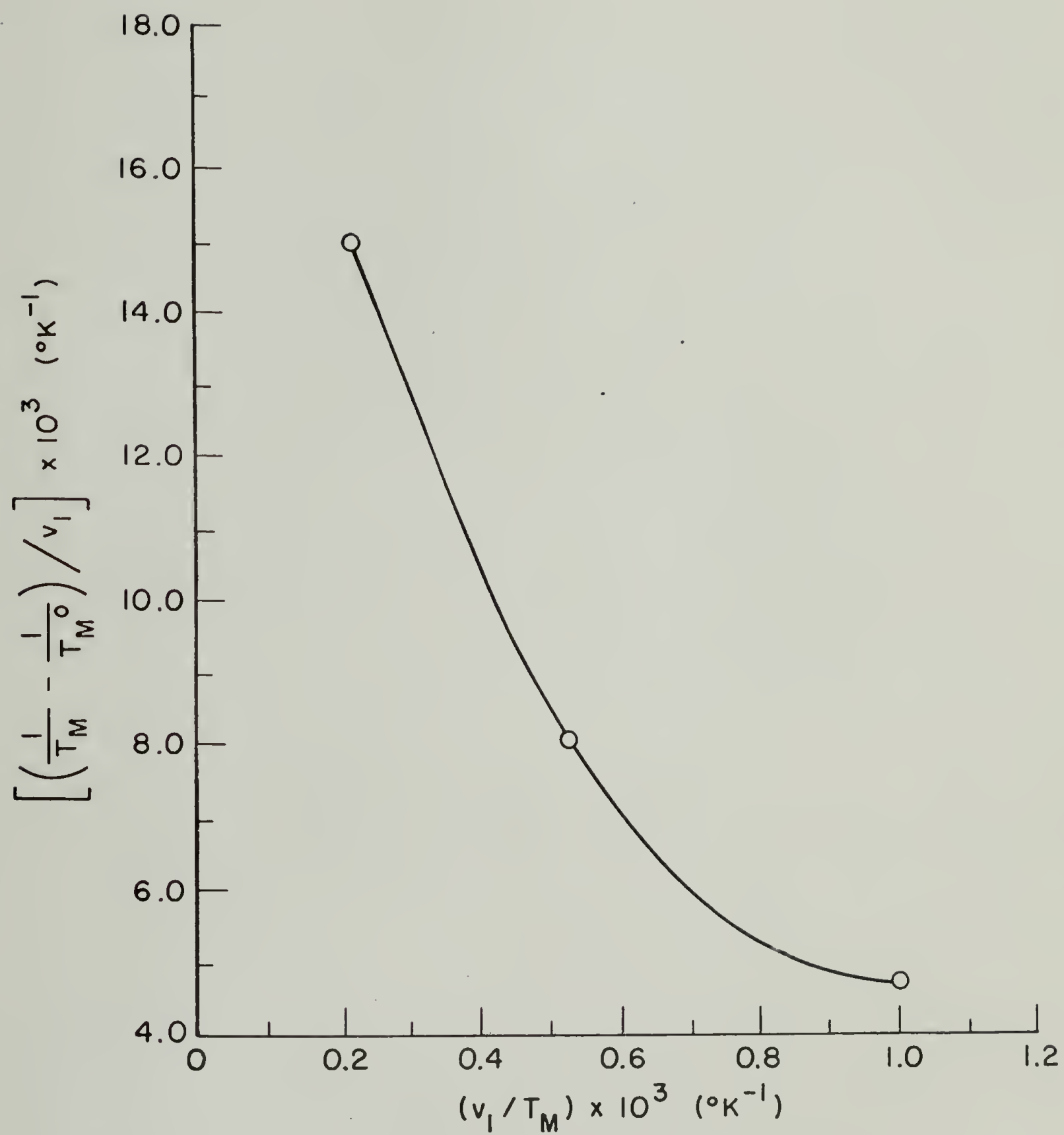


Fig. 11. Plot of  $(1/T_m - 1/T_m^0)/v_1$  against  $v_1/T_m$  for i-PS/PP0 polyblends<sub>m</sub>

