Dynamic Mechanical Properties of Fibers in Liquid Media in Relation to Dyeing

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Synopsis

An apparatus for measurement of dynamic mechanical properties of a polymer immersed in a liquid medium has been developed in this laboratory. The apparatus is based upon modification of the Vibron Viscoelastometer DDV-II. The viscoelastic properties of fibers immersed in liquids are of primary concern in textile processing. The dynamic mechanical properties of poly-(ethylene terephthalate) fibers immersed in dyeing media, such as water and tetrachloroethylene, were measured. The glass transition temperatures of polyester immersed in these dyeing media were significantly depressed from the dry glass transition temperature. A relationship between viscoelastic properties above the glass transition temperature of polyester fibers in tetrachloroethylene and the rate of disperse dyeing from tetrachloroethylene is proposed. The relationship is interpreted in terms of dye diffusion controlled by segmental mobility of amorphous regions of the polymer.

INTRODUCTION

An apparatus for the measurement of dynamic mechanical properties of polymers immersed in a liquid medium has been developed in this laboratory.[1] The apparatus is based upon modification of the Vibron Viscoelastometer DDV-II (Toyo Measuring Instruments).

The viscoelastic properties of fibers immersed in liquids are of primary concern in textile processes such as dyeing, scouring, bleaching, and home laundering. The measurement of dynamic mechanical properties of poly-(ethylene terephthalate) fibers in organic liquids in the temperature interval of interest for dyeing is the subject of this paper. The relationship between viscoelastic properties above the glass temperature of these fibers in liquids and the rates of disperse dyeing from the liquids was also examined.

BACKGROUND

Interest in solvent dyeing and finishing has prompted widespread discussion of the advantages and disadvantages of solvent versus aqueous processing. The interaction of organic liquids with synthetic fibers such as poly(ethylene terephthalate) (PET) during processing has received increasing attention. The adoption of organic liquids as a processing medium means that essentially hydrophobic synthetic fibers will be in intimate contact with hydrophobic liquids at elevated temperatures for extended periods of time. It is entirely possible that interaction of these organic liquids with fibers such as

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polyesters and polyamides may more drastically alter the "fine structure" (morphology) of these fibers than similar processing in water.

Tetrachloroethylene is the dominant nonaqueous medium under development for dyeing. The kinetic and thermodynamic treatments found to describe disperse dyeing of cellulose triacetate, nylon 6 and 66, and polyester from water have been successfully applied to disperse dyeing from tetrachloroethylene.[2-6] The dyeing of hydrophobic fibers by nonionic dyes in aqueous solution is described by a model in which dye molecules diffuse across a boundary layer and are absorbed at the fiber surface and then proceed to diffuse into the polymer. From organic medium, diffusion within the fiber appears to determine the overall rate of dyeing. This diffusion approximately follows Fick's laws of diffusion. Dyeing rates from tetrachloroethylene at a given temperature above 80°C are generally much larger than from water, reflecting the plasticization of the fiber by the organic liquid. Diffusion coefficients and the activation energies for diffusion of disperse dyes exhibit marked dependence on the molecular sizes of the dyes, suggesting involvement of polymer segmental mobility and free volume in the penetration process.

The equilibrium sorption isotherms of disperse dyes on polyester from tetrachloroethylene obey the law of distribution and indicate that the solutions of dye in the fiber and in the liquid obey Henry's law or Raoult's law. The partition coefficients for the dyes between fiber and tetrachloroethylene are much lower than between fiber and water, reflecting the high solubilities of the dyes in the organic liquid. Exhaustion of disperse dyes from tetrachloroethylene is typically low. Heats of dyeing are generally exothermic and much smaller from tetrachloroethylene than from water, indicating a greater effect of temperature on equilibrium sorption from water than from the organic liquid. The standard free energy difference or the affinity of dyeing is smaller for tetrachloroethylene dyeing than for aqueous dyeing, indicating that the driving force for dye to enter the fiber is smaller for the anhydrous dyeing than for aqueous dyeing.

Tetrachloroethylene exhibits a constant diffusion coefficient with time for sorption into polyester in the temperature range from 60° to 120°C.[7] The activation energy of diffusion is approximately 25–30 kcal/mole.[7,8] At 100°C, the diffusion coefficient for tetrachloroethylene is of the order of 1 to 2 × 10^{-9} cm^2/sec,[3,7,8] whereas typical disperse dyes diffuse into polyester from tetrachloroethylene with similar diffusion coefficients.[2-6] Indications are that for some dyes, sorption of solvent and dye may nearly coincide with an approximately common diffusion front.

The rate of sorption and equilibrium sorption of tetrachloroethylene also depends upon the morphology of the poly(ethylene terephthalate) fiber.[7] The sorption of perchloroethylene above 80°C by commercial fibers and films results in changes in the polymer morphology.[8,9] These structural reorganizations accompanying sorption have been demonstrated for a number of liquids.[9,10,11]

EXPERIMENTAL

The Vibron Viscoelastometer DDV-II is used for measuring dynamic mechanical properties of fibers. The Vibron applies a sinusoidal tensile strain

to one end of a sample and measures the stress output at the other end. The instrument operates at frequencies of 3.5, 11, 35, and 110 cps. Two transducers used to read directly the absolute dynamic modulus E^* (the ratio of maximum stress amplitude to maximum strain amplitude) and the phase angle δ between stress and strain. From these two quantities, the real part E' (dynamic modulus) and the imaginary part E'' (loss modulus) can be calculated. The principles of this direct-reading method and instrument are described in detail by Takayanagi.[12]

To measure the dynamic properties in a liquid medium, it was necessary to devise an apparatus to keep the sample immersed in liquid medium and the transducers outside the liquid, yet aligned with the sample. The liquid medium was pumped from another bath into the sample bath at a flow rate which maintained the liquid level 1 in. above the sample. This apparatus and procedure is described in detail by Murayama and Armstrong.[1] Samples were heated at a rate of 1°C/min in a liquid medium under relaxed conditions, and measurements of the tensile modulus E and loss tangent (tan δ) were made at 5° or 10°C increments. Samples were allowed to equilibrate at each temperature for 20 min before measurements were made. In some cases, the fibers had been immersed in the liquid for a specified time and temperature prior to the measurement.

MacLean and Murayama[13] have examined the question as to what parts of the dynamic modulus and loss tangent are due to the intrinsic property of a polymer film in the liquid and what parts are due to the drag forces exhibited by the liquid on the surface of the solid where the liquid does not penetrate the solid. The analysis indicated that the effect of viscous drag was small except in very viscous liquid at high frequencies and for a film of low modulus. The following conclusion was reached: "Thus, in the capability of the Vibron DDV-II, larger differences between the dynamic properties in dry and in liquid will be seen if chemical or physical interaction of the liquid with the film is present." The drag effect analysis of MacLean and Murayama[13] might be extended to the case of diffusion of liquid into the polymer during the dynamic measurement. The magnitude of the flow into the film might be calculated and substituted into the analysis to estimate the effect of flow into the film on the measurement.

Rates of dyeing were measured from a well-agitated semiinfinite dye bath of 40 g C.I. Disperse Red 13 per liter of perchloroethylene. The dye uptake of the fibers was measured by the extraction procedure of Dumbleton, Bell, and Murayama.[14] The dye uptake was not corrected for the amount of unabsorbed dye that was deposited in the fiber from the dye solution that was retained in the fiber after rinsing the fiber with cold acetone until clear rinses were obtained. The dye concentration was measured spectrally using the measured molar absorptivity of 30,930 l./mole-cm at 525 nm for purified C.I. Disperse Red 13. No chemical instability of the dye to the extraction procedure at 95°C with dimethylformamide was found such as that reported by Kissa[15] for extractions at higher temperatures. Diffusion coefficients were calculated from the rate of dyeing curve by Hill's equation for diffusion into a semiinfinite cylinder.[16] The required linear relationship between per cent dye sorbed and square root of dyeing time was established. A poly(ethylene terephthalate) filament bundle of 1200 denier (6 denier per filament) which has been uniaxially oriented by drawing 5.0× and had a density of 1.400

