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National Bureau of Standards
Center for Materials Science
Polymer Science and Standards Division
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First Annual Report

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

PREDICTION OF THE LONG TERM STABILITY OF POLYESTER-BASED RECORDING MEDIA

by

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ABSTRACT

The stability of poly(ethyleneterephthalate) is being studied in order to predict its long term behavior as the base of the film and tape used to record archival information. This report contains results of the first year's work. Film base, with and without photographic and other coatings, was aged at several temperatures and humidities. Mechanical and calorimetric properties and molecular weights were measured at intervals. Degradation was relatively rapid at temperatures of 115, 100, and 85 °C at 100% relative humidity. The scission rate at 85 °C was about 10^{-6} mol scission/g-day and the activation energy was 113 kJ/mol. Rates decreased strongly with relative humidity, becoming negligible in dry air and nitrogen. At 55 °C and 100% relative humidity degradation was not significant in 163 days. Samples were seriously embrittled by the introduction of about one scission per molecule--about 10^{-4} mol scission/g. In its present state, gel permeation chromatography probably is not precise enough to be a good degradation monitor, since one would like to know when degradation had exceeded a fraction of the damaging level. Differential scanning calorimetry showed little change in melting behavior of samples aged at 55 and 85 °C. Glassy samples crystallized during aging at 85 °C but not at 55 °C.

Magnetic tapes based on poly(ethylene terephthalate) usually have a polyester polyurethane binder that holds the magnetic particles. The

binder is thought to be more sensitive to hydrolysis than the tape base. Results obtained with a thermoplastic polyester polyurethane imply that there may be an equilibrium extent of degradation for any storage condition. At 20 °C and 50% relative humidity, about 70×10^{-5} mol scissions/g might occur. The corresponding molecular weight is only 1400 and it is expected that binder of this molecular weight would be too soft.

It is anticipated that the study will go on for four more years. Agings at 35 °C at several humidities are going on and samples will be examined at intervals. Attempts will be made to develop more sensitive methods to detect degradation.

Key Words: degradation; film base; hydrolysis; photographic film; polyester; poly(ethylene terephthalate); recording media; stability

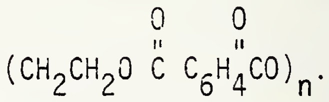
1.0 Introduction

Many of the cultural, historic, and commercial records are now kept in forms other than that of the traditional paper books or documents. Tapes for audio, video, or digitally encoded information as well as microfilm are increasingly popular storage media because of their higher storage density and their compatibility with automated data access and retrieval systems. Newer electrographic imaging systems combine the advantages of microfilm with the ability to update pages, thereby totally eliminating the need for paper records even for active files.

Poly(ethylene terephthalate) (PET) is the supporting base in much of the photographic film and most of the magnetic tape that is used to record archival information. The lifetime of PET is unknown under conditions of archival storage. Similarly, polyester polyurethane binder, used to hold magnetic particles on magnetic tapes, has an unknown lifetime.

Over twenty years ago, similar considerations prompted the Library of Congress, with support from the Rockefeller Foundation, to sponsor a study of the archival qualities of phonograph discs and the types of magnetic tapes available at that time. The report of that study, "Preservation and Storage of Sound Recordings" by A. G. Pickett and M. M. Lemcoe, contains a discussion of the probable modes of deterioration of those recording media and recommendations for storage conditions that still seem reasonable today. The present study was begun in 1981 under the sponsorship of the National Archives. It begins a five-year program aimed at producing measurement methods and data for predicting the lifetimes of polyester-based materials under archival storage conditions. It is hoped that the results will be general enough to be applicable to the products which will be available during the next ten to twenty years and is therefore not merely an assessment of the stability of specific current products. This report describes the results of the first year of the study.

2.0 Background

2.1 PET. This polymer has the chemical structure,  $(CH_2CH_2O\overset{O}{\overset{\|}{C}}\ C_6H_4\overset{O}{\overset{\|}{C}}O)_n$. Industrial production has been described recently [1]. Currently the polymer is made from dimethyl terephthalate by catalyzed ester exchange with ethylene glycol. Two exchange steps are involved. In the first, bis (hydroxyethyl) terephathalate is formed at about 150-200 °C and methanol is distilled off. Reaction catalysts are acetates of cobalt, magnesium or zinc. PET is formed in the second step by heating the first product to 280 °C with antimony trioxide. Ethylene glycol is formed, which is removed under vacuum, thereby favoring polymer formation. At 280 °C, residual catalyst from the first step would convert some ethylene glycol to bis-(hydroxyethyl) ether. This could enter the polymer through ester exchange and affect its properties. To prevent this, phosphoric acid or triphenyl phosphate is added along with the antimony trioxide. These complex the acetate catalysts and render them innocuous.

Recently high purity terephthalic acid has become available in large quantities and may become the starting material of choice. In this process bis-(hydroxyethyl) terephthalate would be made directly from terephthalic acid and ethylene glycol, using titanium alkoxides or dialkyl tin oxides or carboxylates. With these present, conversion of bis (hydroxyethyl) terephthalate to PET does not require antimony trioxide, although some may be used.

Storage qualities of the finished product may be affected by the process used. Specifically, since catalysts must act on forward and reverse reactions, residual esterfication catalyst will promote hydrolysis. If the catalyst is destroyed by side reactions (hydrolysis, for example) the residual activity may not be great. In a study of the hydrolysis of poly(butylene adipate) glycol we found that it hydrolyzed with a smaller rate constant if it had been prepared without catalyst.

A side reaction that occurs during polymerization of PET may also be important to its subsequent storage qualities. This is the self disproportionation of the polymer chain to form vinyl ($\text{--}CH = CH_2$) and acid ($HO\overset{\overset{O}{\|}}{C}C_6H_4CO\text{--}$) end groups. Hydrolysis of esters is known to be acid catalyzed so manufacturers strive to keep the acid content low. Acid concentrations of 15-50 μ eq/g are typical of commercial polymers [2].

The number (M_n) and weight (M_w) average molecular weights of commercial PET are about 20,000 and 45,000 g/mol respectively. About 1.3-1.8 wt. %

of cyclic compounds-dimers, trimer, tetramer, and pentamer, are present. The most abundant is a cyclic trimer [2,3]. Conceivably, these compounds may migrate out of the polymer in prolonged or high temperature agings, affecting physical properties and the measured M_n.

PET is weak, brittle, and opaque unless subjected to a complex thermomechanical treatment [2] to be described. Polymer is heated above the melting temperature, T_m (about 250 °C), extruded, and quenched. Then it is heated to about 135 °C (the glass temperature, T_g, is about 70 °C) and stretched biaxially. Subsequently the polymer is heated to about 150 °C, under restraint, and some crystallization occurs. It is then cooled and may be "tensilized" by stretching it unidirectionally. The result is a clear film with a tensile strength as high as 200 MPa (30,000 psi) and an elongation at break of about 150%. Although the film is quite clear, the amount of crystallinity is appreciable--from 30 to 50% is estimated by calorimetry.

Glassy PET, prepared by simply melting and quenching the polymer, is clear but is weaker and less deformable than fully treated film. Therefore, the tremendous improvement in mechanical properties brought about by the thermomechanical treatment is due to residual orientation and stress in the film. The presence of residual stress is shown by the two fold shrinkage in length and width that occurs if a film is heated quickly to 285 °C.

Temperatures in previous aging studies of PET have generally been above T_g in order to keep aging times from becoming unreasonably long. Archival storage temperatures are normally of the order of 20 °C or below [4].

Thus a rather rather long extrapolation below T_g is required when applying previous data to the temperature region of interest. There is no convincing evidence that such extrapolation is valid. Indeed, one anticipates some discontinuity at T_g because of changes in mobility. Thus, above T_g one would expect that a scission in an amorphous portion of a polymer chain would be followed by rapid relaxation of any strained configurations that portion had. Considerably below T_g one would expect the broken chain would maintain its strained configuration. Presumably there should be differences in physical characteristics that reflect such contrasting behavior that would not be taken into account by simple extrapolation through T_g.

There have been several aging studies involving PET. We will not attempt to review all but will describe the most important ones. The reaction of primary interest is ester hydrolysis, which breaks the polymer chain generating acid and alcohol groups, i.e. $H_2O + -CO_2- \rightarrow -CO_2H + HO-$.

One of the most thorough of the previous studies is that by McMahon et al. [5]. The hydrolysis of PET was studied at temperatures between 130 and 50 °C at relative humidities, RH, of 0, 20, 50, 75, 95, and 100%. Samples consisted of 0.5 and 10.0 mil-thick film, the former more oriented than the latter, and 1100 denier yarn. The maximum time was 300 days. The amount of chain scission, calculated as the fraction of ester groups hydrolyzed, was deduced from intrinsic viscosities. Measurements were also made of tensile strength, elongation and density. Infra-red spectra were studied.