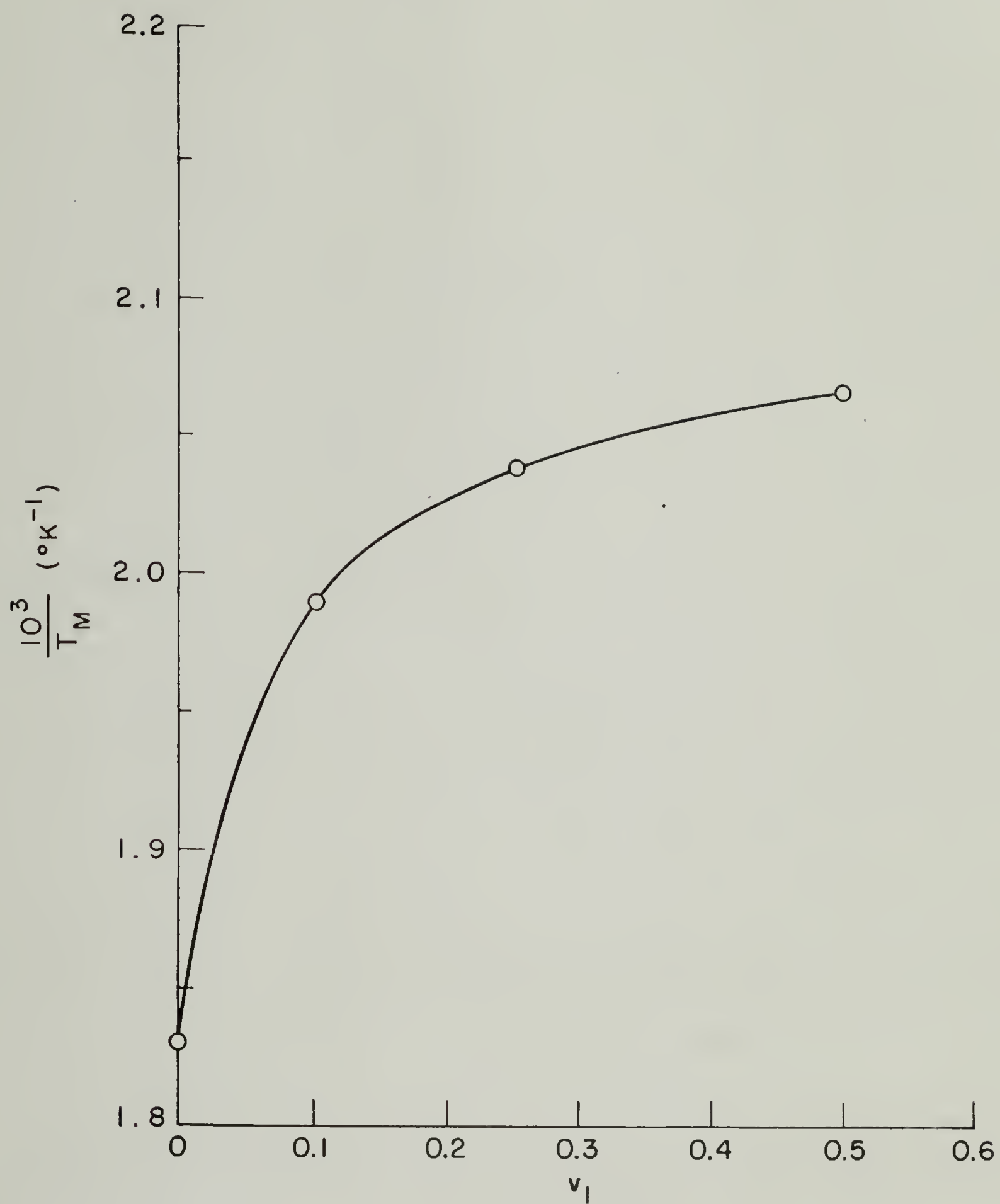


Fig. 12. Plot of  $1/T_m$  against  $v_1$  for i-PS/PP0 polyblends

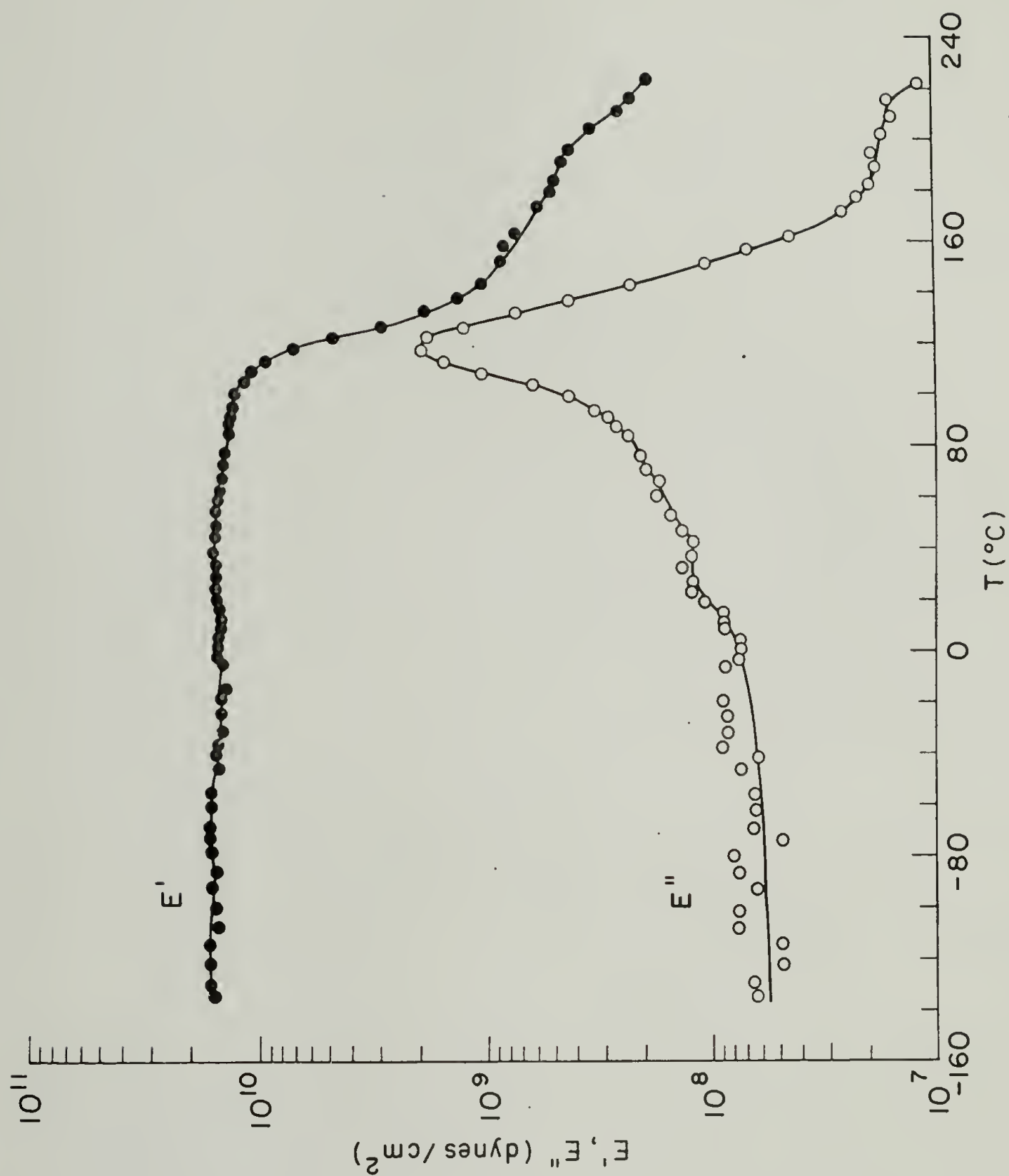


Fig. 13. Dynamic-mechanical storage and loss moduli for crystallized i-PS as a function of temperature at 11 Hz.



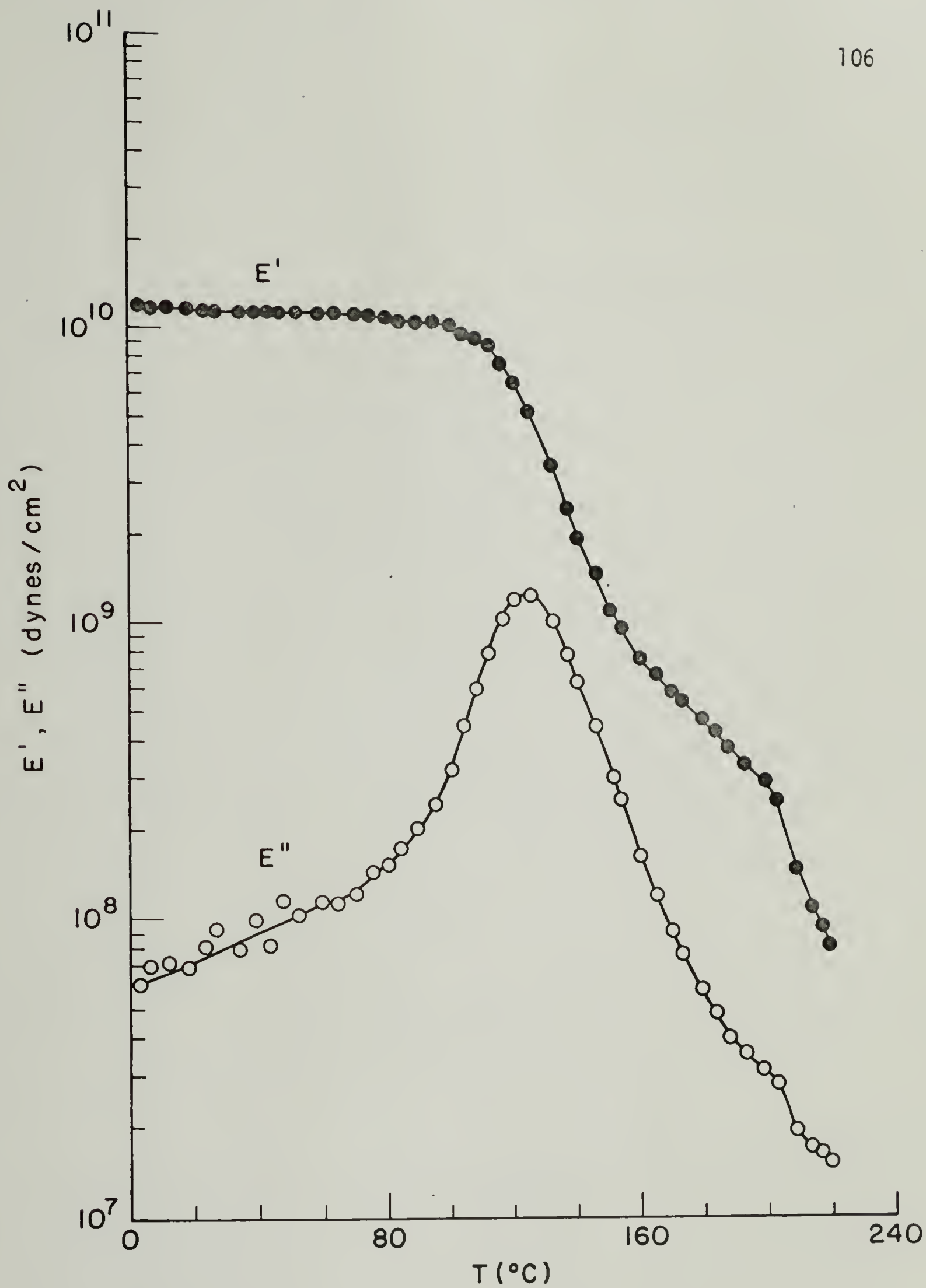


Fig. 14. Dynamic-mechanical storage and loss moduli for crystallized polyblend of 75% i-PS and 25% PPO as a function of temperature at 11 Hz