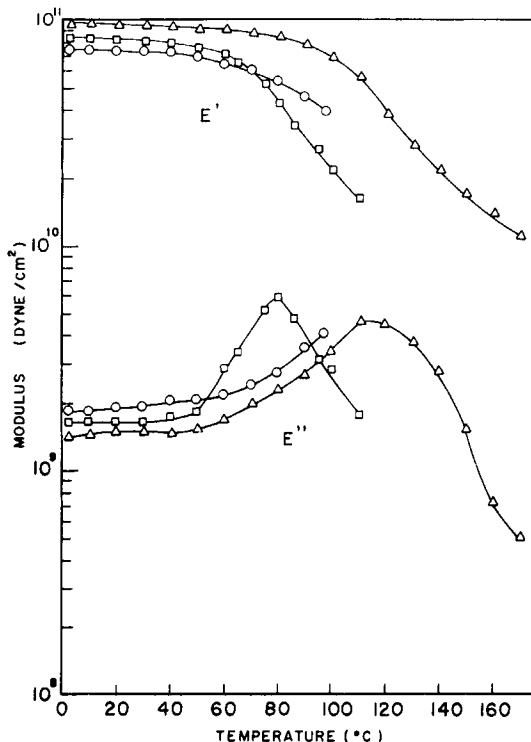Fig. 1. Comparison of dynamic modulus E' and loss modulus E'' of polyester filaments in liquids and dry: ($\triangle$) dry; (O) in D.I. water; ($\square$) in tetrachloroethylene.

g/cm^3 was conditioned in tetrachloroethylene at 120°C for 3 hr prior to dyeing. The bundle remained immersed in tetrachloroethylene at room temperature until being introduced into the dye bath or the Vibron bath. A commercial 2.5-mm biaxially oriented film with a density of 1.384 g/cm^3 was also utilized. Organic liquids were reagent grade. Tetrachloroethane refers to the 1,1,2,2 isomer.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties in Liquids

Using the modified Vibron, Murayama and Armstrong[1] demonstrated that the temperatures at which the maximum occurs in the tan δ peak (α-dispersion peak temperature or glass temperature) of nylon 66 fibers in water and tetrachloroethylene were depressed by about 90 and 40°C, respectively, from the α dispersion peak temperature in air at 0% relative humidity.

Figures 1 and 2 show the dynamic modulus E', loss modulus E'', and tan δ of drawn polyester fibers in deionized water, tetrachloroethylene, and air at 0% relative humidity. The fibers were not preconditioned prior to the measurements. The α-dispersion peak of polyester in deionized water was not reached in this experiment, but the tan δ curve was shifted to the left of the curve for air at 0% relative humidity. Dynamic mechanical data collected on
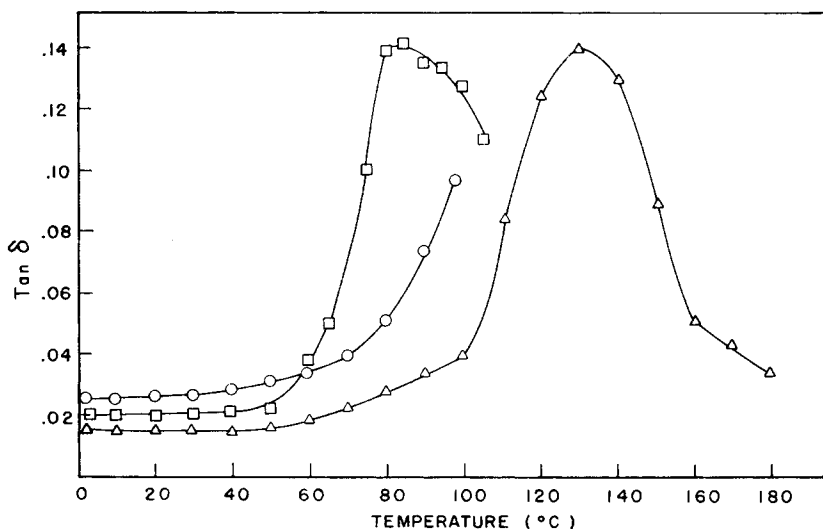
Fig. 2. Comparison of the loss tangent tan δ of polyester filaments in liquids and dry: (□) in tetrachloroethylene; (O) in D.I. water; (△) dry.

the polyester filaments in a 100% relative humidity atmosphere using the Vibron were nearly superimposable on the data collected for the filaments in water shown in Figures 1 and 2. The lowering of the glass temperature in 100% relative humidity atmosphere was previously shown by Dumbleton and Murayama.[17] The α-dispersion peak for drawn polyester in tetrachloroethylene was shifted to 85°C from a value of 130°C in air at 0% relative humidity.

It should be noted that the dynamic mechanical properties were measured after 20 min of equilibration at each temperature, and then the sample was heated at 1°C/min over a 5° or 10°C increment to the next temperature of measurement. If diffusion of the liquid medium into or out of the fiber is slow at this heating rate, then the measured dynamic mechanical properties may be for filaments only partially penetrated by the liquid. Thus, the dynamic properties at a given temperature might exhibit a time dependence reaching equilibrium values when the sorption of the liquid and any accompanying structural reorganization reached equilibrium. However, dynamic mechanical data indicating transitions under nonequilibrium sorption conditions may be related to practical batch dyeing where the fiber in the dye bath is heated at a programmed rate to the dyeing temperature and then dyed over a relatively short time interval.

Dynamic properties have not been extensively studied as function of immersion time in the liquid. However, data from the literature and certain experimentation offer some insight into this area. In Figure 3, the dynamic mechanical properties of fibers conditioned in tetrachloroethylene for 120 hr at 25°C before testing are presented. A fiber which was free to contract is compared to one held at constant length during the conditioning. Sorption data from the literature indicate that an equilibrium uptake of 11% to 12% liquid should have been achieved during this conditioning.[8] During the course of the temperature increase of the Vibron experiment, there would be a desorption of liquid with increasing temperature tendng toward an equilib-
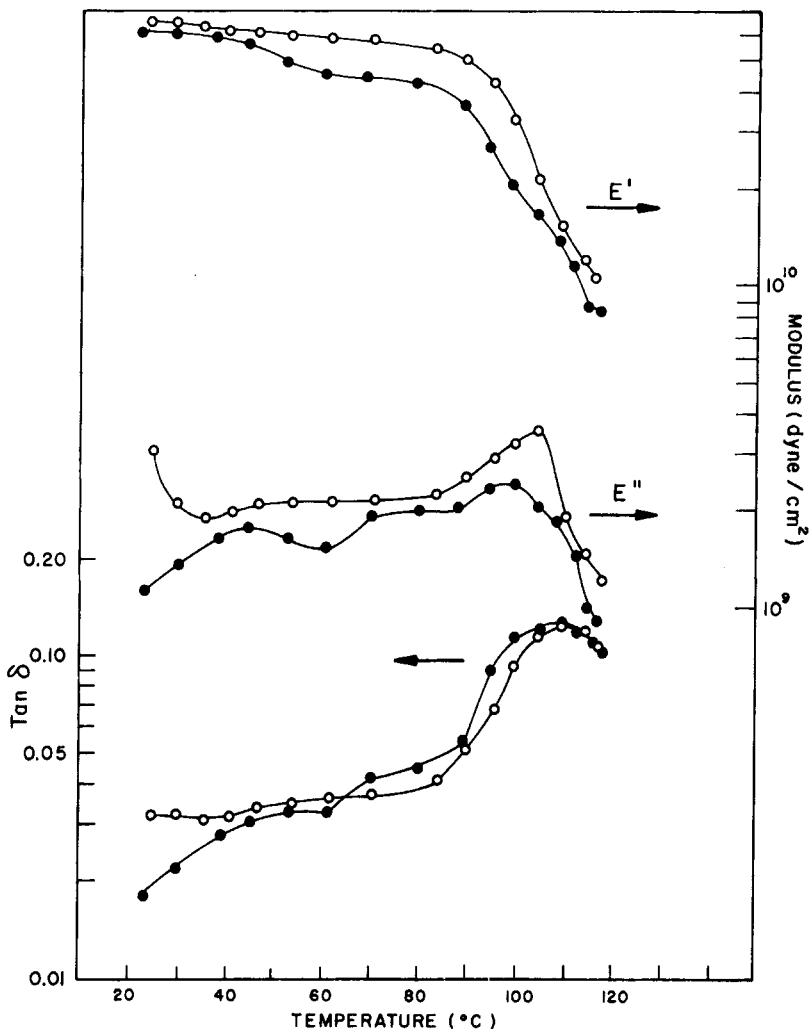
Fig. 3. Comparison of dynamic mechanical properties of fiber preconditioned in tetrachloroethylene at 25°C for 120 hr; open circles = no restraint, filled circles = constant length.