Plots of the amount of chain scission versus time showed upward curvature. However, this became appreciable only after samples had become brittle so rate constants for chain scission were taken as the initial slopes. For the 0.5 mil sheet these were approximately proportional to RH at constant temperature and had an activation energy of about 110 k J/mole, independent of RH. Rate constants for the 10- mil sheet increased more rapidly than relative humidity but were 1/4 to 1/2 those of the 0.5 mil sheet. The activation energy was about 120 kJ/mol. It was assumed that diffusion limited the degradation rate of the 10 mil sheet. The yarn, which had threads thinner than 0.5 mil, was considerably more stable than either sheet. Possibly orientation and/or crystallinity contributed to these rate differences.

The 0.5-mil and 10-mil films were judged to have failed when 0.7 and 0.5% of the ester groups had been hydrolyzed, respectively, which amounts to about one ester group broken per molecule. Extrapolation by the Arrhenius equation gave lifetimes of about 500 and 800 years, respectively, for these films at 25 °C, 50% RH.

The lowest temperature at which work was reported is 60 °C. In 300 days at 100% relative humidity the intrinsic viscosity had decreased from 0.53 to 0.45 dL/g. The decrease was approximately uniform with time. The value of T_g in such a long experiment may be less than 70 °C, so it is uncertain if this degradation is below T_g.

Arguments were given [5] to the effect that degradation due to thermal or oxidative scission is about three orders of magnitude less than hydrolytic scission at 100% RH. The data for films at 90 °C in dry air initially showed a small decrease in intrinsic viscosity followed by an increase to about the initial value.

During degradation of the films there were increases in density, attributed to increases in crystallinity, and also increases in absorbance at 3425 cm^{-1}, attributed to incorporation of -OH groups in the polymer.

A more recent paper described hydrolysis at 100 °C, 100% RH [6]. Carboxylic acid contents were measured at various times for samples having different initial acid contents. These data show clearly that degradation is autocatalytic, the rate increasing proportionally to initial acid content and exponentially with time. Since acid contents of the samples studied by McMahon et al. [5] were not given, it is possible that some of the differences between samples were due to differing initial acid contents.

The above studies did not involve film bearing photographic emulsions, which might affect the degradation. Adelstein and McCrea [7,8] have aged photographic film and also uncoated film base.

Samples were sheets of base, 4 mil thick in the case of PET and also sheets of exposed and developed photographic film, on the same thickness of base. Most of these were preconditioned at 21 °C, 50% RH and then sealed in 2.5 cm diameter glass tubes, about 100 sheets of one kind to each tube. The volume of the tube was made small to minimize evaporation of moisture from the samples. The samples were then placed in ovens at temperatures between 71 and 125 °C for various times. Properties measured included intrinsic viscosity, tensile strength and elongation, emulsion melting and image loss, and brittleness on rapidly bending the film. The last two are qualitative tests.

The results for the first three properties were assumed to obey first order kinetics and rate constants were calculated as the fraction of each property lost per unit time. These rate constants were not used directly in extrapolation but instead were used to calculate times to 20% viscosity loss, 10% loss in tensile strength, and 10% loss in elongation at break. Times to emulsion melting and image loss and onset of brittleness were also judged. These times were extrapolated by the Arrhenius equation to 21 °C. The extrapolated times range from 1000 to 2000 years. Relative humidities at each temperature are unknown and must be different, so the reliability of the extrapolation appears questionable.

Longer experiments were done in which samples were aged at 25 °C - 60% RH, 38 °C -78% RH, and 50 °C - 20% RH for times up to 24 years. After 24 years at 25 °C, 60% RH decreases in intrinsic viscosity and elongation were 3% and 22% respectively; tensile strength appeared to increase slightly, about 5%. The extrapolation described above predicts that in 24 years losses of these three properties will be 0.1, 0.2, and 0.4% respectively at 25 °C. Thus the extrapolation described above predicts rather different changes in properties than were observed.

PET base with a photographic emulsion layer degraded about three times faster than the uncoated support. This was attributed to production of ammonia from the gelatin. Ammonia is known to attack PET quite severely [2]. However, to us it seems that the effect might also be due to humidity differences, since gelatin which sorbs water strongly at 21 °C, might desorb it at oven temperatures. Relative humidities would be greater in these tubes. At high temperature the film with the cellulose triacetate base appears somewhat more stable than the film with the PET base. Below 100 °C this situation is reversed.

2.2 Magnetic Tape. Most magnetic tapes consist of a thin (0.25-1.50 mil) PET substrate with a front coating containing a magnetic material, commonly $\gamma\ Fe_2O_3$ or CrO_2. The magnetic material is embedded in a polymeric binder. Common binders are based on polyester polyurethanes. Sometimes there is a carbon coating on the back, which is also embedded in a polymeric binder. The carbon coating dissipates electrostatic charge.

The polyester polyurethane binders used on tapes are highly cross-linked materials with complex structures. They can be expected to have 5 - 10 times as many ester groups as urethane groups. Aliphatic esters are used; these are more susceptable to hydrolytic degradation than the PET substrate. Thus the degradation of interest in magnetic tapes is primarily that of the binder. On degradation this softens; adjacent layers of tape may stick together or the binder may stick to the recording heads. Ultimately the tape becomes unreadable.

The hydrolytic degradation of soluble aliphatic polyester polyurethanes is quite well understood [9,10]. The reaction proceeds by the equation:

$$H_2O + -CO_2- \xrightarrow{k} -CO_2H(A) + HO- \qquad (1)$$

Here an ester link, $-CO_2-$, reacts with water, breaking the polymer chain and giving an alcohol and a carboxylic acid (A), which catalyzes the reaction. Typically there are about 10^{-2} mol ester groups for one gram of polymer. If 5 - 10% of these are hydrolyzed the polyurethane molecular weight becomes about 1000 - 2000 g/mol. This is far too low to have the mechanical properties of a polymer. Thus severe property degradation can occur without much change in the ester concentration. For any sample, the water content is determined by the relative humidity and the temperature and is not much affected by the extent of degradation. Consequently, ester and water concentrations can be included in the rate constant, k. Scissions in mol/g are equal to the change in the reciprocal of the number average molecular weight, $\Delta(M_n^{-1})$. This equals the change in acid content. Since the reaction is acid catalyzed the applicable differential equations are:

$$\frac{d[A]}{dt} = \frac{d\,\Delta(M_n^{-1})}{dt} = k[A] \qquad (2)$$

where t is time and k is the fractional rate of increase in acid concentration. After integration:

$$[A] = [A_o]e^{kt} \qquad (3)$$

$$\Delta(M_n^{-1}) = [A_o]\,(e^{kt}-1) \qquad (4)$$

where $[A_o]$ is the initial acid content, about 10^{-5}eq/g.

For polyester polyurethanes based on polycaprolactones and polybutylene adipates, k was approximately proportional to relative humidity and, at 100% RH, increased with temperature with an activation energy of about 75 kJ/mol [10].

Carbodiimides are sometimes used as hydrolysis stabilizers in polyester polyurethanes because they react with acid, reducing reaction 1 to negligible proportions. However, there is a slow uncatalyzed hydrolysis, ordinarily negligible, which continually generates acid [11]. This reacts with carbodiimide, eventually consuming it. Subsequently, reaction 1 again becomes significant and destroys the polymer.

Esterification, the reverse of hydrolysis, may be significant at low relative humidities. If k^1 is the rate constant for the reverse of reaction (1) then the rate of ester formation will be $k^1\ [A]^2[HO-]$. The acid concentration is squared because acid was a catalyst for the forward reaction and so must be one for the back reaction. If hydrolysis has occurred to a moderate extent, [A] and the [HO-] will be about equal, since $[A_0]$ is small and acid and alcohol form at equal rates. Thus a sample undergoing degradation at low RH ought to reach an equilibrium described by the equations:

$$k[A] = k^1[A]^3 \text{ or } k = k^1[A]^2 \qquad (5)$$

At 35°C, 100% RH, unstabilized, soluble polyester polyurethanes lasted about 400 - 500 days before becoming very weak. Highly cross-linked materials would be expected to last longer because more scissions would be required to reduce the molecular weight to a critical value. Such samples have been examined. Cross-linked reticulated foams, taken from airplane fuel tanks, have been studied by preaging them until soluble and then aging them for additional periods to measure the rate of increase in acid content [12]. The rate data were extrapolated backward in time to get the acid contents before aging. These correlated well with mechanical properties and the times (5 - 8 years) the materials had been in service. The actual rate constants were about equal to those of soluble polyurethanes.