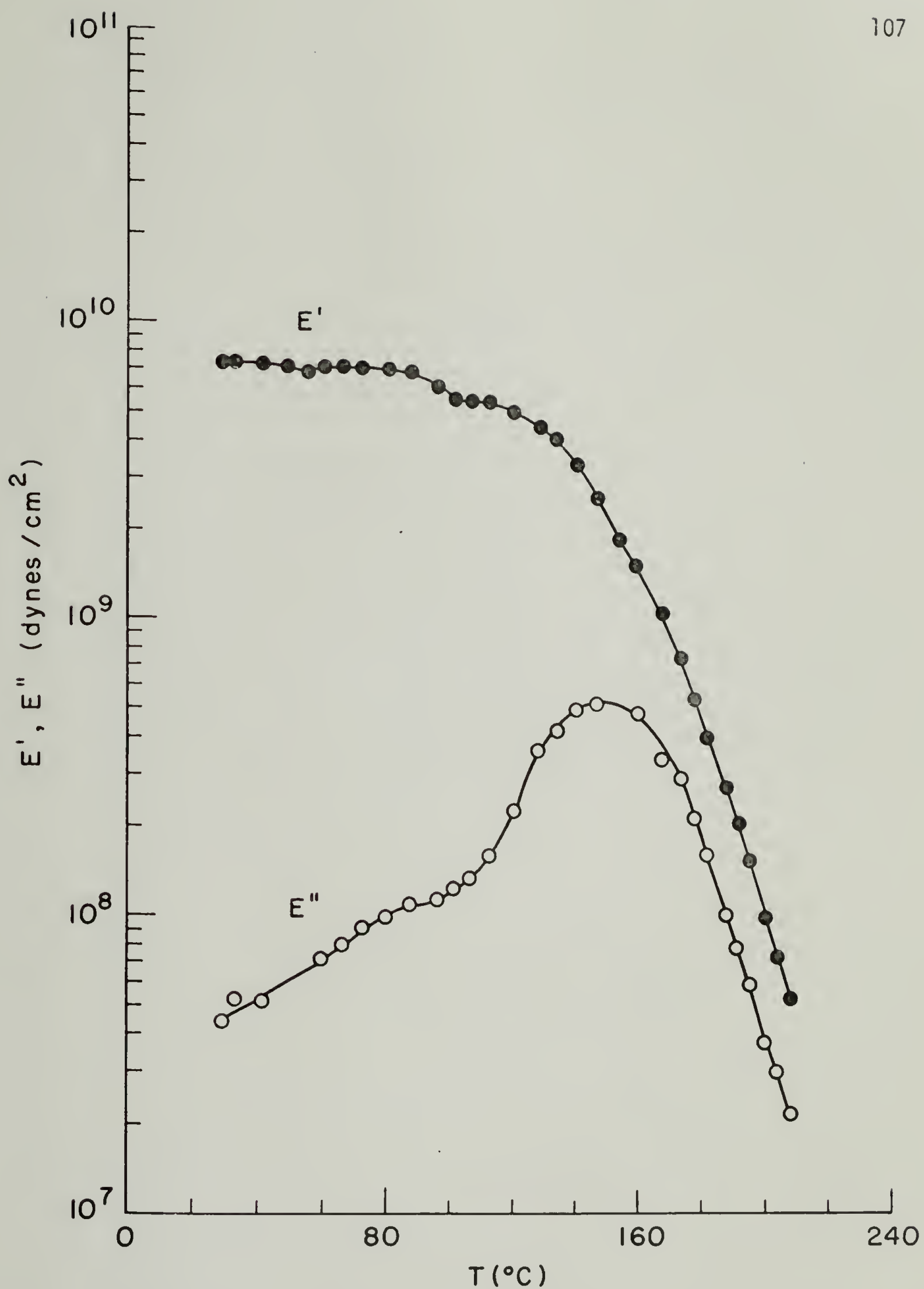


Fig. 15. Dynamic-mechanical storage and loss moduli for crystallized polyblend of 50% i-PS and 50% PPO as a function of temperature at 11 Hz