rium value of 8% to 9% at 120°C.[8] Fiber shrinkage also occurs as the temperature of measurement increases.[18] Diffusion rates would indicate that these equilibrium values of desorption could be readily approached during the heating schedule of the Vibron experiment above 60°C. The maximum of the α-dispersion peak for fibers held for 120 hr in tetrachloroethylene is shifted to 110°C versus 80°C for fibers not preconditioned. This shift is probably a result of constraints[17] placed on the amorphous regions induced during the prolonged immersion.[11] Knox et al.[11] have cited evidence for such morphological rearrangement during liquid immersion and proposed that the rearrangements induced by chemical energy at room temperature with certain strongly interacting liquids are similar to the rearrangements induced by annealing below 175°C. Although tetrachloroethylene is not among the strongly interacting liquids, the dynamic mechanical data indicate an alteration of the segmental mobility of the fiber during prolonged immersion. Knox et

al.[11] have also noted that perceptible changes in sorption and shrinkage values for fibers in weakly interacting liquids such as tetrachloroethylene occur between 2 days and 90 days of immersion. Such behavior may be indicative of very slow viscoelastic relaxation processes occurring in the fiber during long-term immersion at room temperature.

Shrinkage data[9,11,18] indicate that tetrachloroethylene induces chain relaxations in fibers at temperatures as low as 20°C. The values of the maximum in the loss modulus, E''_{max}, are decreased by preconditioning in tetrachloroethylene (compare Figs. 1 and 3). The changes in the tan δ and E'' peaks are indicative of possible morphological rearrangement[17] due to preconditioning at 25°C. The effects of crystallite size and distribution and orientational factors on the α-dispersion have been studied in detail for thermally annealed fibers.[17] Comparison of the fiber held at constant length during the conditioning with the unrestrained fiber shows that orientational changes may have also occurred. The dynamic modulus and tan δ curves for the restrained fiber differ considerably in the 50° to 100°C range from those observed for the unrestrained fiber. This difference for the restrained fiber probably reflects the relaxation of tensions in oriented amorphous regions which were relaxed during the immersion for the unrestrained fibers. The greater shrinkage while being heated in the Vibron for the fiber preconditioned at constant length compared to the fiber preconditioned without restraint shown in Table I is indicative of disorientation during the unrestrained preconditioning.

Even though the general shapes and features of the dispersion curves are not typical of those for oriented poly(ethylene terephthalate) fibers in a dry medium, the reproducibility of the dynamic mechanical data in the liquid media was found to be similar to that observed for dry fibers. It should be noted that a slight initial tension of 0.005 g per denier was applied to the filament bundle prior to measurement at each temperature in order to obtain equal stress-bearing characteristics across the bundle.

The tan δ, E', and E'' values for unrestrained fiber conditioned in tetrachloroethylene at 110°C for 3 hr are presented in Figure 4. This conditioning allowed attainment of equilibrium sorption of 9% liquid; and being at or above the glass temperature of fiber in tetrachloroethylene, considerable morphological rearrangement occurred. The sample was held at room temperature in liquid for 16 hr prior to Vibron experiment. The E'' curve is peculiar in shape, exhibiting two humps, one centered at 50°C and one at 90°C. The maximum of the tan δ curve is located at 95°C, and the maximum value is of lower magnitude than that shown in Figure 2 or Figure 3. Since the E'' peak may be associated with the energy dissipated as heat per cycle in the amorphous regions of the polymer in the T_g transition region, the broadening of the peak is probably evidence for a morphological rearrangement resulting in a highly plasticized amorphous region. Such broadening is often cited as evidence for an increased range of order.

During the Vibron experiment, the sample was first heated to 115°C and then cooled to room temperature at the programmed rate. The dynamic data at a given temperature were nearly superimposable whether approached from room temperature or from 115°C. Such reversibility in the α-transition region indicates that no further morphological rearrangement is occurring

TABLE I

Shrinkage and Resonance Peak Data for Sample While Being Heated in Liquid During the Vibron Experiment

| Figure no.	Preconditioning in immersion medium	Immersion medium	Temperature interval, °C	Shrinkage in Vibron, %	Temperature at which maximum occurs in E'' peak, °C	Maximum E'', dynes/cm²	Temperature at which maximum occurs in tan δ peak, °C	Maximum tan δ (E''/E')
1 and 2	none	dry air	0–160	6.1	110	4.8×10^9	130	0.140
1 and 2	none	water	0–98	1.1	—	—	—	—
1 and 2	none	tetrachloroethylene	0–110	6.3	80	5.8×10^9	85	0.142
3	120 hr at 25°C, unrestrained	tetrachloroethylene	25–117	8.6	105	3.6×10^9	110	0.125
3	120 hr at 25°C, constant length	tetrachloroethylene	25–118	9.3	98	2.5×10^9	110	0.130
4	3 hr at 110°C, unrestrained	tetrachloroethylene	25–115	0	91[a]	9.6×10^{8}[a]	91	0.084
5	18 hr at 110°C, unrestrained	tetrachloroethylene	25–115	0	70 to 85[a]	1.1×10^{9}[a]	85	0.086
6	none	tetrachloroethylene	25–115	0	74	1.1×10^9	103	0.096
7	3 hr at 85°C, unrestrained	trichloroethylene	25–83	0	62[a]	1.4×10^{9}[a]	81[a]	0.086[a]
8	none	1,1,2,2-tetrachloroethane	0–94	38.2	67	4.4×10^9	73	0.098
9	120 hr at 25°C, unrestrained	1,1,2,2-tetrachloroethane	25–98	31.4	95	2.1×10^9	95	0.074
10	120 hr at 25°C, constant length	1,1,2,2-tetrachloroethane	25–102	25.9	71	1.0×10^9	75	0.110

[a] Very broad and ill-defined peak.
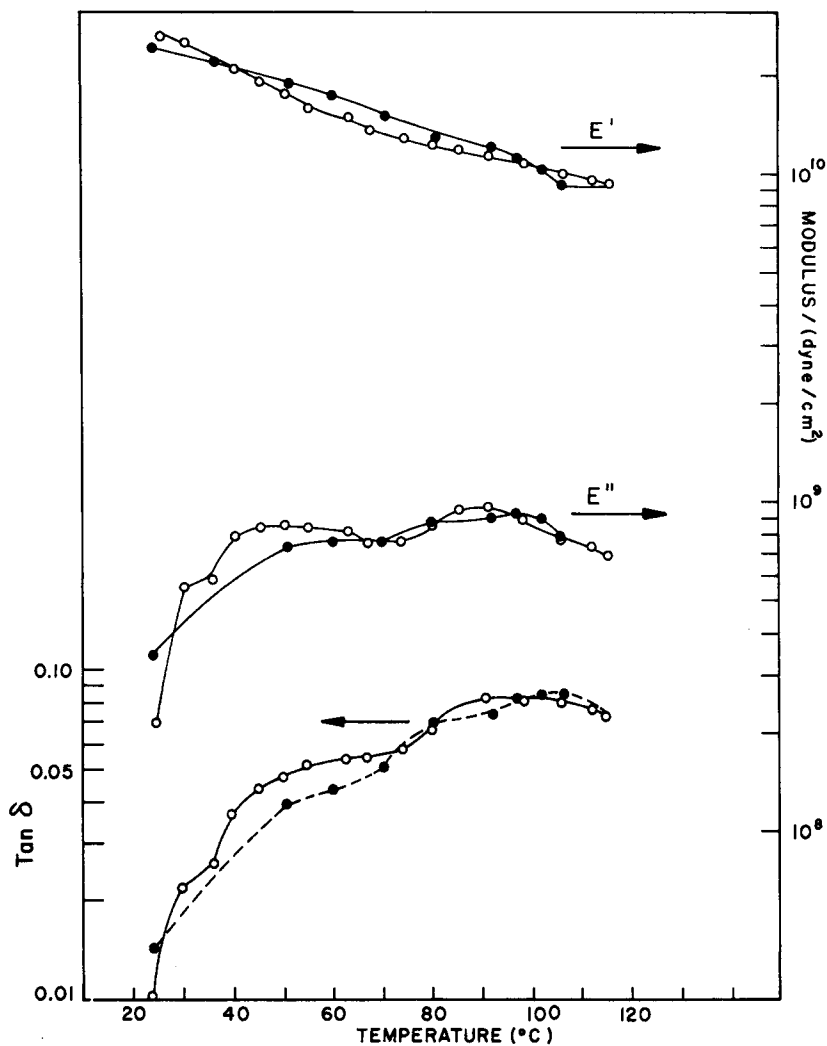
Fig. 4. Dynamic mechanical properties of fiber preconditioned in tetrachloroethylene at 110°C for 3 hr; open circles = increasing temperature; filled circles = decreasing temperature.

during the time interval of the Vibron experiment and that the rate of heating is slow enough for absorption and desorption toward equilibrium values at a given temperature not to affect the dynamic data.