Two studies have been concerned with the hydrolytic stability of magnetic tape binder. E. F. Cuddihy measured the weight of acetone-soluble components and evaluated the adhesion between binders and PET [13]. Agings were done in air and in nitrogen at relative humidities of 0, 11, 30, and 100% at temperatures of 36, 48, 61, and 75 °C. Samples that had been hermetically sealed at relative humidities of 30, 60, and

100% at each temperature were also aged. The weight of the acetone soluble materials decreased at 0 and 11% RH and in all the hermetically sealed samples, indicating that crosslinking occurred. The other samples showed increases in sol fraction. These increases were attributed to scissions caused by hydrolysis. The crosslinking was attributed to the reverse process, esterification.

The adhesive strength between binder and PET was estimated by rubbing the tape with a swab that had been soaked in tetrahydrofuran and measuring the time required to dislodge the binder layer. Values were 14±2 seconds for unaged tape. They ranged down to as little as one second for a sample aged 14 weeks at 75 °C, 100% RH and up to 30 seconds for samples aged 14 weeks in dry air or nitrogen at 75 °C. Thus the results parallel the sol fraction observations.

The crosslinking effect found for hermetically sealed samples is puzzling since the samples were supposedly equilibrated at humidities high enough to cause degradation. Thus, unless the binder initially had considerable acid and alcohol, one would expect that the sol fraction would increase and the humidity decrease until hydrolysis and esterification went on at equal rates. Relative humidity was measured in several experiments and found to increase. As noted above, sol fractions decreased. Possibly the iron oxide particles contain some $Fe(OH)_3$, which reacted with carboxylic acid to give water and an iron carboxylate.

Cuddihy concluded that at a relative humidity of 24% at 21 °C the binder should be stable, neither crosslinking nor degrading.

The second study of tape stability was undertaken for the U.S. Air Force [14]. The effect of humid aging was only part of the study; much of the effort went into mechanical characteristics of tape winding and their effect on long term tape readability.

To study the effect of humidity, reading error rates were measured before and after aging tapes at: 55 °C, 100% RH; 20 °C, 50% RH; and 20 °C in a hemetically sealed container (conditions at closure were not stated). Tapes were examined at three month intervals for 12 - 15 months. Low density and high density multitrack systems were used. At 20 °C it was concluded that the error rate increased somewhat but remained small, about one error in 10^6 to 10^7 bits. However there were some unreadable blocks and tracks, usually on the outer part of the reel or on the outer edge of the tape, that were eliminated from consideration. At 55 °C there was severe binder degradation, to the point where binder flaked off the tape if it was stretched. Reading difficulties started after six months of aging and became worse. However, with the multitrack system, information could be recovered after 15 months aging at 55 °C, 100% RH by combining results from several tracks.

The authors of the report were aware of the Cuddihy work and attempted to use it to calculate a relative humidity-temperature line along which there would be no hydrolysis. However, they set up the equilibrium as $k = k^1[A]$, which appears contrary to the law of mass action. Consequently, their recommended storage conditions, 18 °C at 40% RH, are suspect in our estimation. Our own experience with a variety of polyester polyurethane elastomers suggests that considerable degradation would occur under such conditions, but we have no experience yet with tape binder.

3.0 Present Approach

3.1 PET. Samples of several materials are being aged at 25, 50, and 100% relative humidity at 35, 55, and 85 °C. In addition to two exposed and developed photographic films, there are samples of two electrographic systems, some uncoated PET film base, and NBS 1470, a PET film having known permeation characteristics. Samples for each condition are in one large test tube closed with a rubber stopper. The samples are suspended on a frame above the LiCl humidifying solution. In addition, samples of the leader are being aged in sealed tubes under dry air, dry nitrogen, and nitrogen at 100% RH. The coating has been removed from some of the commercial samples in order to get results with and without coatings. At 35°C some samples contain test patterns in order to see effects on the gelatin layer.

Samples are removed at intervals, tested for brittleness by creasing, and their molecular weights are determined by gel permeation chromatography. Tensile strengths, TS, and elongation, E, are measured in many cases. A differential scanning calorimeter (DSC) is used to observe glass and melting behavior and measure ΔH_f, the heat of fusion. A potentiometric titrator has been received and acid contents will be determined. Some infrared measurements were made and more are planned.

Two sets of smaller scale experiments are being run. These involve glassy samples and samples preaged at 85 °C, 100% RH. These are being aged only at 100% RH, the last set only at 55 °C and 35 °C.

Properties of unaged samples are in Table I. The first three materials (all photographic products) and coated electrographic film D have similar properties. Other materials have somewhat lower values of M_n and TS and higher values of ΔH_f. Values between 113 and 144 J/g have been estimated [15] for 100% crystalline PET, so our samples appear to be 30-50% crystalline by calorimetry.

Uncoated electrographic film C has particulary high values of ΔH_f and E and a low value of TS. It "necks" in the tensile tester suggesting that it was not prestretched as much as the other materials.

The lower molecular weights of the glassy polymer indicate that it degraded during preparation. When heated in the calorimeter it exhibits a strong glass transition, then crystallizes, and finally melts. This behavior is shown later. Pieces of the glassy polymer were small and contained bubbles. Consequently, their tensile properties were not measured.

3.2 Tapes. To date we have not aged magnetic tapes but have been studying equilibrium characteristics of esterfication at different humidities and temperatures. Materials studied include a polyester polyurethane elastomer and several polyester diols used to make polyester polyurethanes.

4.0 Results

4.1 PET

4.1.1 Mechanical Properties. Table II lists the number of days of aging after which samples cracked when creased, a qualitative test designated "Finger Brittleness." These times depend on humidity and temperature. No failures have yet been observed in samples aged at 85 °C, 25% RH or at 55 °C. At 85 °C, 100% RH, approximately 100 days cause failure of all samples. Electrographic film C was embrittled more rapidly than the others.

Figures 1 and 2 show elongation at break as a function of aging time at 85 °C. The figures show effects of surrounding gas, relative humidity, and removal of any coating. The lines indicate the general trends of the data. At 100% RH almost all elongation is lost between 80 and 100 days, whether in air or in nitrogen, whether coated or not. Specimens of uncoated and coated electrographic film C, aged at 100% RH, were not run in the tensile tester. The former was too brittle to handle after 61 days, at which time only a small piece of the latter was taken. After 81 days the latter was too brittle to handle. At 50, 25, and 0% RH all samples show progressively less loss of elongation.

Figures 3 and 4 show tensile strength as a function of aging time at 85 °C. Decreases on aging are not nearly as severe as found for elongation. The influence of humidity and the lack of any consistent difference associated with the presence of a coating are qualitatively as found with elongation.

4.1.2 Chain Scissions in PET. Molecular weights were measured by use of gel permeation chromatography using four microstyragel columns having pore sizes 10^1, 10^2, 10^2, and 10^4 nm. The solvent was hexafluoroisopropanol containing 0.01 M sodium trifluoroacetate. This salt tends to prevent adsorption of polymer on the packing. Calibration was performed by using published chromatograms and intrinsic viscosities of PET in hexafluorisopropanol [16] to calculate the Mark Houwink equation between intrinsic viscosity and molecular weight at the chromatogram peak. This relationship was assumed valid for our polymers. Then we determined the intrinsic viscosities and chromatographed several of our degraded and undergraded samples. Use of the Mark Houwink equation gave molecular weight at the peak as a function of retention volume on our column set.

This calibration technique is being used on a tentative basis. Efforts were also made to develop a calibration with a better theoretical basis. Narrow fractions of polymethyl-methacrylate were purchased and a universal calibration was developed (polystyrene is insoluble in hexafluroisopropanol and so could not be used). When applied to PET this calibration gave values between 3000 and 200 for undegraded and degraded samples and thus was seriously in error. The reason for the failure is unknown. Also, in our preliminary work we found that metastable solutions of PET could be formed by dissolving it first in hexafluoroisopropanol and then diluting 30 fold with chloroform. These solutions were stable for

7-10 days and so could be chromatographed. The mixed solvent, being effectively chloroform, dissolved polystyrene fractions, which were chromatographed and the results made the basis of a universal calibration. When applied to PET the result was as above, unbelievably low molecular weights.

Several chromatograms of degraded and undegraded PET in hexafluoroisopropanol are in Figure 5. The secondary maximum at about 37 cm^3 was found with all materials. The progressive shift of the peak maxima to higher retention volumes as aging time increases means that the molecular weight decreases on aging. Aging at 100 °C and 115 °C for short times caused severe degradation. There are small peaks at higher retention volumes than shown here, 40 - 60 cm^3. These are observed if polymer-free solvent is injected and so are ignored.

The molecular weights are calculated from the chromatograms by assuming that the height above the baseline is proportional to the concentration of polymer, whose molecular weight is determined from the retention volume at which that height occurs. Therefore, the weight fraction of polymer in a certain molecular weight range is proportional to that fraction of the total area under the chromatogram between certain retention volumes. A digital computer is used to make the necessary summations and calculate M_w and M_n.