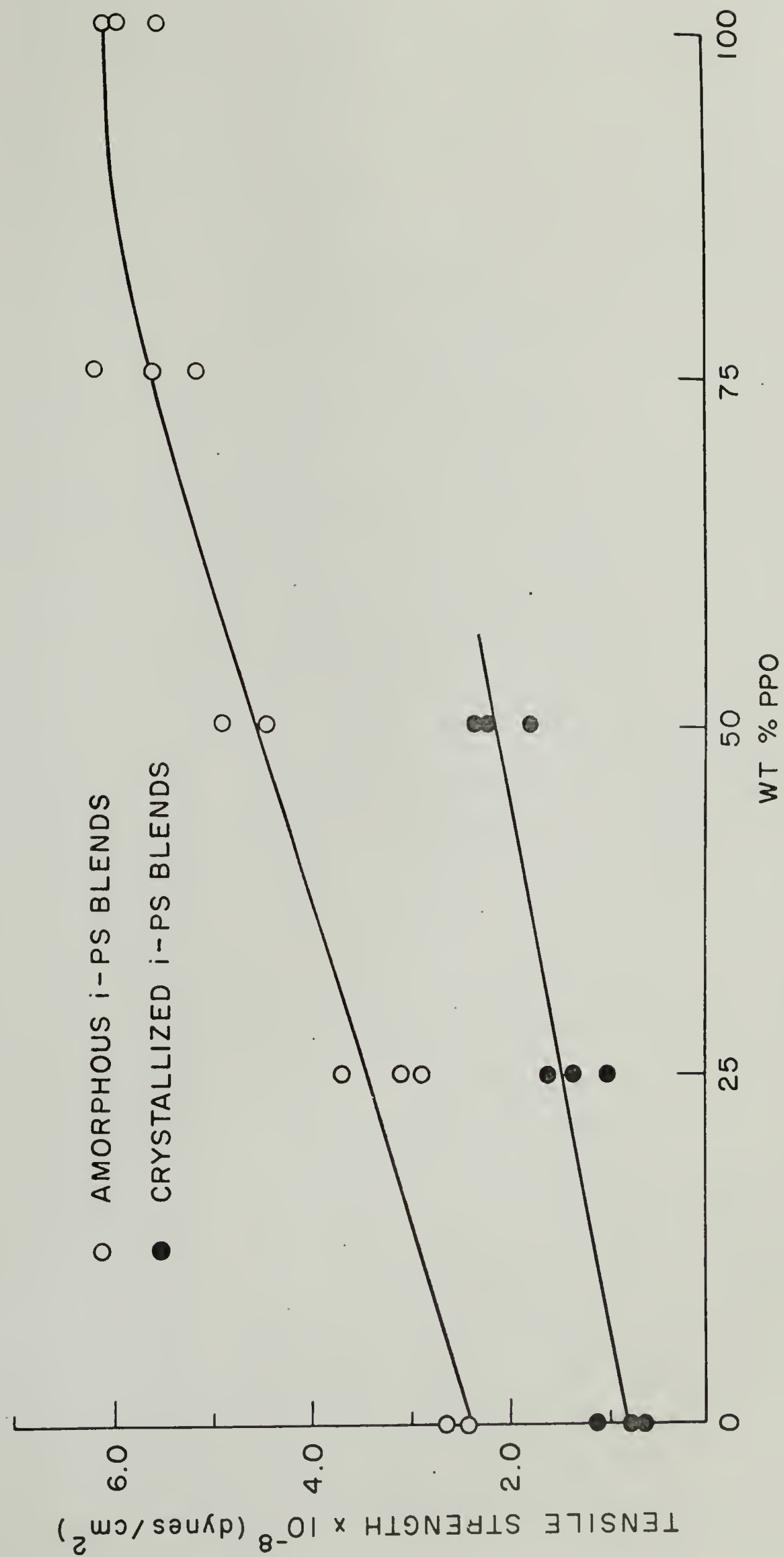


Fig. 16. Tensile strength as a function of composition for i-PS/PP0 polyblends

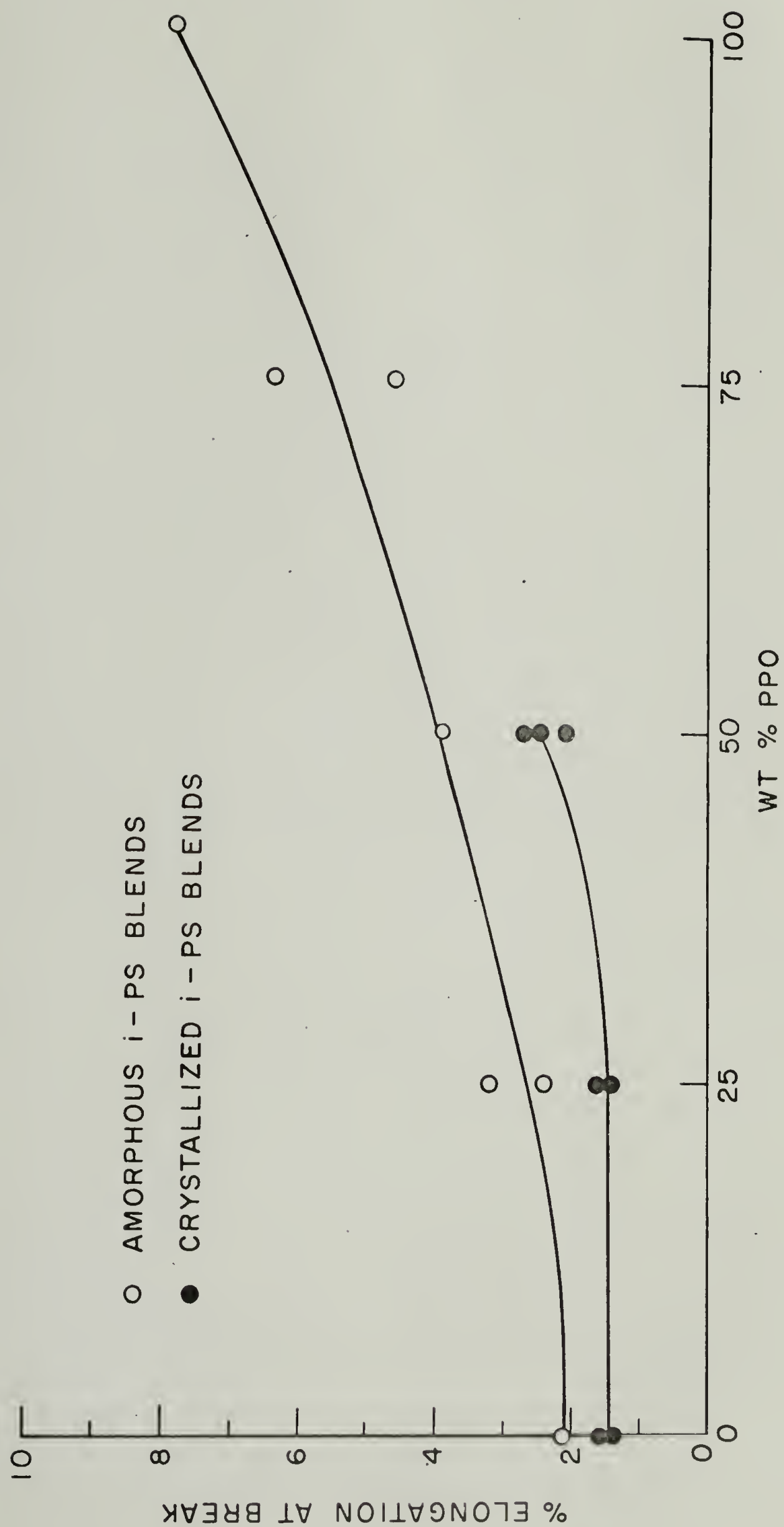


Fig. 17. Per cent elongation at break as a function of composition for i-PS/PP0 polyblends