Data for an unrestrained fiber conditioned in tetrachloroethylene at 110°C for 18 hr are presented in Figure 5. The curves are comparable with those of Figure 4 with some shifts. The maximum value of the tan δ curve appears to be shifted from 91°C for 3-hr preconditioning to 85°C for the 18-hr preconditioning.

The dynamic mechanical data for an unconditioned commercial biaxially oriented polyester film are shown in Figure 6. The Vibron data were obtained by heating the sample from room temperature to 116°C and then cooling back to room temperature. The data are not superimposable for the increasing temperature versus decreasing temperature. This may reflect mor-
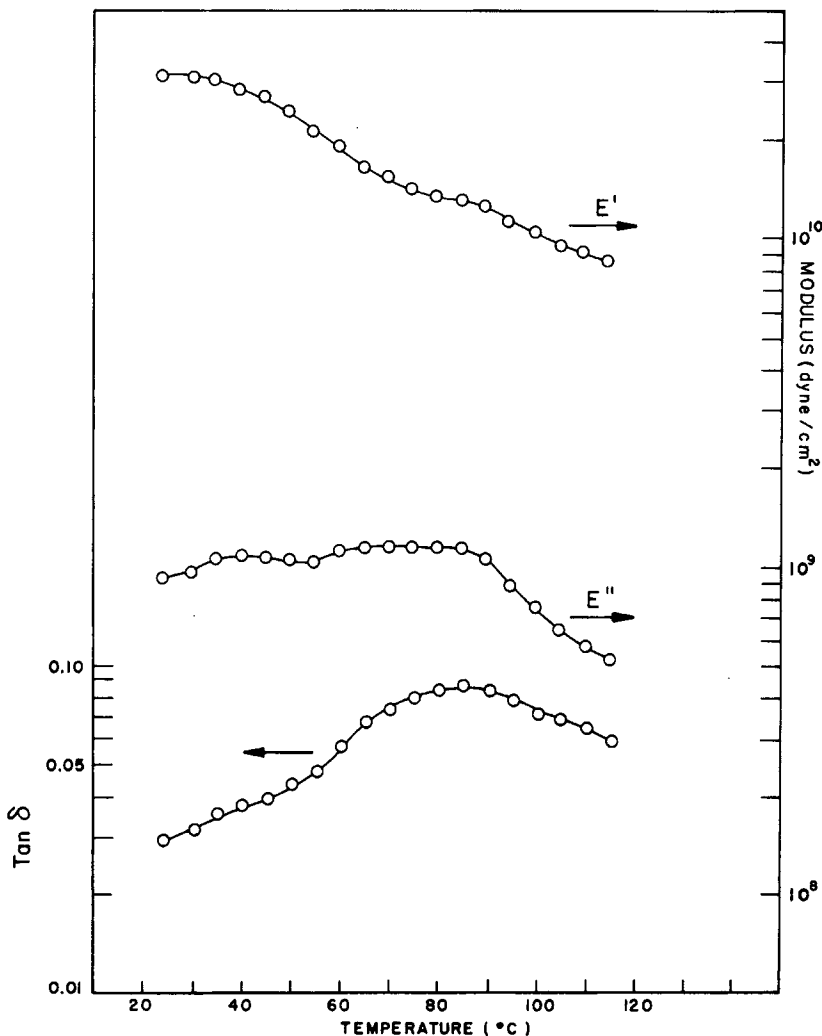
Fig. 5. Dynamic mechanical properties of fiber preconditioned in tetrachloroethylene at 110°C for 18 hr.

phological changes induced during the liquid immersion and/or the nonattainment of equilibrium sorption of tetrachloroethylene at lower temperatures. The disagreement is more pronounced at lower temperatures than at higher temperatures.

Trichloroethylene is another liquid from which nonaqueous dyeings of polyester have been studied.[3,4] The dynamic mechanical properties of fiber preconditioned for 3 hr at 85°C in the trichloroethylene and held in the liquid at room temperature prior to measurement are shown in Figure 7. During this preconditioning, the fiber would be completely penetrated by the liquid.[7] The data are plotted for heating the sample from 25° to 83°C and then cooling back to 25°C. The near-superimposability of the measurements at a given temperature, whether approached from 25°C or from 83°C, indicates the attainment of steady-state properties in the liquid medium. The tem-
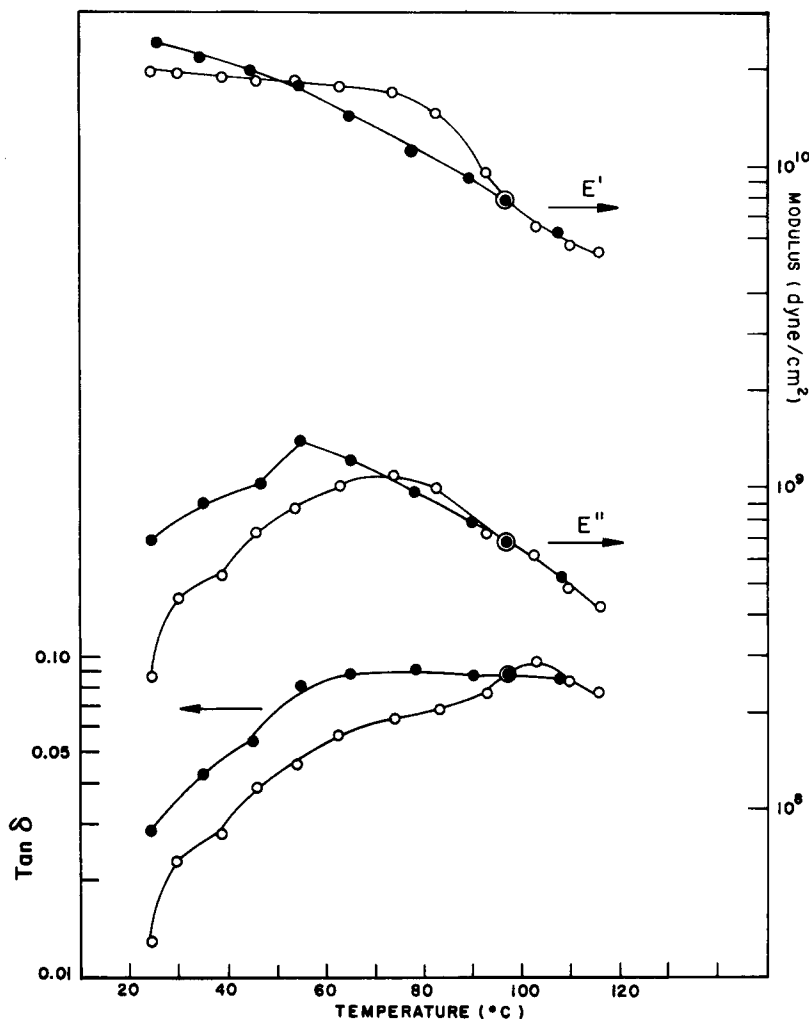
Fig. 6. Dynamic mechanical properties of film in tetrachloroethylene; open circles = increasing temperature; filled circles = decreasing temperature.

perature of the maximum of the tan δ curve appears to be roughly 80°C. The E' and E'' curves indicate distinct plasticization of the fiber above 20°C and do not clearly indicate the location of the α-transition (glass transition). The dyeing data in trichloroethane of Perkins and Hall[4] indicate that the dyeing transition temperature as defined by Gwi-Arish and Ingamells[19] is located in the 50° to 70°C temperature interval. The dyeing transition temperature is that temperature at which dye absorptions and dyeing rates suddenly increase; this temperature parallels the glass temperature measured by other means. Ingamells and co-workers[19,20,21] have offered extensive evidence that the onset of segmental mobility at the glass temperature of a polymer is directly related to the entry and diffusion of dyes into a polymeric substrate.