One characteristic of the results is that M_n is quite sensitive to location of the baseline. This is shown in Fig. 6, which gives M_w and M_n for two baseline locations. The location of the baseline is really somewhat subjective, particularly in the low molecular weight region because of the solvent impurities and because there is probably some adsorption of the polymer on the column packing. The larger standard deviation found for M_n than M_w in table I for film base reflects this situation.

In calculating scissions, M_n is the quantity of interest because M_n^{-1} represents mol polymer per gram. Therefore $\Delta(M_n^{-1})$ is the increase in mol polymer per gram. This is equal to the mol of scissions per gram, since each scission adds one to the number of polymer molecules. Probably $\Delta(M_n^{-1})$ is uncertain by about 2×10^{-5} mol scission per gram.

Figures 7 and 8 are plots of $\Delta(M_n^{-1})$ versus time at 85 °C. At 100% RH a linear extrapolation of $\Delta(M_n^{-1})$ at longer times to zero time falls below the origin, suggesting that the scission rates increase with time; the line is drawn so as to emphasize this trend. The scatter is great and it is thought there are no significant differences in scission rates between samples. This is true even of coated and uncoated electrographic films C despite their early mechanical failures, compared with those of the other samples. At 100 days there is about 6×10^{-5} mol scission/g, indicating that values of M_n have been reduced from about 17000 to 8000. Thus, there has been about one scission per original molecule at failure, in agreement with the work of McMahon et al. [5]. Degradation is much less at 50, 25, and 0% RH.

Figure 9 shows scissions formed in the glassy polymer at 100% RH at 85 °C and also at 55 °C. At 85 °C the scission rate is about four times as large as with the other samples. At 55 °C the number of scissions is negligible.

Table III shows results from a variety of samples aged at 55 °C, 100% RH for 163 days. No property decreases very much and some increase slightly. Consequently, we have as yet no evidence of degradation at 55 °C.

Single aging experiments were done in sealed tubes at higher temperatures than 85 °C. At 115 °C there were 26×10^{-5} mol scissions/g in 13 days and at 100 °C there were 22×10^{-5} mol scissions/g in 39 days. At 85 °C at 100% RH there were 11 x 10^{-5} mol scission/g in 123 days. Overall rates are plotted in Fig. 10. The activation energy is about 113 k J/mol or 27 kcal/mol in reasonable agreement with 29 kcal/mol found by McMahon et al. [5]. Their rates at 85 °C, 100% RH are about 2 x 10^{-6} and 10^{-6} mol scissions/g, day for 0.5 mil and 10 mil film, respectively. Our value for the same conditions is 0.9 x 10^{-6} mol scissions/g, day.

4.1.3 Calorimetry with PET. Some scans between 45 and 180 °C from the differential scanning calorimeter are in fig. 11. For each curve the starting ordinate value is arbitrary and the slope is made approximately zero. The curves for the unaged commercial samples show deflections at about 75 °C that are indicative of glass temperatures, although they are very weak. That for unaged film base is typical of most of our materials. The deflection for the uncoated electrographic film C is the largest for any of the commercial samples. Aged samples do not show a normal T_g but their curves appear to have weak melting peaks about 30-45 degrees above the aging temperature. Interpretation will not be attempted now because the effects of time, humidity, and extent of degradation are unknown.

Curves for the same polymer and also for some aged NBS 1470 between 180 and 280 °C are in Fig .12; the ordinate sensitivity is one tenth that in Fig. 11. Curves 1 and 2 cover the range found for unaged polymers except for the glassy one. The temperatures at the peak maxima, T max, and the heats of fusion are listed in Table IV. Long heating does not affect these quantities much at 55 °C and 85 °C. The changes with samples aged at 100 °C and 115 °C probably are significant.

Fig. 13 and 14 show calorimeter scans for the glassy material. The ordinate scales are both made the same as in Fig. 12 in order to keep the crystallization peaks on scale. The transition at T_g for unaged glassy material is much stronger than for the other unaged materials. Aging at

85 °C permits crystallization, which greatly reduces the size of the glass transition and eliminates crystallization during the scan. Aging at 55 °C did not cause crystallization but it did shift the glass transition temperature. It is encouraging that crystallization did not occur since this process might destroy the orientation of commercial films.

4.2 Polyester Polyurethanes. Cuddihy's work suggests that hydrolysis of polyester polyurethane tape binder may be equilibrium limited at low relative humidity [13]. Binder insolubility and the presence of iron oxide prevent reliable kinetic analysis so we made a preliminary study of equilibrium using soluble polyester polyurethane and polyester diols. In this study hydrolysis was followed by measuring the acid content as a function of time.

A thermoplastic polycaprolactone polyurethane elastomer with an initial acid content of 10^{-5} eq/g was aged at 85 °C, 100% RH until the acid content was 25.5×10^{-5} eq/g. Portions of this material were then re-aged at 85 °C at relative humidites of 27, 12, and 0%. The variation in acid content during the re-aging experiments is shown in Fig. 15. At 27 and 12% RH the equilibrium acid contents are 60 and 35×10^{-5} eq/g, respectively. Samples were also aged at 8% RH at 55 °C and at 11% RH at 35 °C. Equilibrium acid contents were 33 and 28×10^{-5} eq/g respectively. Thus equilibrium acid contents change little with temperature at the same relative humidity.

Polyester diols were also equilibrated at 85 °C and nominal relative humidities of 95, 50, and 25%. At 85 °C these materials are liquids with viscosities of about 30 Pa.s (300 cp). [A] in eq/g of poly(butylene adipate) and poly(caprolactone) diols at equilibrium were 3.9×10^{-3} and 3.2×10^{-3} at 95% RH, 1.4×10^{-3} and 1.2×10^{-3} at 50 % RH, and 0.6×10^{-3} [poly(butyleneadipate)] at 25% RH. The equilibration is now being studied at 55 °C and it appears that the equilibria [A] are not much different from those at 85 °C at the same relative humidity.

Rate constants for the hydrolysis are known from previous work [10]. Therefore, rate constants for the back reaction can be calculated, by equation 5 for the polyurethane and by its modification for the polyester diols. Modification is required because the polyester diols initially contain about 10^{-3} eq/g of -OH groups; consequently [A] and [-OH] are not equal. Secondly, at high relative humidity the ester concentration is changed by hydrolysis. The equation is:

$$\frac{k[E]}{[E_0]} = k^1[A]\,([-OH_0] + [A]) \qquad (6)$$

Here $[E_0]$ and $[-OH_0]$ are initial concentrations of ester and -OH groups and E is the equilibrium concentration of ester. At equilibrium, $[A] \gg [A_0]$, so that the [-OH] is nearly equal to $([-OH_0] + [A])$. $[E_0]$ and $[-OH_0]$ are known characteristics, being 10^{-2} and 2.1×10^{-3} eq/g, respectively, for poly(butyleneadipate) diol and 8.77×10^{-3} and 10^{-3} eq/g, respectively, for the poly(caprolactone) diol.

At 0% RH there is no hydrolysis so k^1 for the polyurethane was calculated from the kinetic data for this condition in Fig. 15. If third order kinetics are assumed then k^1 is half the slope of $[A]^{-2}$ versus time. The three points fit third order kinetics rather well (Fig. 15, x's and dashed line).

The values of k^1 are listed in Table V. As humidity increases k^1 decreases for all three materials. The polyester diols have smaller k^1 values than the polyester polyurethane.

The k^1 at about 10% RH for the polyurethane were extrapolated to 20 °C by the Arrhenius relation to obtain 1.2×10^3 $g^2/eq^2 \times$ day. The corresponding value of k, obtained by extrapolating data in reference [10], is 1.2×10^{-4} day^{-1}. If these rate constants are substituted in eq. (5) the equilibrium acid content is calculated to be 32×10^{-5} eq/g, about as observed at 85 - 35 °C at this humidity. If one neglects any change in k^1 with relative humidity and takes k as being proportional to relative humidity then the equilibrium acid content will vary as the square root of the relative humidity ratios, giving 50×10^{-5} and 70×10^{-5} eq/g at 25 and 50% RH at 20 °C. The reticulated foams studied earlier had lost substantially all their tensile strength at acid contents of 22×10^{-5} and 36×10^{-5} eq/g. About 65% of the strength was retained at 9×10^{-5} eq acid/g.

Alternatively, one can neglect equilibrium and use k to calculate the time to reach some limiting acid content from the initial acid content, which is probably about 10^{-5} eq/g. Values of k are 3×10^{-4} and 6×10^{-4} day^{-1} at 25 and 50% RH at 20 °C. If the limiting acid content is 15×10^{-5} eq/g then, by solving eq. (3) for t, one obtains times equal to about 25 and 12 years respectively for the above conditions.