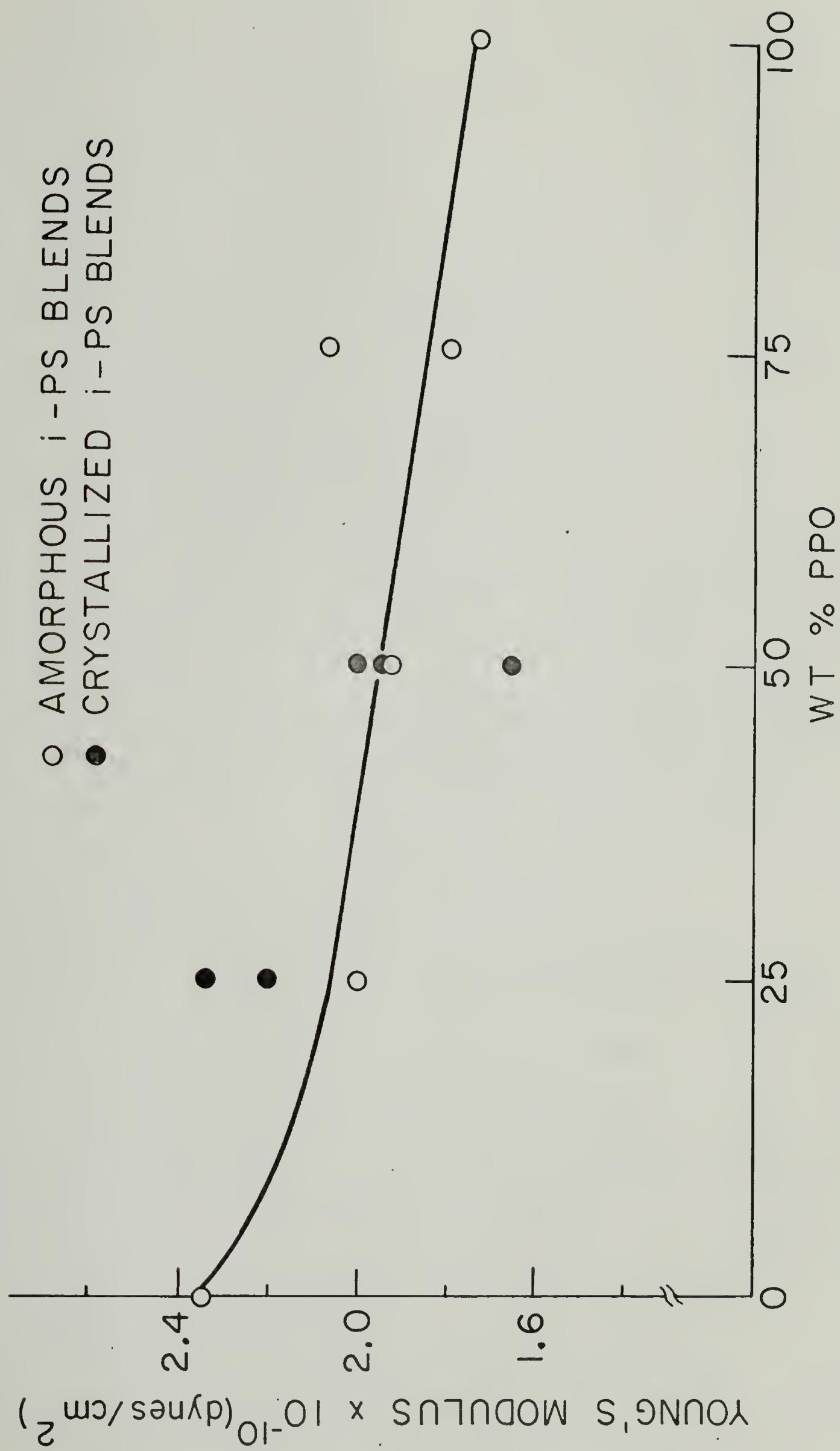


Fig. 18. Young's modulus as a function of composition for i-PS/PP0 polyblends



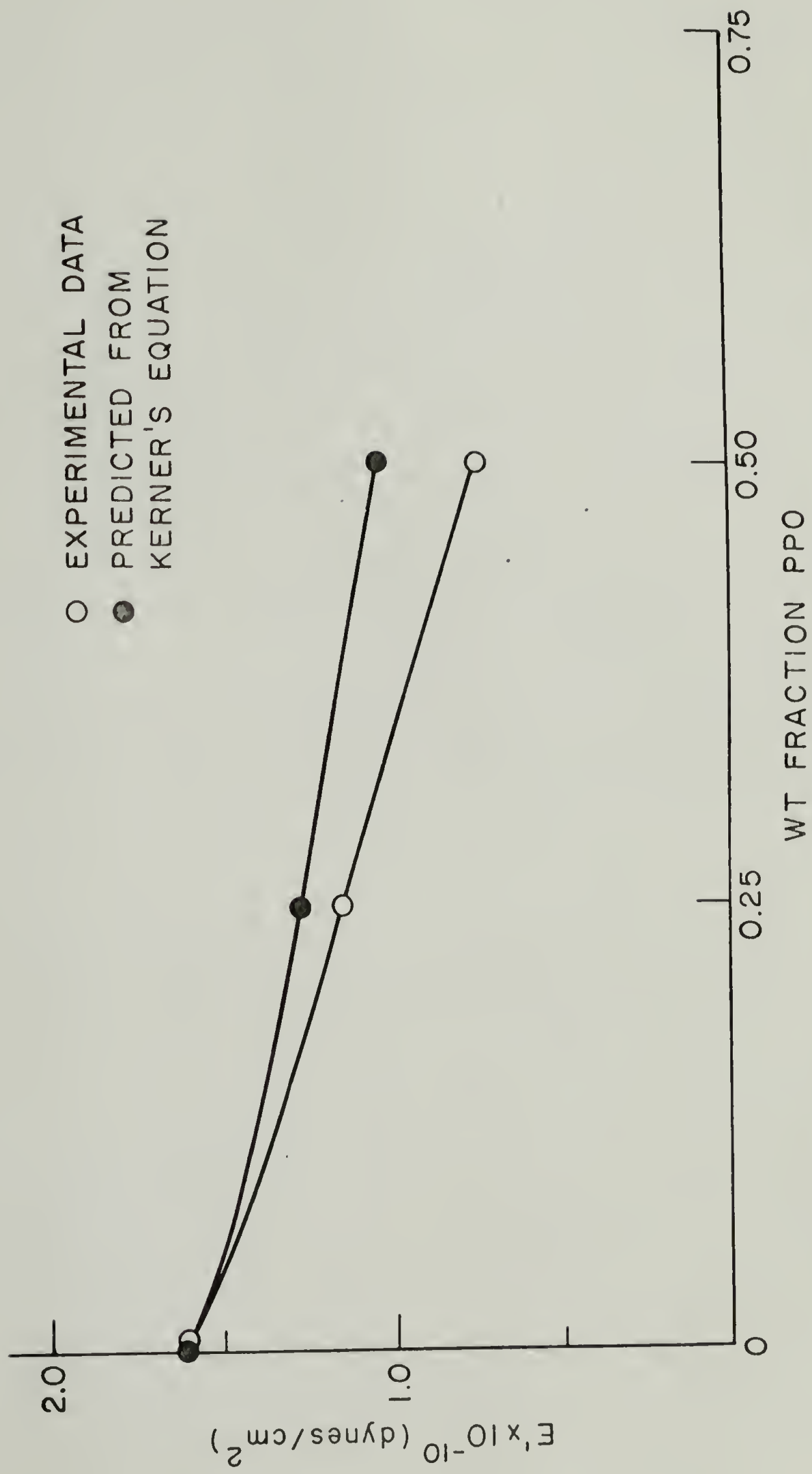


Fig. 19. Comparison of experimental and theoretical dynamic-mechanical storage moduli as a function of composition for i-PS/PP0 polyblends