Several authors have noted wide discrepancies in the cited T_g values for polyester in tetrachloroethylene.[5,8] However, it should be remembered that
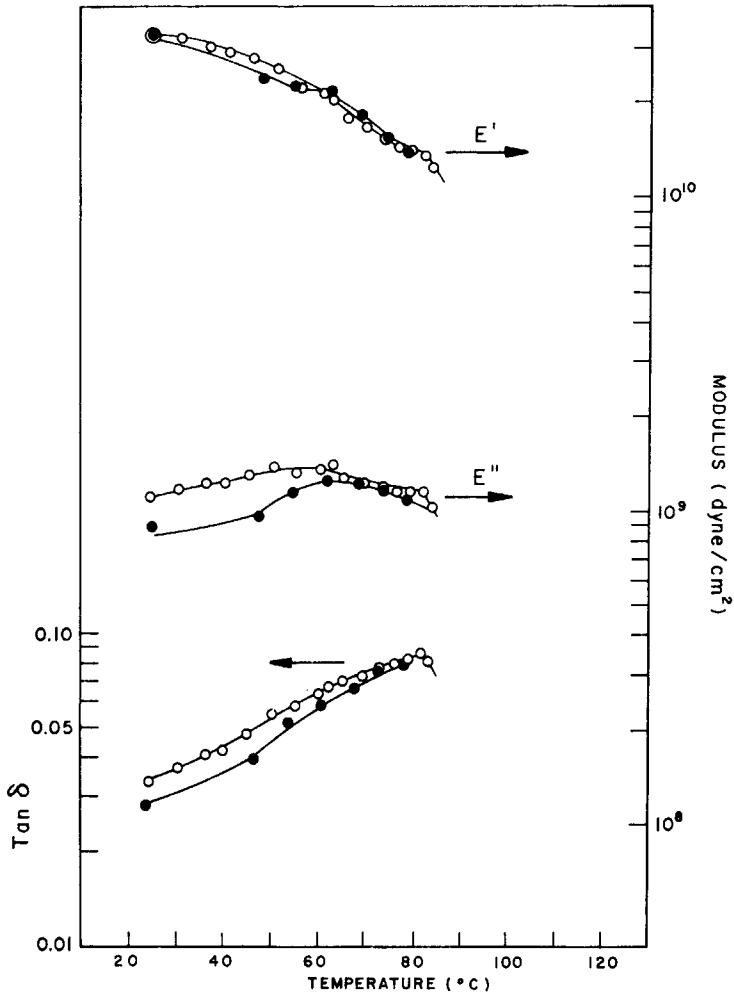
Fig. 7. Dynamic mechanical properties of fiber preconditioned in trichloroethylene at 85°C for 3 hr; open circles = increasing temperature; filled circles = decreasing temperature.

the temperature of the onset of segmental mobility is time dependent and that this measured temperature must be defined relative to the experimental technique used. In dynamic mechanical measurements, the temperature corresponding to the maximum of the E'' curve at a given frequency is often cited as T_g.[14,17] It has been shown, however, that the breadth, shape, and maximum of the E'' curve can be drastically altered by morphological changes of PET, making this assignment rather arbitrary.

Resonance peak data are summarized in Table I. The loss modulus E'' curves of Figures 1 through 6 indicate that the maximum of E'' for PET in tetrachloroethylene can be widely shifted depending upon interactions with the liquid which alter the polymer morphology. In some cases, the E'' curves show unusually high values from 20° to 60°C and flat shape, probably reflecting a distinct plasticization of the polymer. This behavior is pronounced for polymers conditioned at elevated temperature in the liquid. It would appear

that the morphological rearrangements at 110°C in tetrachloroethylene produce structures more susceptible to plasticization (compare Fig. 3 with Figs. 4 and 5).

Suzuki et al.[10] have shown that significant changes in the crystallinity, crystallite size, and amorphous and crystalline orientation functions occur for commercial poly(ethylene terephthalate) fibers immersed at 60°C in a number of liquids. Of course, the magnitude of these changes is dependent upon the interaction of the particular liquid with the polymer. The morphological rearrangement is also dependent upon the tension applied to the filaments during the immersion. Knox et al.[11] have presented x-ray evidence for morphological changes induced at 20°C by several liquids during sorption into commercial fibers.

Figure 8 shows the dynamic mechanical properties of unconditioned polyester in tetrachloroethane. The temperature of the maximum of the tan δ peak is about 73°C. The magnitude of the α-dispersion peak of polyester fibers in tetrachloroethane was much smaller than in tetrachloroethylene. Since the E'' peak is directly proportional to the energy dissipated as heat per cycle in the amorphous regions of the polymer at T_g and the tan δ peak is a measure of the ratio of energy dissipated as heat to the maximum energy stored per cycle, the decrease in peak sizes reflects a decrease in amorphous content of the fiber as a result of increased crystallinity induced by tetrachloroethane or increased resistance to segmental mobility from interaction of polymer with tetrachloroethane in the amorphous regions. Ribnick and Weigmann[9] have proposed that tetrachloroethane lowers the T_g of polyester to allow annealing and increased crystallization at temperatures well below the dry T_g. Zachmann and co-workers[22,23] have examined the effect of sorbed liquids on the molecular motions in polyester by nuclear magnetic resonance and dynamic mechanical measurements and have concluded that swelling significantly increases the tension of chains in amorphous regions.

The drastic changes that are induced in oriented fibers by immersion in tetrachloroethane are illustrated by comparison of Figures 8, 9, and 10. Fibers were conditioned for 120 hr at 25°C in tetrachloroethane with and without restraint. Approximately 19% shrinkage occurred in the unrestrained sample. Knox et al.[11] have shown that such a treatment would induce appreciable increases in crystallinity. The dynamic data are clearly shifted by prolonged exposure to the liquid or by tension applied to the fibers preventing shrinkage and disorientation. In Figure 10, the extreme plasticizing action of the liquid is evidenced by the dynamic data obtained upon cooling the sample from 102°C to 25°C. This sample had shrunk 26% while being heated from 25°C to 102°C under relaxed conditions in the Vibron experiment.

The expected lowering of E'' and tan δ as the sample was cooled was not observed. Apparently, the sample underwent such drastic rearrangement at the elevated temperatures during the Vibron experiment that it remained in a rubbery state when cooled. Ribnick and Weigmann[9] have noted that commercial fibers lose their fibrous structure (dissolve) above 120°C in tetrachloroethane. Since the fibers were conditioned for an extended period at 25°C in tetrachloroethane prior to the Vibron experiment, it appears unlikely that the increased plasticization upon cooling is due to an increased penetration of the fiber at the higher temperatures. It might be speculated that the ex-
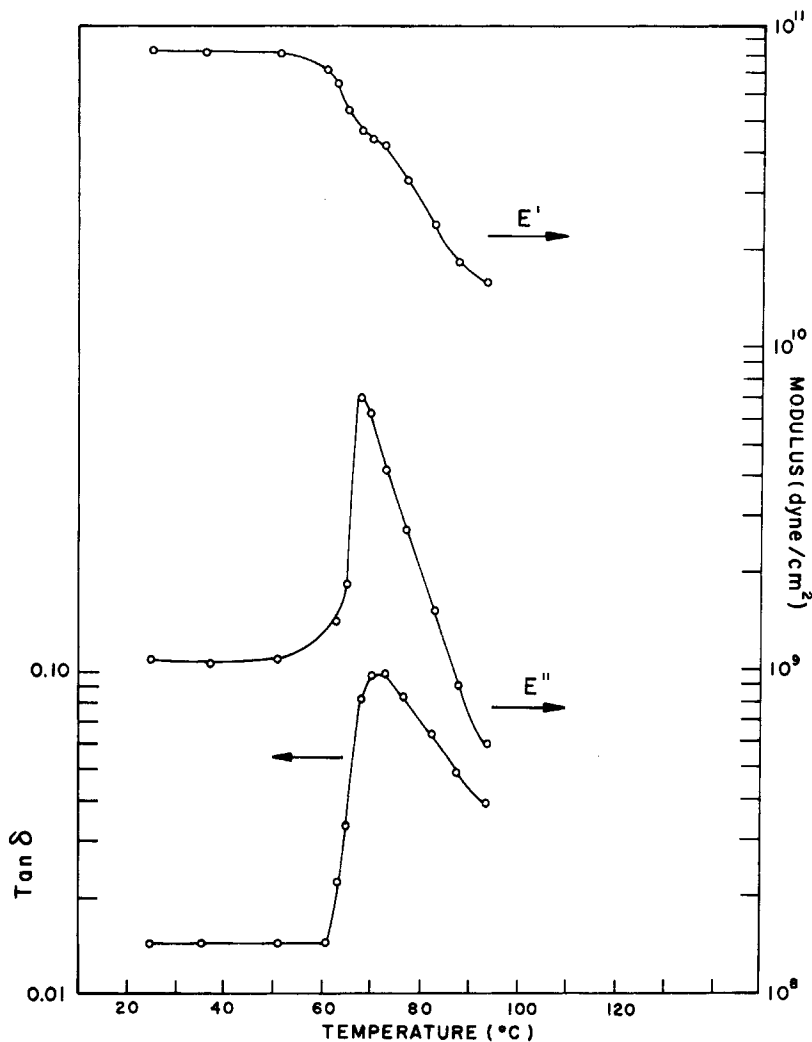
Fig. 8. Dynamic mechanical properties of fiber in 1,1,2,2-tetrachloroethane.