These calculations were all based on data from a thermoplastic polyester polyurethane and it is not known how closely they will apply to tape binders. The ideas should be valid for any aliphatic polyester polyurethane and modifications exist if stabilizers are present [11].

5.0 Discussion

5.1 PET. The degradation observed is consistent with previous work and supports the idea that the most likely cause of degradation under ordinary conditions will be hydrolysis. It is somewhat surprising that serious loss in physical properties occurs with only one scission per molecule. However the molecular weight of the polymer is quite low so one scission per molecule may bring M_n below a critical value. In addition, the highly oriented nature of the material may furnish an explanation. One picture of a strained semicrystalline polymer is that much of the stress is carried by strained amorphous portions of chains that tie crystalline regions together [17]. Another concept is that mechanically strained bonds are sensitive to chemical attack [18]. If one combines these ideas then the attack would tend to be localized at bonds that are critical for mechanical strength.

The results with the glassy material appear somewhat in conflict with these ideas, since nominally unoriented, glassy polymer degraded faster than the oriented PET. However, the DSC results indicate that the sample crystallized during aging. This might have had some effect because the degradation that occurred during heating prior to forming the glass probably introduced acid groups, which would be expected to have a catalytic effect on hydrolysis. Being on chain ends, they would probably be located preferentially in non-crystalline regions.

In the coming year the agings at 55 °C and 35 °C will be continued and others will be started at 70 °C. Acid contents will be measured by use of a potentiometric titrator, which was delivered recently.
Some agings will be also be started in the presence of small concentrations of sulfur dioxide and nitrogen oxides. These may be environmentally significant for the degradation since the concentration of acid pollutants is likely to increase as lower grade fuels become more common.

Finding that severe mechanical degradation requires very little chemical degradation has made us rather skeptical of the value of gel chromatography as a method of monitoring samples, unless the precision of the measurements can be improved by a factor of ten or more. Infrared methods will be investigated more thoroughly in an effort to find a sensitive means for detecting degradation. Other methods to be considered are transmission of sound and light [19].

5.2 Magnetic Tape. Two problems involved in studying degradation of tape binder are the presence of crosslinks and iron oxide. The latter may represent 80% of the coating. Methods employed will be like those used to study crosslinked foams--pre-aging to render the binder soluble, additional aging, and then determination of the acid contents. Filtration or centrifugation will be used to remove the iron oxide particles. Infrared spectroscopy will also be used to get evidence for reaction between binder and iron oxide.

Experiments will be carried out at several temperatures and humidities. The hydrolysis of tape binder is expected to be much more rapid than that of PET.

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Table I. Properties of Unaged PET[1]

	$10^{-4}M_w$ g/mol	$10^{-4}M_n$ g/mol	TS, M Pa	E, %	ΔH_f, J/g
Uncoated Film Base	4.90 ±0.11	1.77 ±0.34	204 ±5[2]	144 ±8	47 ±3
Microfilm A	5.04	2.15	200 ±14	126 ±13	48
Microfilm B	4.80	1.69	193 ±11	122 ±11	48
Encapsulating Film	4.16	1.59	177 ±22	80 ±15	56
Uncoated Electrographic Film C	4.20	1.44	116 ±7	185 ±22	59
Coated Electrographic Film C	4.07	1.54	167 ±5	105 ±7	55
Coated Electrographic Film D[3]	4.60	1.68	201 ±10	99 ±16	47
PET Film NBS 1470[4]	4.50	1.45	150 ±11	96 ±29	54
PET, NBS 1470 Glassy Polymer[5]	2.60	0.88	--	--	-32 56

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[1] Samples 0.01 cm (4 mil) thick except as indicated. Uncertainties are standard deviations of three or more measurements.

[2] 1 M PA = 145 psi

[3] 4.8 mil

[4] 1 mil

[5] Made by heating and quenching NBS 1470. About 10 mil thick.

Table II. Days Aging of PET at 85 °C to Induce Finger Brittleness

Material	100% RH	50% RH
Film Base	105	>146
Microfilm A	97	>146
Microfilm B	97	>146
Encapsulating Film	105	>146
Uncoated Electrographic Film C	61	81
Coated Electrographic Film C	81	146
Coated Electrographic Film D	>81	>84
PET Film NBS 1470	90	--

Table III. Percentage Change in Properties of PET Aged at 55 °C, 100% RH, for 163 days

Material	M_w	M_n	TS	E
Film Base	0	10	-8	-8
Microfilm A	-8	-2	-3	+10
Microfilm B	-2	28	6	6
Uncoated Electrographic Film C	-7	15	-9	12
Coated Electrographic Film C	3	20	-9	-2
Encapsulating Film	-1	28	6	6
Arithmetic Mean	-2.5	15	-5.3	9

Table IV. Effect of Aging on T_{Max} and ΔH_f

Material	Aging Conditions			T_{Max}, °C	ΔH_f, J/g
	°C	days	%RH		
Film Base		Unaged		251 ±0[1]	47 ±3[1]
Film Base	55	163	100	252	49
Film Base	85	154	25	252	46
Film Base	85	105	100	253	52
Uncoated Electrographic Film C		Unaged		260	59
Uncoated Electrographic Film C	55	163	100	257	65
Uncoated Electrographic Film C	85	154	25	257	62
NBS 1470		Unaged		255	54
NBS 1470	55	90	100	254	52
NBS 1470	85	39	100	255	48
NBS 1470	85	60	100	253	53
NBS 1470	85	90	100	255	59
NBS 1470	100	39	100	249	64
NBS 1470	115	13	100	243	62

---

[1] Uncertainties are standard deviations of three measurements.

Table V. Rate Constants for Esterfication

Material	Temp./°C	RH/%	$10^{-5}k^1/g^2/eq^2\cdot day$
Poly(caprolactone) polyurethane	85	0	4.1
Poly(caprolactone) polyurethane	85	12	1.9
Poly(caprolactone) polyurethane	85	27	1.4
Poly(caprolactone) polyurethane	55	8	0.17
Poly(caprolactone) polyurethane	35	11	0.06
Poly(caprolactone) diol	85	50	0.47
Poly(caprolactone) diol	85	95	0.13
Poly(butyleneadipate) diol	85	25	0.42
Poly(butyleneadipate) diol	85	50	0.26
Poly(butyleneadipate) diol	85	95	0.07