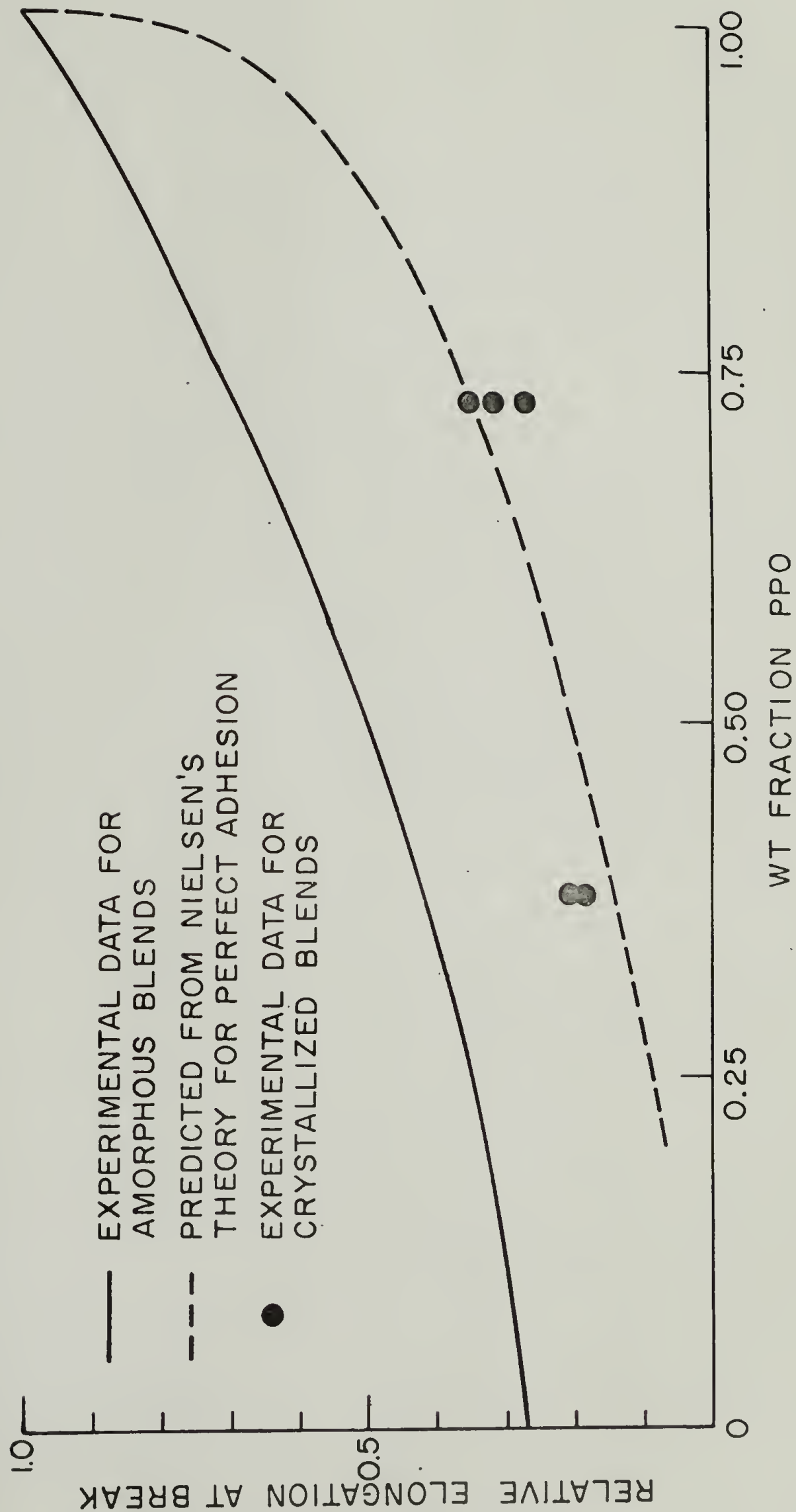


Fig. 20. Comparison of experimental and theoretical relative elongation at break as a function of composition for i-PS/PPO polyblends

## APPENDIX A

## THERMODYNAMIC PROPERTIES OF POLY- $\epsilon$ -CAPROLACTONE

A study was made of the thermodynamic properties of poly- $\epsilon$ -caprolactone (PCL) during the course of this work. Differential scanning calorimetry (DSC) was used to measure the melting point depressions of mixtures of the polymer with 1-chloronaphthalene, and from these data the heat of fusion of PCL was calculated. Such data have been subsequently published by Crescenzi, et al.,<sup>1</sup> with somewhat different results.

A sample of PCL-700 was obtained from the Union Carbide Corporation and was used as received. The polymer had a number average molecular weight of 8,050 as determined by vapor phase osmometry. Mixtures of the polymer and 1-chloronaphthalene were placed in test tubes which were evacuated and sealed. The resulting capsules were then heated to dissolve the polymer and were ultimately quenched into ice water. Final compositions were determined by chlorine analysis.

The melting points of 5 - 15 mg samples of these mixtures were determined from DSC traces at a heating rate of 0.625°C/min. The melting point ( $T_m$ ) was taken as the temperature at which the trace through the endothermic peak returned to the baseline.

The melting points of mixtures of PCL and 1-chloronaphthalene up to a volume fraction  $v_1$  of 0.39 diluent are shown in Figure A-1. These results were analyzed in the customary manner in which  $(1/T_m - 1/T_m^0)/v_1$  is plotted against  $v_1/T_m$ . In these expressions  $T_m^0$  and  $T_m$  are the melting points of the pure polymer and of a polymer diluent

mixture of volume fraction  $v_1$  of diluent, respectively. The intercept of such a plot is proportional to  $\Delta H_u^{-1}$ . A value of 26.4 cal/g was determined for  $\Delta H_u$  from the plot shown in Figure A-2.

Such results are in conflict with those reported by Crescenzi, et al.,<sup>1</sup> who obtained values of 32.3 - 36.2 cal/g using similar techniques. Since the techniques involved are subject to limited accuracy, the value for the heat of fusion is only known within some uncertainty.



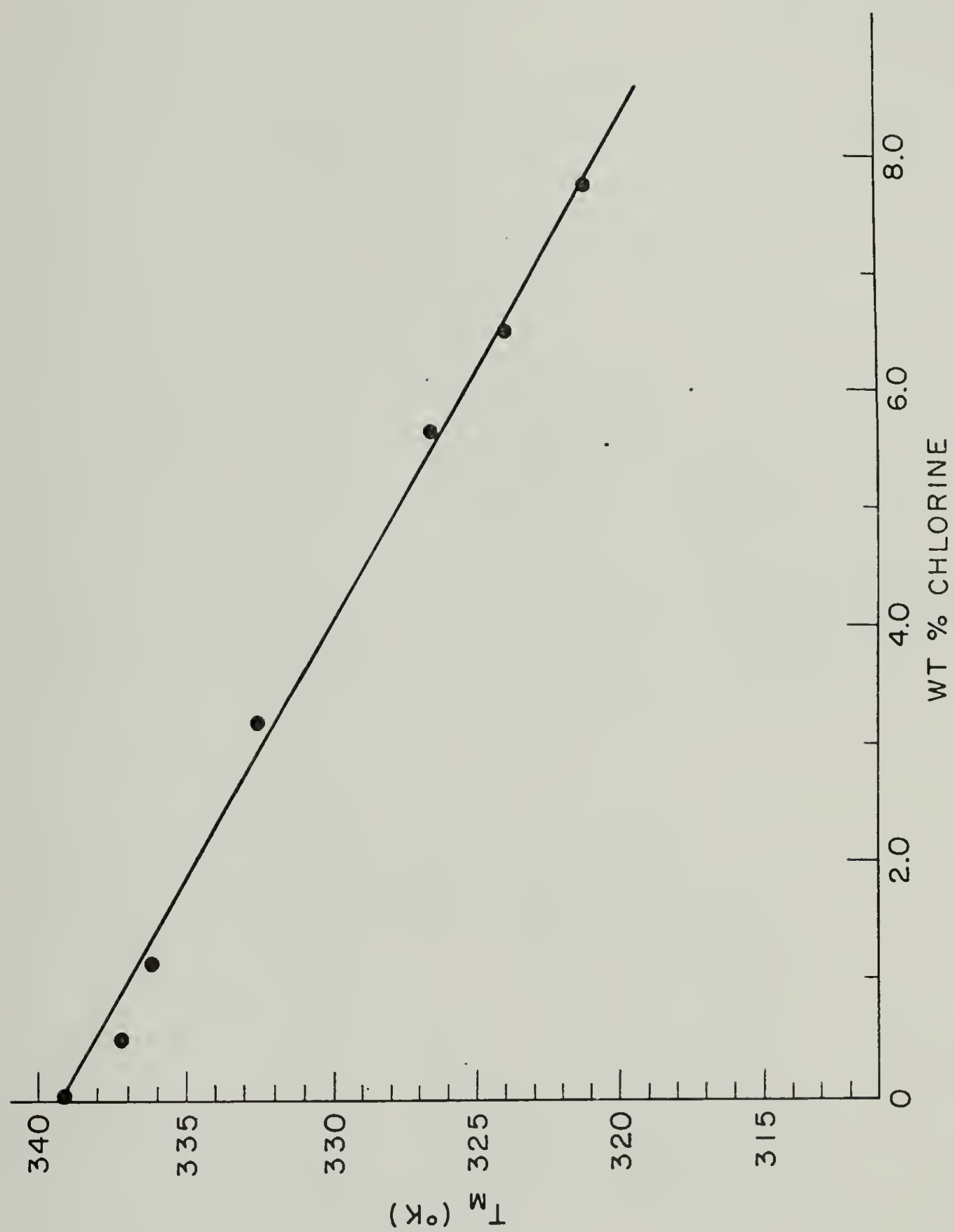


Fig. A-1. Melting temperature as a function of composition for mixtures of PCL and 1-chloronaphthalene