treme interactions (as evidenced by crystallite dissolution above 120°C) of tetrachloroethane with the fiber results in a plasticized rearranged structure that remains rubbery to below room temperature over the time interval of the Vibron experiment. This state of the fiber might be related to the formation of sol-gel structures in concentrated polymer solutions.[24] The crystallites in the polymer would essentially melt at 110°C in tetrachloroethane and reform small crystallites as the temperature was lowered, resulting in an elastic non-flowing gel. The role of loss of polymer and oligomer from the fiber due to dissolution in the liquid also needs clarification. Tetrachloroethane[39] and other liquids[8,10,40] leach considerable material from the fiber at elevated temperatures.

This interpretation of the dynamic mechanical data implies that there is a larger depression of melting point for fibers in the powerfully interacting liquid tetrachloroethane than in the weakly interacting tetrachloroethylene and
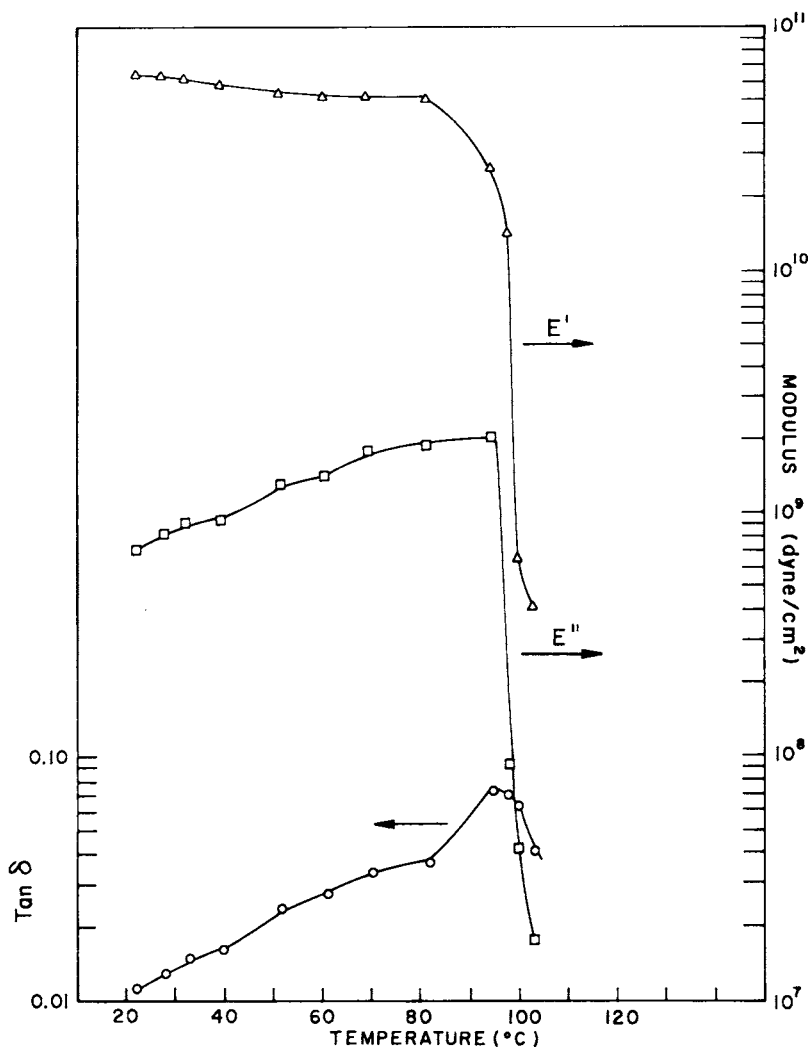
Fig. 9. Dynamic mechanical properties of fiber preconditioned without restraint for 120 hr at 25°C in 1,1,2,2-tetrachloroethane.

that the depression of the glass temperature is of similar magnitude for the powerfully and weakly interacting liquids.

The structural alterations due to immersion in tetrachloroethane and the powerful interaction of the polymer with tetrachloroethane are illustrated by the following comparisons. For the unconditioned fiber over the tempera-ture interval of 70° to 94°C, E'' decreases from 4.4×10^9 to 7.2×10^8 dynes/cm², while E' decreases from 4.2 to 1.9×10^{10} dynes/cm². For the unres-trained fiber preconditioned at 25°C for 120 hr, from 80° to 103°C, E'' de-creases from 2.0×10^9 to 1.7×10^7 dynes/cm², and E' decreases from 5.3×10^{10} to 4.2×10^8 dynes/cm². The fiber preconditioned at constant length also exhibits large decreases in E'' and E over the 70° to 95°C temperature interval: E'' from 1.0×10^9 to 8.0×10^7 dynes/cm² and E' from 2.8×10^{10} to 1.1×10^9 dynes/cm². These large decreases in E'' are further evidence for
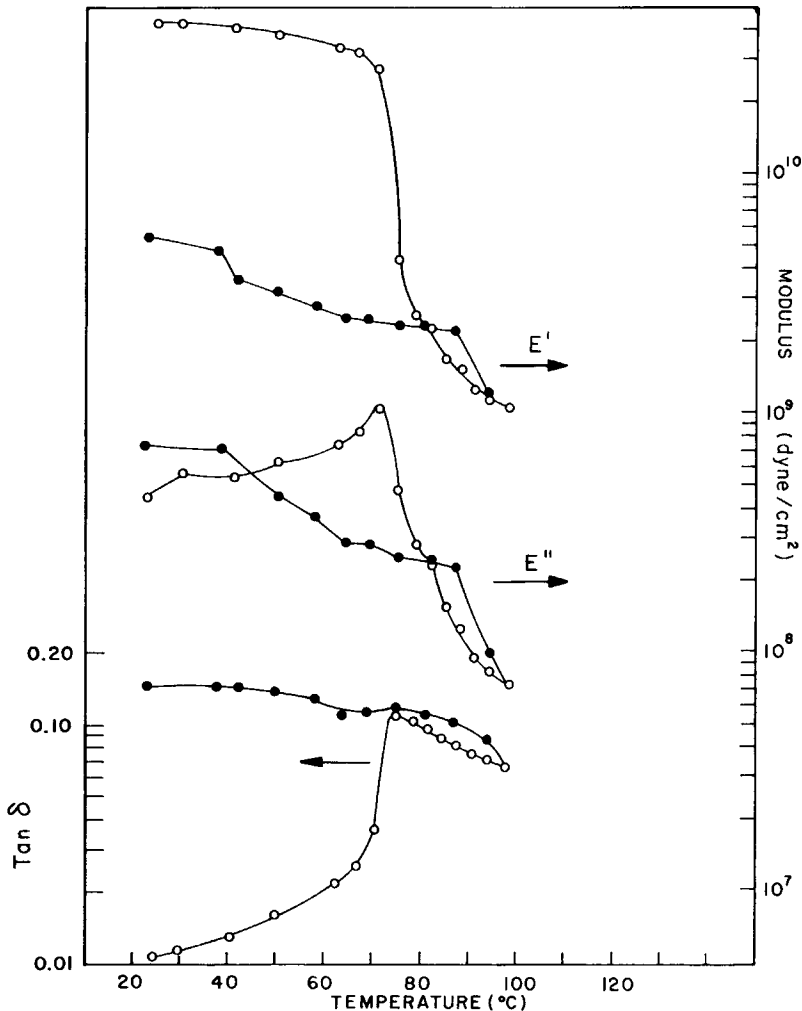
Fig. 10. Dynamic mechanical properties of fiber preconditioned at constant length for 120 hr at 25°C in 1,1,2,2-tetrachloroethane; open circles = increasing temperature; filled circles = decreasing temperature.

the solvated (rubbery) state of the fiber in tetrachloroethane at temperatures approaching 110°C. For fiber preconditioned at constant length in the less interacting tetrachloroethylene, E'' would typically decrease from 2.0×10^9 dynes/cm^2 at 70°C to 1.9×10^9 dynes/cm^2 at 110°C and E' from 4.6×10^{10} to 1.4×10^{10} dynes/cm^2.