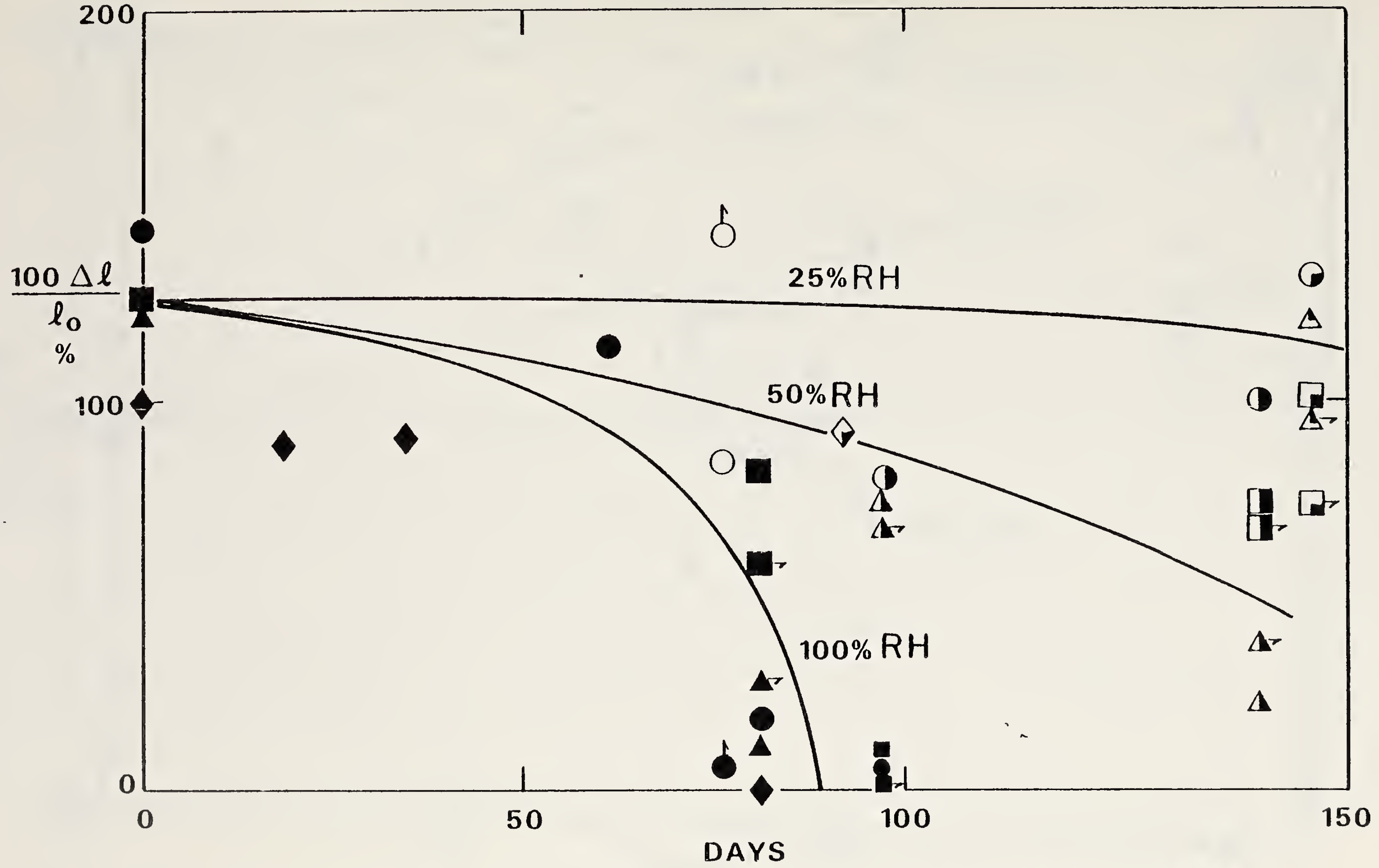

Fig. 1. Elongation at break versus aging time at 85 °C. ○, ◔, ◑, ● film base; ◱, ◧, ■, microfilm A; △, ◭, ▲ microfilm B; ◆, coated electrographic film D. Shadings indicate relative humidity: Unshaded, 0%, quarter shaded, 25%; half shaded 50%; fully shaded, 100%; flags indicate special exposure condition: horizontal, gelatin-layer removed; vertical, under N_2.

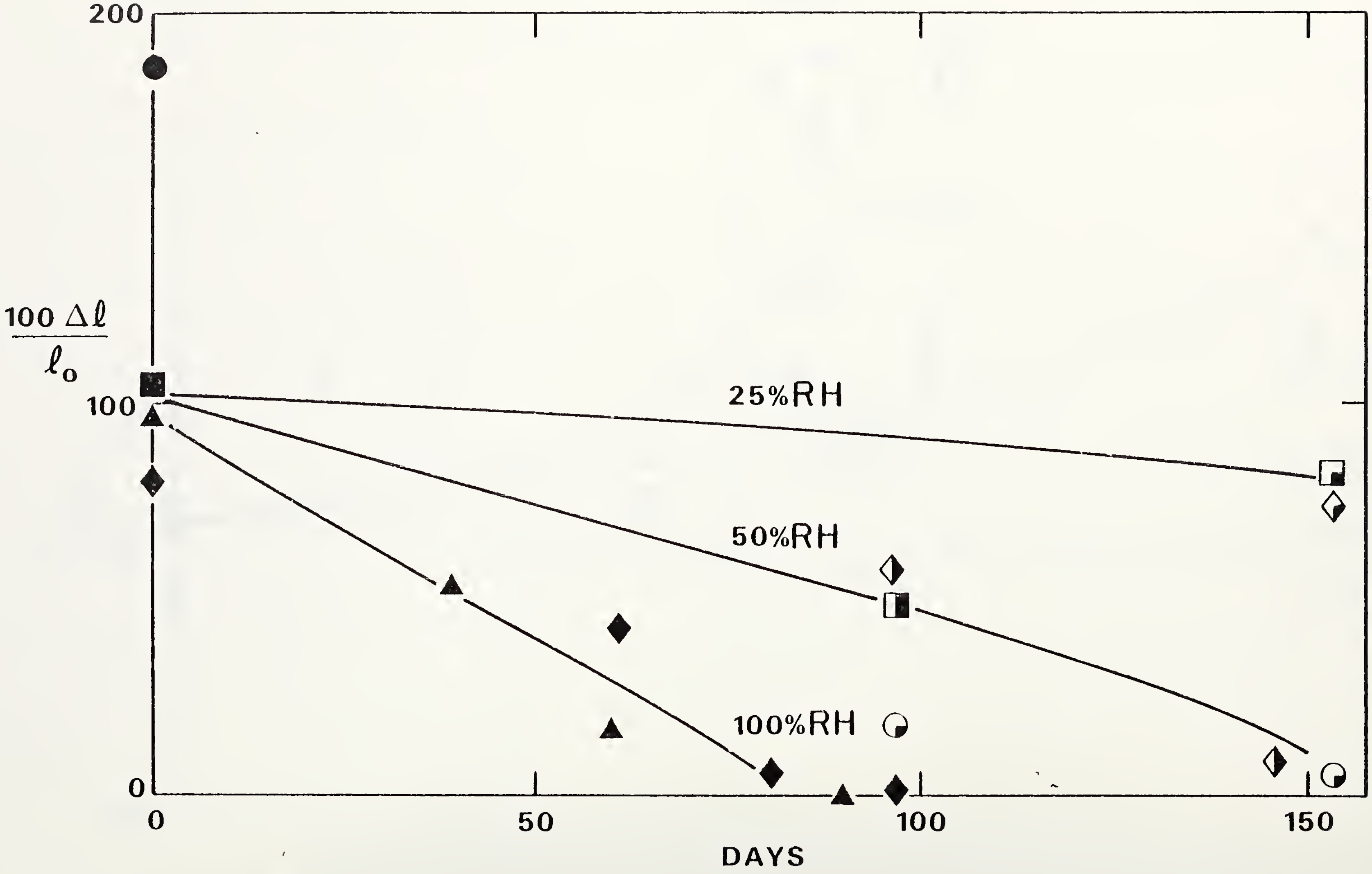

Fig. 2. Elongation at break versus aging time at 85 °C. ◔, ● uncoated electrographic film C; ◪, ◧, ■ coated electrographic film C; ▲, NBS 1470; ◇, ⬖, ◆ encapsulating film. Shading code as in Fig. 1.

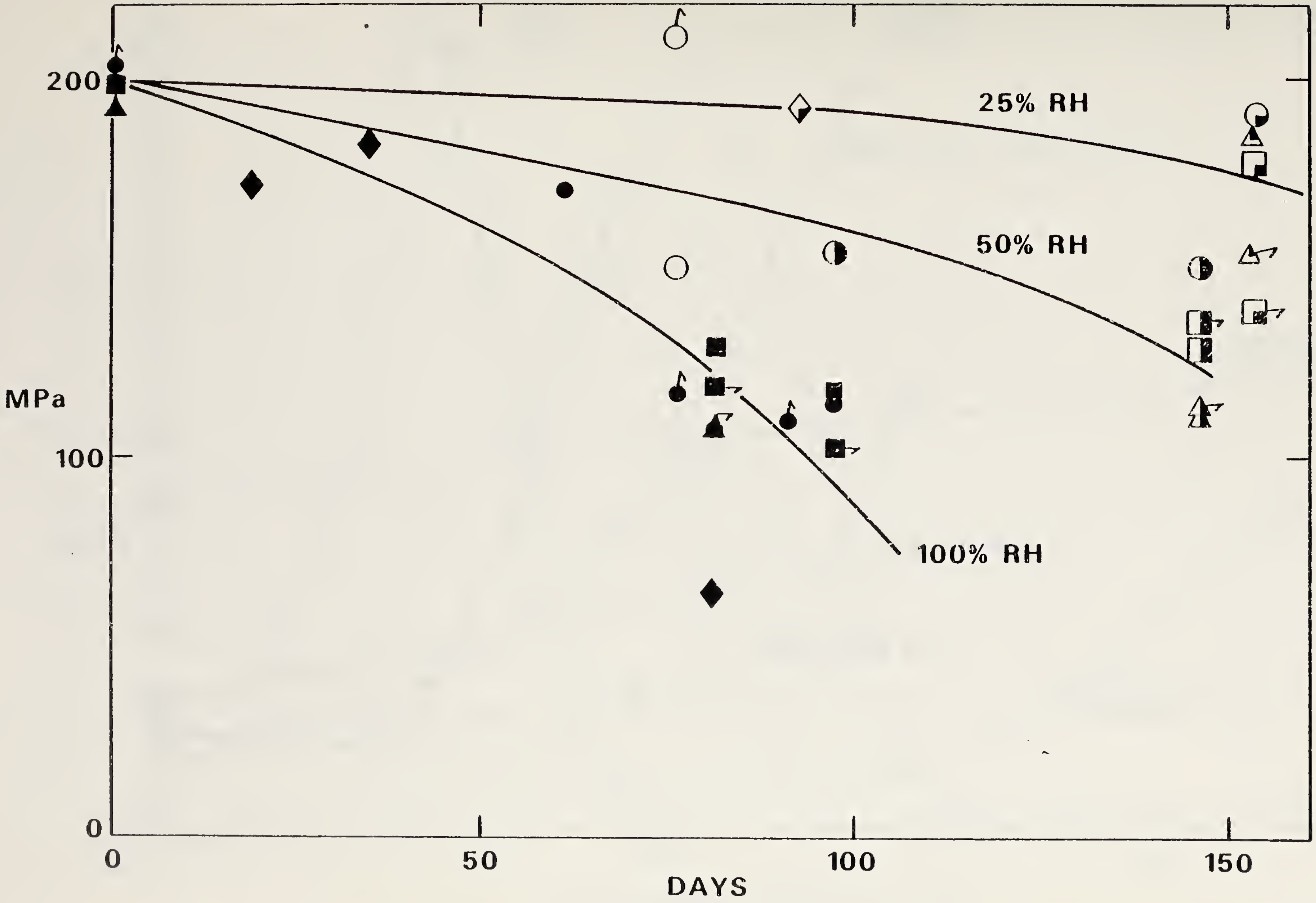

Fig. 3. Tensile strength versus aging time at 85 °C. ○, ◐, ◑, ● film base; ◪, ◧, ■ microfilm A; △, ◭, ▲ microfilm B; ◇, ◆ coated electrographic film D. Shadings and flags as in Figure 1.