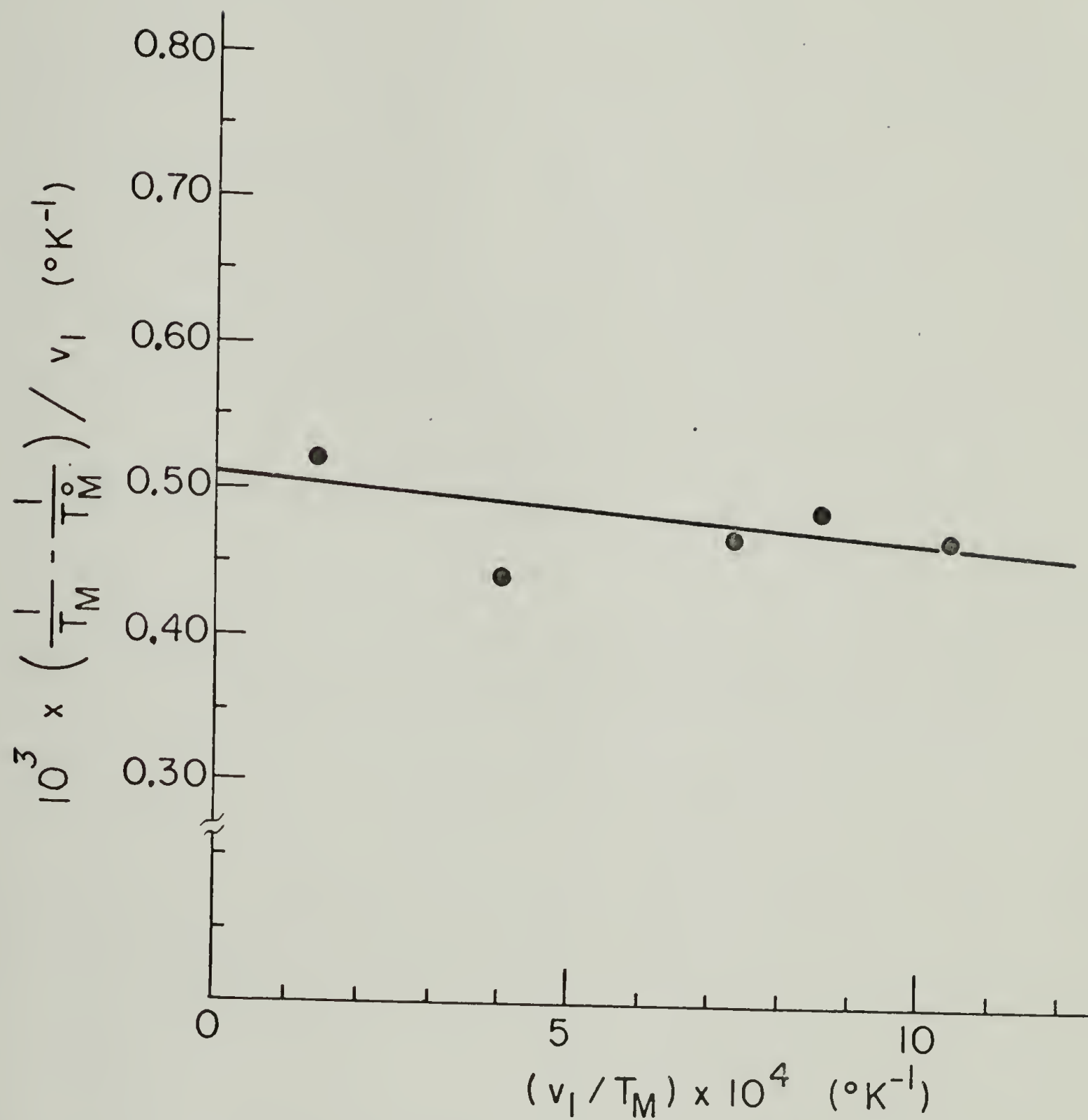


Fig. A-2. Plot of  $(1/T_m - 1/T_m^0)/v_1$  against  $v_1/T_m$  for mixtures of PCL and <sup>m</sup>1-chloronaphthalene

## APPENDIX B

07/30/70

## PROGRAM DIELECT

C THIS COMPUTER PROGRAM CALCULATES THE DIELECTRIC CONSTANT AND THE DIELECTRIC LOSS AS A FUNCTION OF FREQ AND TEMP. IT DOES THIS FOR TWO TYPES OF CELLS VIZ. A LOW TEMP CELL WITH A GUARD ELECTRODE (HALSBANDUM CELL) AND A HIGH TEMP CELL WITHOUT A GUARD ELECTRODE. IN THE LATTER CASE, KIRCHHOFF'S FORMULA IS USED FOR CALC EDGE CAP ASSUMING THE CELL ELECTRODES ARE 53 MM IN DIAM AND 0.5 CM THICK. ALSO THAT EDGE CAP IS INDEX OF TEMP AND FREQ. IN ALL CASES TAN DELTA IS CORRECTED FOR DC CONDUCT. AND DIELECTRIC CONSTANT IS CORRECTED FOR HIGH TAN DELTA WHEN TAN DELTA IS MEASURED DIRECTLY.

\*\*\*\*\* WRITTEN BY ROLAND J. TETREault \*\*\*\*\*

C LH = CODE FOR CELL USED. IN COLUMN 11 BELOW TEMP, 1=HIGH TEMP CELL

C THICK = SAMPLE THICKNESS IN MILS

C CONDT = TOTAL CONDUCTANCE IN MICROMHOS

C TEMP = TEMPERATURE IN DEGREES C

C TAND = TAN DELTA

C FREQ = FREQUENCY IN KHZ

C ACCON = AC CONDUCTANCE IN MICROMHOS

C CO = CONDUCTANCE IN AIR IN MICROMHOS

C DIAM = DIAMETER OF ALUMINUM ELECTRODES IN MM

C DICCN = DIELECTRIC CONSTANT

C CAP = CAPACITANCE IN PICOFARADS

C ECAP = EDGE CAPACITANCE IN PICOFARADS

C RESIS = RESISTANCE IN MEGOHMS

C D = SAMPLE THICKNESS IN MM

C DILOS = DIELECTRIC LOSS

C RTMP = RECIPROCAL TEMPERATURE \* 1000 IN DEGREES K

C CRT = AIR CAPACITANCE AT 21 DEGREES C IN PICOFARADS  
 C EO 45 REPRESENTS CALIBRATION OF TEFLON COATED CELL VBP 62K 1-24-71  
 C

```

2400 DIMENSION ID (10)
      KPAGE = 0
4900 READ (5,4900) (ID(I), I = 1,10)
      FORMAT (11A8)
      IF (EOF,5) 999, 2500
2500 READ (5,5000) THICK, LH, DIAM
5000 FORMAT (F10.0, I10, F10.0)
2000 READ (5,5010) TEMP, FREQ, TAND, CONDI, CAP, RESIS
5010 FORMAT (OF10.0)
3000 IF (EOF,5) 2400, 3000
      CRT = ( 565.31 / THICK ) + 8.98
      TANSQ = 1.
      IF ( TAND .GT. .00000001 ) TANSQ = 1./ (1. + TAND * TAND)
      IF ( TAND .GT. .00000001 ) CONDI = 6.26 * FREQ * CAP * TAND / 1000.
      DCCON = 0.0
      IF ( RESIS .LT. .00000001 ) GO TO 10
      DCCON = 1./RESIS
      ACCON = CONDI - DCCON
      TAND = (ACCON * 1000.) / (0.28 * FREQ * CAP)
      RTEMP = 100. / (TEMP + 273.)
      TERM = 1.
      IF ( DIAM .GT. .00000001 ) TERM = (2809. / (DIAM * DIAM))
      IF ( LH .EQ. 0 ) GO TO 15
      CO = ( 1.0835 - 3.74120E-4 * TEMP + 2.45599/E-6 * TEMP * TEMP )
      1 * CRT