The assignment of the resonance peak in the 60° to 100°C temperature interval for fiber immersed in tetrachloroethane as the α-dispersion peak is in conflict with the interpretation by Ribnick and Weigmann[9] of the shrinkage behavior of fibers in tetrachloroethane. From a linear extrapolation of dynamic shrinkage data to the temperature of zero shrinkage, Ribnick and Weigmann[9] concluded that the T_g of fibers equilibrated with tetrachloroethane was approximately −130°C. The experimentally observed[9] onset of shrinkage in tetrachloroethane at the heating rate of 4.17°C/min was in the

40° to 60°C temperature interval corresponding to the onset of the resonance peak observed in the dynamic mechanical experiment at a slower heating rate. Ribnick and Weigmann[9] have reasoned the following: (1) that the sorption of tetrachloroethane into the filaments is very slow below the 40° to 60°C interval; (2) that shrinkage onset at 40° to 60°C corresponds to rapid penetration of the fiber by tetrachloroethane as the dry T_g is approached; (3) that equilibrium shrinkage values are obtained above 60°C for 4°C/min heating rate; (4) that a linear extrapolation of shrinkage data above 60°C to zero shrinkage temperature is valid; (5) that the heating rate is sufficiently rapid to prevent crystallization which follows the disorientation of amorphous regions which causes shrinkage[44] from interfering with the dynamic shrinkage experiment; and (6) that if sufficient time were allowed for sorption of tetrachloroethane into the fibers, shrinkage would be observed at temperatures below 40°C in the dynamic experiment.

The dynamic mechanical data for fibers preconditioned in tetrachloroethane at 25°C for 120 hr exhibit a resonance peak in the 60° to 100°C interval. It should also be noted that even though dynamic data do indicate considerable plasticization of these preconditioned fibers, the dynamic modulus E' is greater than 10^{10} dynes/cm^2 prior to the onset of the resonance peak in the 60° to 100°C interval, which is consistent with the amorphous regions being in a glassy rather than a rubbery state. Unfortunately, extensive data on the rate of sorption of tetrachloroethane into the polymer do not exist from which degree of penetration of fibers after 120 hr at 25°C preconditioning can be evaluated. Data from Knox et al.[11] indicate at 21°C significant sorption of tetrachloroethane approahcing steady-state values after 48 hr. Shrinkage data[11,18] also indicate essentially complete penetration after 48 hr. Sorption data[7] for other powerfully interacting chlorinated hydrocarbons such as chloroform, 1,2-dichloroethane, and 1,1,2-trichloroethane indicate that essentially steady-state sorption values would be reached during 120 hr of immersion at 25°C. Thus, it appears that the dynamic mechanical data of Figures 9 and 10 were obtained upon fibers that were penetrated by tetrachloroethane and that the dynamic mechanical data indicated these fibers to be in a glassy state below 60°C rather than the rubbery state predicted by the T_g value proposed by Ribnick and Weigmann.[9]

The estimation of T_g values by extrapolation of shrinkage data to the temperature of zero shrinkage is probably valid for those cases where shrinkage is a result of a relaxation process which involves disorientation of amorphous regions. This disorientation (the shrinkage process) may then be followed by a separate crystallization process of the newly relaxed polymer chains if sufficient time is allowed at the temperature of the relaxation process.[44] The shrinkage process in weakly interacting liquids such as tetrachloroethylene is a result of disorientation in amorphous regions which begins at T_g possibly followed by crystallization of relaxed chains. However, in tetrachloroethane, the shrinkage process above 60°C probably not only involves disorientation in amorphous regions but the dissolution of existing crystalline regions resulting in a drastic morphological rearrangement of the semicrystalline fiber structure. Thus, extrapolation of shrinkage data to the temperature of zero shrinkage would not be valid since shrinkage would not only be a result of amorphous disorientation but also of drastic rearrangements in the crystal-

line areas. The dynamic mechanical data appear to be consistent with such a process.

Changes in the dynamic mechanical properties of polymers after immersion in a liquid may reflect alteration of viscoelastic properties of the polymer due to interaction with the liquid and also alteration of the polymer structure due to changes in crystallinity and orientation induced by the interaction. The degree of disorientation of fibers occurring during the heating interval of the Vibron experiment is indicated in Table I by the shrinkages of fibers with and without preconditioning.

Murai and Kuroda[25] have reported measurements of dynamic mechanical properties of polyester immersed in liquids. Their measurements were on amorphous films immersed in aqueous phenol solutions using the Iwamoto Manufacturing Company viscoelastic spectrometer. They found large depressions of the polymer glass temperature which depended upon the concentration of phenol in the fiber. They also measured changes in E' and E'' at given temperatures during sorption of phenol into the film. Murai and Kuroda[25] have presented dynamic mechanical data indicating that for nonequilibrium sorption of phenol, both the glass transition of the regions of the polymer penetrated by the liquid and the glass transition of the unpenetrated polymer can be detected.

Zachmann and Scherman[22] have measured dynamic mechanical properties of polyester films swollen with organic liquids under several conditions. The glass temperatures of the swollen films were markedly depressed. Similar experiments were performed by Illers and Breur[27] in their pioneering work on dynamic mechanical properties of polyester.

Desai and Wilkes[26] have modified the Rheovibron so as to study crystallization of amorphous films immersed in liquids. However, as noted by these workers, this modification utilized a sample clamp rod with a bend in the rod so that an error due to the "out of axis" vibration was introduced. Also, their modification has no means to agitate the immersion bath, such agitation being essential to the study of two-component liquid media where one component may be preferentially depleted from the layer of liquid at the polymer surface.

Relationship Between Loss Modulus in Liquids and Diffusion Coefficients of Disperse Dyes

These dynamic parameters (E', E'', and tan δ) of fibers in solvents are not only useful information for mechanical properties of fiber but also for relating dye diffusion. In previous studies[14] on the diffusion of a disperse dye, 1-amino-4-hydroxyanthraquinone (C.I. Disperse Red 15), into poly(ethylene terephthalate) fibers as a function of heat-setting temperature and draw ratio, it was found that the dynamic loss modulus E'', measured at the dyeing temperature and 100% relative humidity, was related to the dye diffusivity. This indicated that the diffusion is controlled by the mobility of the polymer chain segments.

Fujita et al.[28,29] also have shown that above the glass transition, the diffusion coefficient D of organic liquids in an amorphous polymer, poly(methyl acrylate), is related to the steady-state viscosity η by the equation

$$\ln (D/RT) = -B \ln \eta + C \tag{1}$$

where B and C are constants; their experimental results indicated that B is near unity.

The shear viscosity η may be replaced by E''/ω, where E'' is the tensile dynamic loss modulus measured at frequency ω and at temperature T.[30] Since E'' is the tensile dynamic loss modulus, the quantity E''/ω is equivalent to the tensile viscosity ηT, which is equal to 3η. Substitution of E''/ω in eq. (1) leads to

$$\ln (D/RT) = -B \ln (E''/\omega) + (C - B \ln \tfrac{1}{3}) \tag{2}$$

Strictly speaking, this replacement is rigorous only for E'' measured at zero frequency.