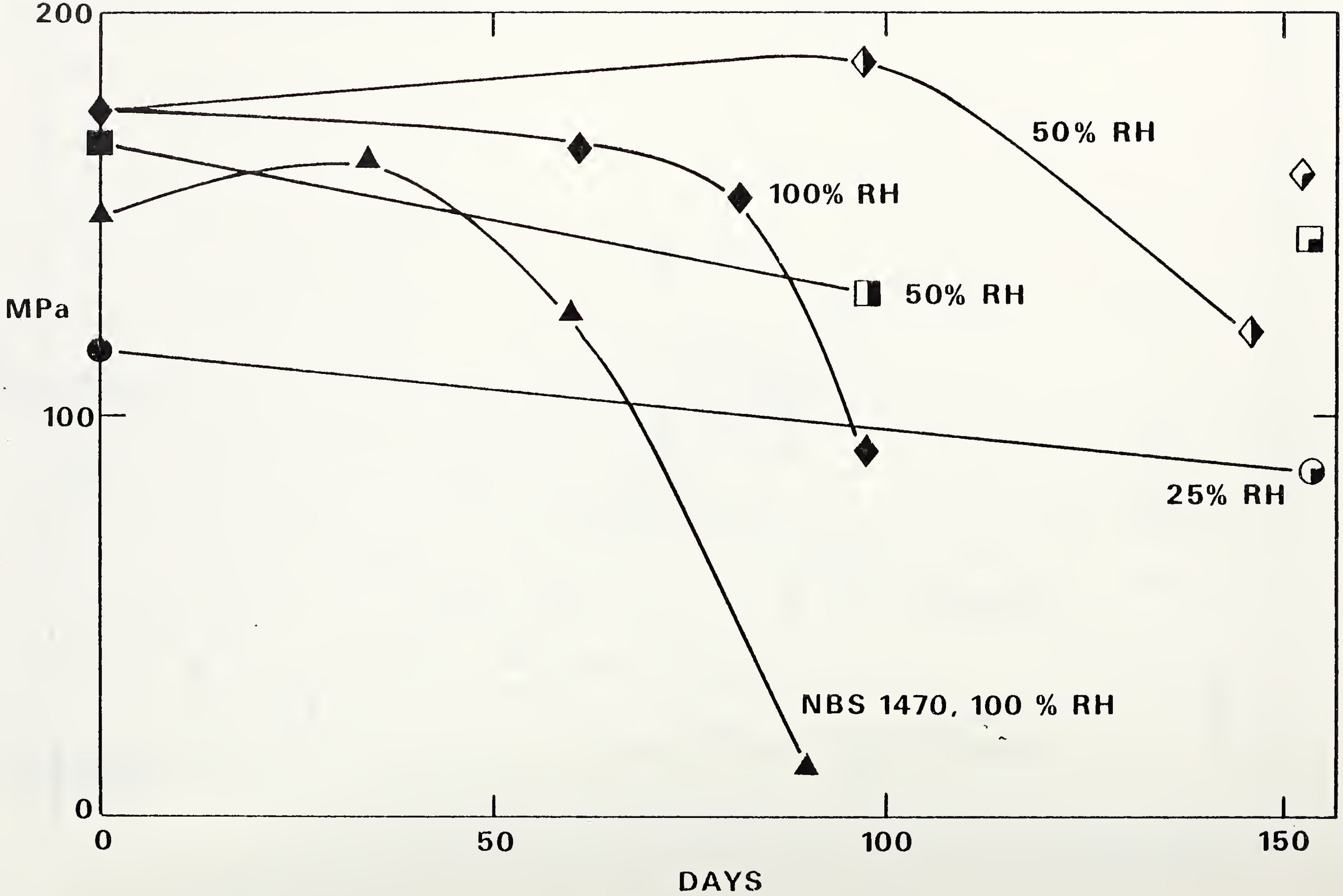

Fig. 4. Tensile strength versus aging time at 85 °C. ◐, ●, uncoated electrographic film C; ◲, ◨, ■ coated electrographic film C; ▲, NBS 1470; ◇, ◈, ◆ encapsulating film. Shading code as in figure 1.

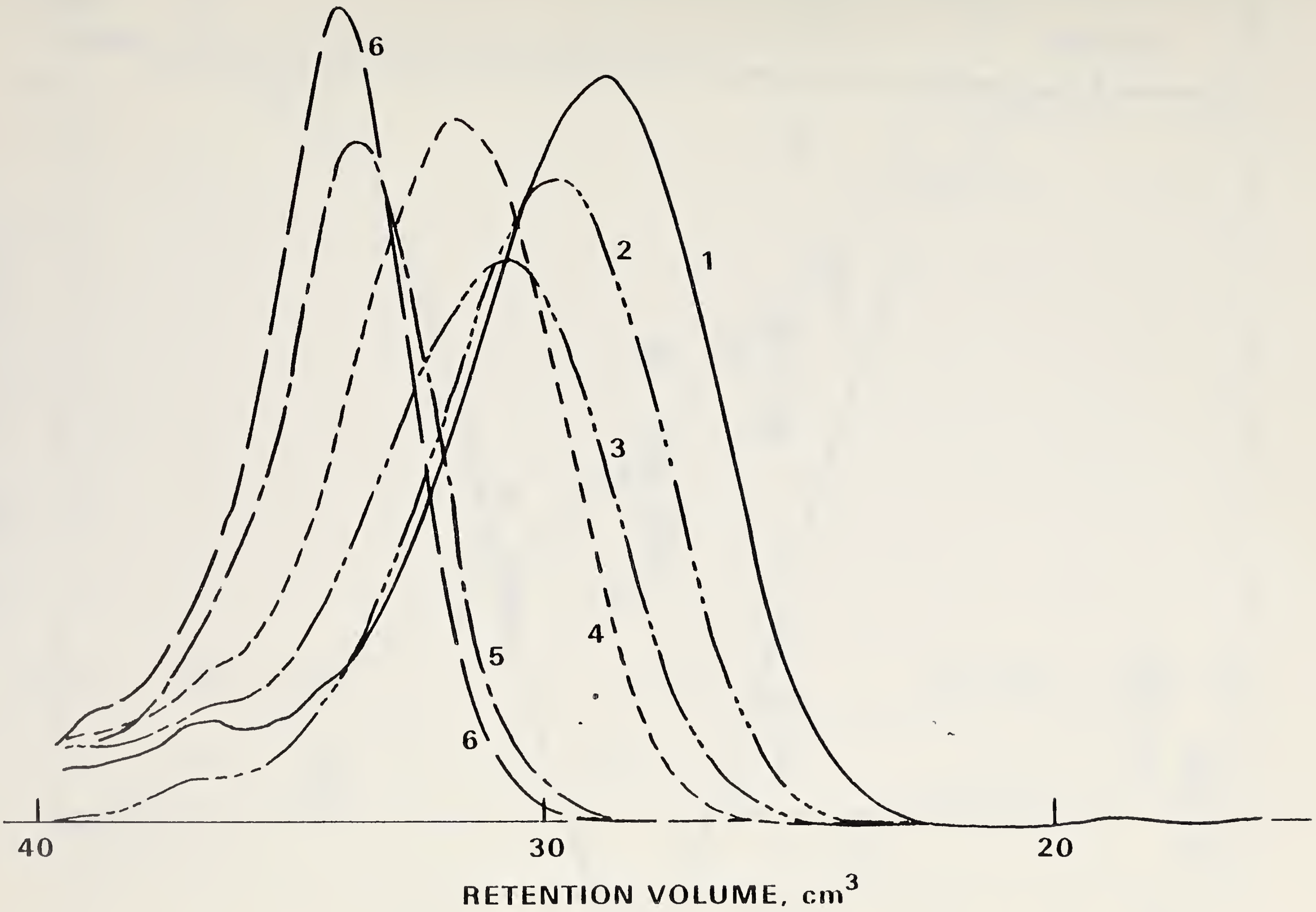

Fig. 5. Gel permeation chromatograms of NBS 1470 unaged and aged at 100% RH. Curve; 1, unaged; 2, 85°, 39 days; 3, 85°, 60 days; 4,85°, 90 days; 5, 100°, 39 days; 6, 115°, 13 days.