```



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```

      D = THICK * U.0254
      ECAP = 0.2344 * ( LOGF( 133.136 * ( C.5 + D) / (U * D)) + U.5 * LOGF ( (
1  U.5 + D) / U.5) - 3.)
      DICON = (( CAP - ECAP) / CO) * TANSQ * TERM
      DILOS = UICON * TAND
      GO TO 20
15  CO = ( 1.02044 - 1.07010E-3 * TEMP + 1.54223+E-6 * TEMP * TEMP -
1  2.0963E-8 * TEMP * TEMP * TEMP ) * CHT
      DICON = ( CAP / CO ) * TANSQ * TERM
      DILOS = UICON * TAND
20  CALL OUTPUT (TEMP, RTEMP, FREQ, DCCON, TAND, UICON, DILOS, APAGE,
1  IU)
      GO TO 200)
999  STOP
      END

```

07/30/77

SUBROUTINE CUIPUL (TEMP, RTEMP, FREQ, DCCON, TAND, DICON, DILOS,

1 KPAGE, 10)

DIMENSION ID(10)

IF (KPAGE .EQ. 0) 100, 250

100 WRITE (6,6000) (ID (1), J = 1,10)

6000 FORMAT (\*10, 10A8/ 1X)

WRITE (6,6100)

6100 FORMAT (\* TEMP (C) RECIP TEMP (K) FREQ DC CONDUCTANCE

1 TAN DELTA DIELECT. CONST. DIELECTRIC LOSS

2

WRITE (6,6200) TEMP, RTEMP, FREQ, DCCON, TAND, DICON, DILOS

6200 FORMAT (3X, F7.1, 2X, F11.4, 5X, F6.2, 4X, F12.8, 6X, F8.5, 5X,

1 F12.4, 2X, F12.5)

KPAGE = 2

TEMPS = TEMP

RETURN

250 NAUD = 1

IF (ABS (TEMPS - TEMP) .GT. .00000001) NAUD = 2

IF ((KPAGE + NAUD) .GT. 40) 100, 300

300 IF (NAUD .EQ. 2) WRITE (6,6300)

6300 FORMAT (1X)

WRITE (6,6200) TEMP, RTEMP, FREQ, DCCON, TAND, DICON, DILOS

KPAGE = KPAGE + NAUD

TEMPS = TEMP

RETURN

END

F8.6  
F8.6

## APPENDIX C



```

DC 6001 = 1,200
TEMP(I) = 0,0
GG(I) = 0,0
U(I) = 0,0
P(I) = 0,0
AAL(I) = 0,0
EPRIME(I) = 0,0
REP(I) = 0,0
SS(I) = 0,0
DELTA(I) = 0,0
AND(I) = 0,0
SLOPE(I) = 0,0
EDDOUBLE(I) = 0,0
600 PRINT 4000
4000 FORMAT(1H ,//)
22 READ 1,(HEADING(I), I=1,9)
1 FORMAT(9A8)
6 FORMAT(1H1,9A8)
PRINT 6,(HEADING(I), I=1,9)
PRINT 89
89 FORMAT(1H ,///)
PRINT 82
J = 0
K = 0
7 READ 2, THICKO,WIDEO,ALO
5 FORMAT(3F10,2)
AREA = THICKO*WIDEO*0.00254
VO = THICKO*WIDEO*ALO
2 J = J + 1

```



U7/23/71

FTN5:48

```

      READ 17, TEMP(J), GAGE, D, DELTA(J), AF
      10 FORMAT(5F10,2)
      IF(D)90,90,1000
      C   THE VALUE OF D- WILL BE THE TEST NUMBER
      1000 X = ATANF(DELTA(J))
      43 IF(AF - 2.)42,43,42
      42 AF = SORTF(10.)
      Y = COSF(X)
      AL = ALD + (GAGE* .001)
      SS(J) = GAGE
      AAL(J) = AL
      EPRIME(J) = ((200.*AL*Y)/(AREA*AF*D))
      EDOUBLE(J) = EPRIME(J)*DELTA(J)
      GG(J) = LOGF(1000000.*EPRIME(J))
      REP(J) = 1./TEMP(J) + 273.)
      DJ(J) = EDOUBLE(J)/((EPRIME(J)**2.) + (EDOUBLE(J)**2.))
      PJ(J) = EPRIME(J)/((EPRIME(J)**2.) + (EDOUBLE(J)**2.))
      PJ(J) = LOGF(PJ(J))

```

```

DJ(J) = LOGF(DJ(J))
AND(J) = LOGF(DELTA(J))
P = AND(J)
SLOPE(J) = LOGF(1000000.*EDOUBLE(J))
B = REP(J)
K = K + 1
IF(K - 1) 9, 100, 9
100 PRINT 18, EPRIME(J), EDOUBLE(J), DELTA(J), GG(J), SLOPE(J), TEMP(J), B,
1 DJ(J), PJ(J)
18 FORMAT(2F12.3, 3X, F9.3, 5X, F8.3, 4X, F9.3, 4X, F9.1, 5X, F10.5, 4X, 2F10.3)
GO TO 2
9 CONTINUE
PRINT 18, EPRIME(J), EDOUBLE(J), DELTA(J), GG(J), SLOPE(J), TEMP(J), B,
1 DJ(J), PJ(J)
GO TO 2
90 CONTINUE
532 GO TO 22
80 END

```

## APPENDIX D

## RECOMMENDATIONS

Knowledge of the interactions of polymer molecules with other polymer molecules in the bulk is an important aspect of polymer science and needs to be further studied in order that progress continue in this area. The modification of the properties of polymers by blending with other polymers continues to result in novel polyblends having desirable properties.

Specifically, polyblends involving PCL should be examined in greater detail for their potential usefulness. Blends with low density polyethylene seem to be among the more promising, at least in proportions of 90% or more polyethylene. Such blends are a potential source of novel and valuable information in view of the fact that both polymers involved are highly crystalline.

Although the dielectric relaxation properties of PCL homopolymer have been examined in detail in this work, the assignment of a definite relaxation mechanism to the sub-glass transition has not been made. It is suggested that further information regarding this mechanism may be obtained by chemical modification of the polymer such as the introduction of side groups to the hydrocarbon portions of the chains and the subsequent study of the dielectric relaxation properties of the substituted polymer.

The question of what dimensions dispersed aggregates must have in order to exhibit a glass transition has also been raised here. It is suggested that different experimental techniques differ in their

sensitivity in detecting such glass transitions. A coordinated effort involving DSC and dynamic-mechanical experiments along with electron microscopy may help to answer this question.

Anomalies have been observed in this work in the melting of crystalline polyblends of i-PS and PPO. The reasons for the occurrence of multiple melting peaks is by no means clear, and further studies at various heating rates involving various annealing conditions is indicated. X-ray studies may be helpful in determining the effect of crystal size on anomalous melting peaks.

The interactions between crystalline and "diluent" polymers in polyblends which result in large melting point depressions is not well documented and is worthy of future considerations. Again, X-ray studies may be indicated to determine the effect of crystal size on such depressions.

High deformation experiments may be done as a function of temperature to further characterize the engineering properties of i-PS/PPO polyblends.

Finally, various substituted polystyrenes and polyphenylene oxides can be blended and characterized for their potential usefulness.