Equation (1) with E''/ω substituted for η was applied to the diffusion of acid dyes in drawn nylon 66 fibers by Bell.[31] It was assumed that measurement frequency of 11 cps was low enough for the substitution to be valid. A relation

$$\ln (D/RT) = -4.5 \ln (E''/\omega) + C'$$

was found to exist, where E'' was measured at the dyeing temperature and 100% relative humidity. The fact that the value of B was 4.5 instead of near 1 was attributed to the fact that the polymer was oriented (E'' was necessarily measured parallel to the fiber axis, whereas diffusion takes place primarily perpendicular to the fiber axis) and semicrystalline and also, possibly, to the substitution of E''/ω for η. Dumbleton et al.[14] have discussed the theoretical basis, applicability, and assumptions involved in these equations. Kojima and Iijima[41] have presented further experimental evidence of the applicability of Fujita's free volume theory to the diffusion of disperse dyes in semicrystalline poly(ethylene terephthalate).

It should be noted that Fujita et al.[28] originally derived their equations in a manner similar to the phenomenological Williams, Landel, and Ferry (WLF) equation[32] of linear viscoelasticity, both being based upon the free volume equation for the viscosity of simple liquids established by Doolittle.[33] Fujita[29] later derived his equation from the theory of Cohen and Turnbull.[34]

Rosenbaum[35] suggested that variations in diffusion coefficients of dye into acrylic fibers with temperature could be represented by an equation having the WLF form. Ingamells[19,20,21] and co-workers have gathered extensive evidence for acrylics and polyester indicating that diffusion behavior above T_g can be represented in terms of the WLF equation. They stress that the dyeing process is controlled by the segmental mobility of the polymer. Their studies indicate that dye carriers depress T_g and increase this segmental mobility. Kitamura[36] has also demonstrated that temperature dependence of diffusion coefficients for disperse dyeings of polyester from water or tetrachloroethylene may be expressed in terms of the WLF equation. Sakai et al.[42,43] have discussed the interrelationship between treatments of the temperature dependence of dye diffusion coefficients above the glass temperature in terms of the WLF equation and the Fujita equation.

The diffusion coefficients of C.I. Disperse Red 13 from perchloroethylene into fibers preconditioned for 3 hr at 110°C in the liquid and dynamic me-

TABLE II

Diffusion Coefficients D of C.I. Disperse Red 13 and Loss Modulus E'' for PET Fiber in Tetrachloroethylene at Various Temperatures[a]

Temperature, °C	D, cm²/sec	E'', dynes/cm²
95	4.15×10^{-9}	9.2×10^{8}
100	6.26×10^{-9}	8.5×10^{8}
110	1.01×10^{-8}	7.4×10^{8}
115	1.13×10^{-8}	6.8×10^{8}

[a] Fiber was preconditioned for 3 hr in liquid at 110°C.

chanical data for this preconditioned fiber in tetrachloroethylene are listed in Table II. The conditioned fiber was held at room temperature in the liquid prior to these measurements. In Figure 11, the log of the molecular mobility, log (D/RT), is plotted against log (E''/ω). A linear relationship is indicated as predicted by eq. (2).

Viscoelastic data are not only of value for studying dye diffusion as controlled by segmental mobility but also equilibrium sorption of dye. Takashi and Omori[37] have proposed a relationship between the dye uptake of polyester fibers and viscoelastic properties of the fibers measured in the dry state.
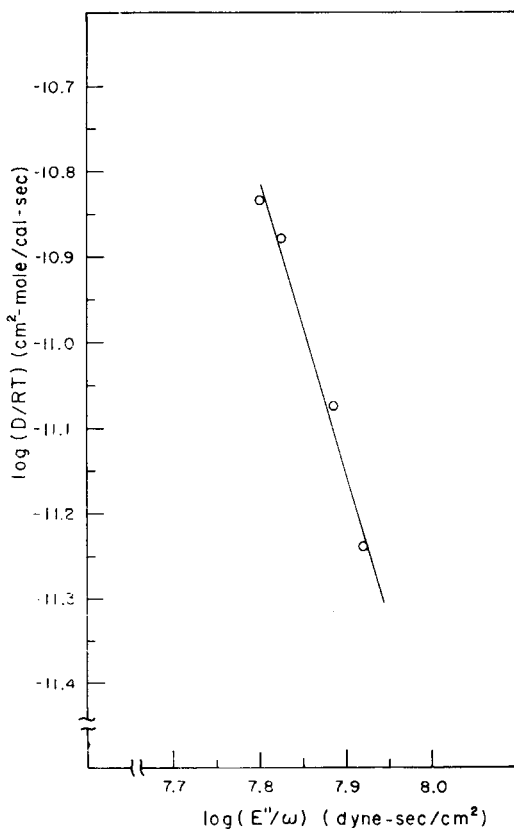

Fig. 11. Relationship between molecular mobility (D/RT) (in cm²-mole/cal-sec) of C.I. Disperse Red 13 and ratio of loss modulus to frequency (E''/ω) (in dynes/cm²-cps) of fiber in tetrachloroethylene.

Namely, the dyeability or concentration of dye on fiber, DY, for a given dyeing condition was expressed as

$$DY = k \int_{20}^{T_0} (\tan \delta)_c \cdot dT$$

where k is the proportionality constant, $(\tan \delta)_c$ is the calibrated loss factor, and T_0 is the characteristic temperature determined by the dyeing condition. This characteristic temperature which served as the upper limit for integration increased with increasing molecular weights of the dyes. This characteristic temperature was always above the temperature corresponding to the maximum value of tan δ (temperature of the α- or glass transition in polyester). The numerical values of the integral at T_0 decreased with increasing crystallinity of the polyester and the corresponding DY values decreased linearly. The authors suggested "that the temperature dependence curve of loss factor tan δ can be treated roughly as the distribution curve of the highest order in the texture that can absorb the dyes." The area under the integrated curve might be considered as a measure of the amorphous polymer capable of absorbing the particular dye. A similar relationship was suggested between DY and the dynamic storage moduli E' at 20°C and the characteristic temperature T_0 as follows:

$$DY = k' \ln (E'_{20}/E'_{T_0})$$

Dumbleton et al.[14] have demonstrated that dynamic mechanical data on polyester fiber reflect the fiber crystalline structure and thus the equilibrium sorption capability.

Supanekar and Daruwalla[38] have proposed that the kinetics of dyeing cellulose triacetate, nylon, and polyester with disperse dyes can be represented by an equation of the same form as the viscoelastic equation for creep in fibers. Dye uptake was described by the equation

$$\frac{C_t}{C_\infty} = 1 - A e^{-Bt}$$

where C_t is the concentration of dye on the fiber at time t, C_∞ is the equilibrium concentration of dye on the fiber, and A and B are constants of the canonical equation. This equation is similar in form to first term of the truncated form of Hill's diffusion equation, which was written as

$$\frac{C_t}{C_\infty} = 1 - 0.692\, e^{-5.782Dt/r^2}$$

where D is diffusion coefficient and r is the radius of the fiber. It was suggested[38] that A from the rate of dyeing equation is associated with the irreversible energy losses in the viscoelastic displacement associated with diffusion of dye into the fiber. The second parameter B was proposed as the reciprocal of the relaxation time for the system. However, no experimental evidence was presented to demonstrate that the measured viscoelastic parameters for the dye–fiber system correspond to the measured values of A and B from dyeing experiments. The experimental evidence did indicate that B was nearly constant for polyester fibers with several disperse dyes.

CONCLUSIONS

The glass temperature of drawn polyester fibers immersed in liquids were significantly depressed over the dry glass temperatures.

The following relationship between diffusion coefficient D of disperse dyes into oriented and crystalline polyester from tetrachloroethylene and loss modulus E'' of polyester in tetrachloroethylene at temperatures above T_g was demonstrated:

$$\ln \frac{D}{RT} = -B \ln \frac{E''}{\omega} + C'$$

where R is the gas constant, T is the absolute temperature, and B and C' are constants. The relationship was interpreted in terms of diffusion controlled by segmental mobility of amorphous regions of the polymer above T_g. Bell[31] has suggested that for semicrystalline and oriented fibers, the value of E''/ω approaches the steady-state viscosity and "represents the product of the activation energy for motion per chain segment and the number of segments moving." Liquid media produced significant morphological rearrangements of PET fibers that were evidenced by changes in dynamic mechanical properties.

The utility of the modified Rheovibron for studies of fiber response to textile processing in liquid media was demonstrated.

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