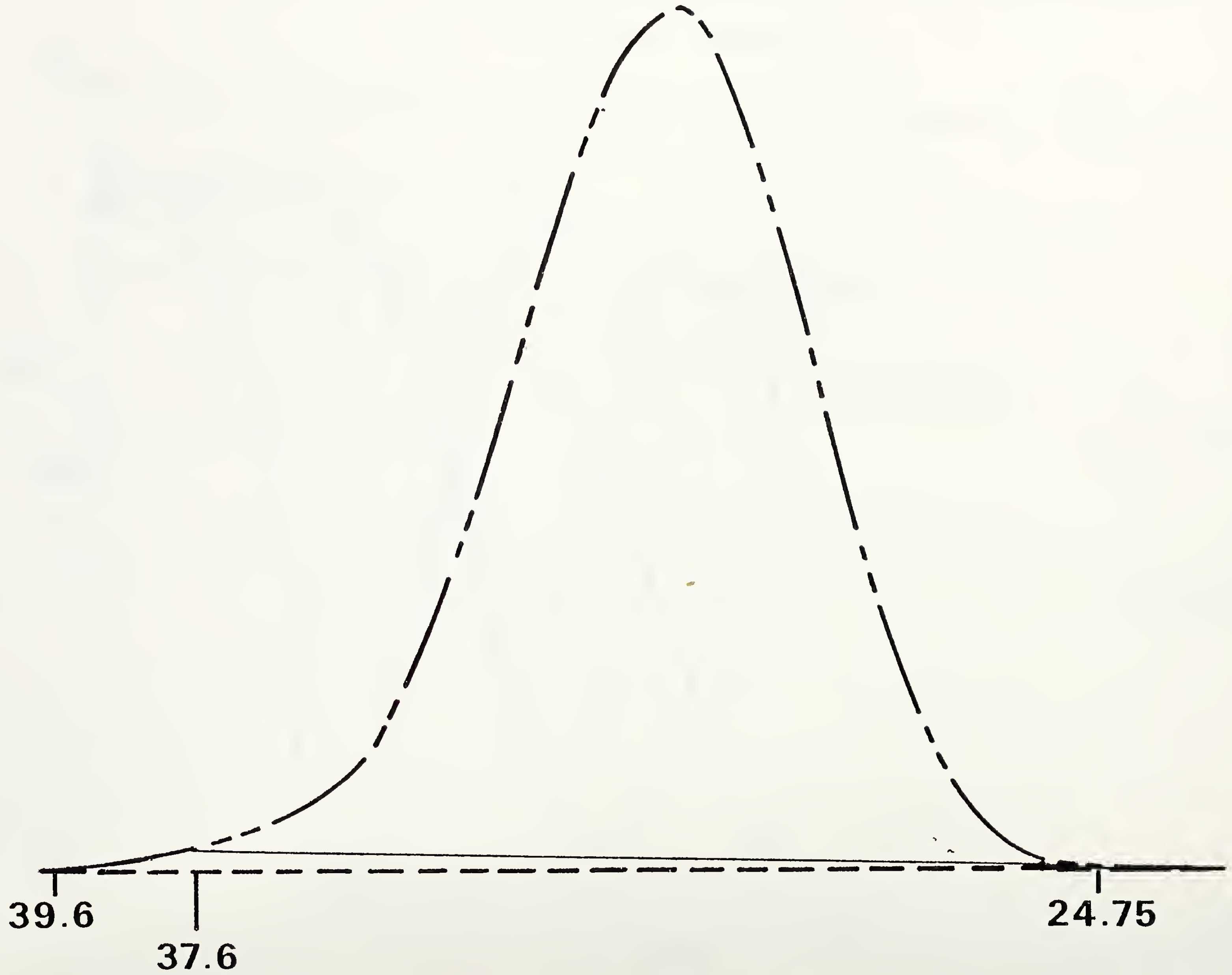

Fig. 6. Effect of chromatogram baseline on M_w and M_n. Film Base aged 85 °C, 100% RH, 81 days. Final volume 39.6 cm^3, area = 247, M_w = 23400, M_n = 10700. Final volume 37.6 cm^3, area = 242, M_w = 23600, M_n = 11900.

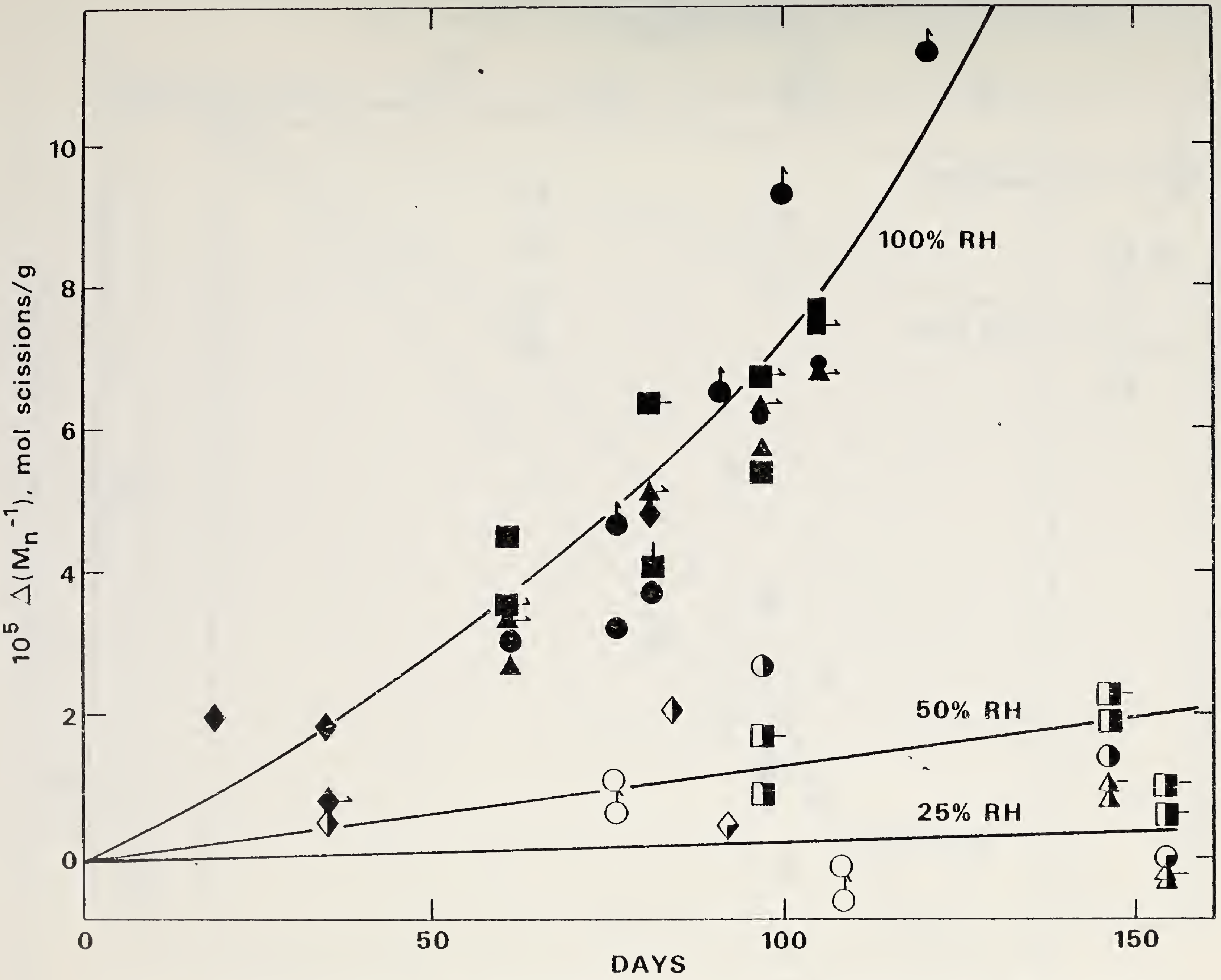

Fig. 7. Chain scissions versus aging time at 85 °C ○, ◐, ◑, ● film base; ◨, ■ microfilm A; △, ▲ microfilm B; ◇, ◈, ◆ coated electrographic film D. Shading and flags as in Figure 1.

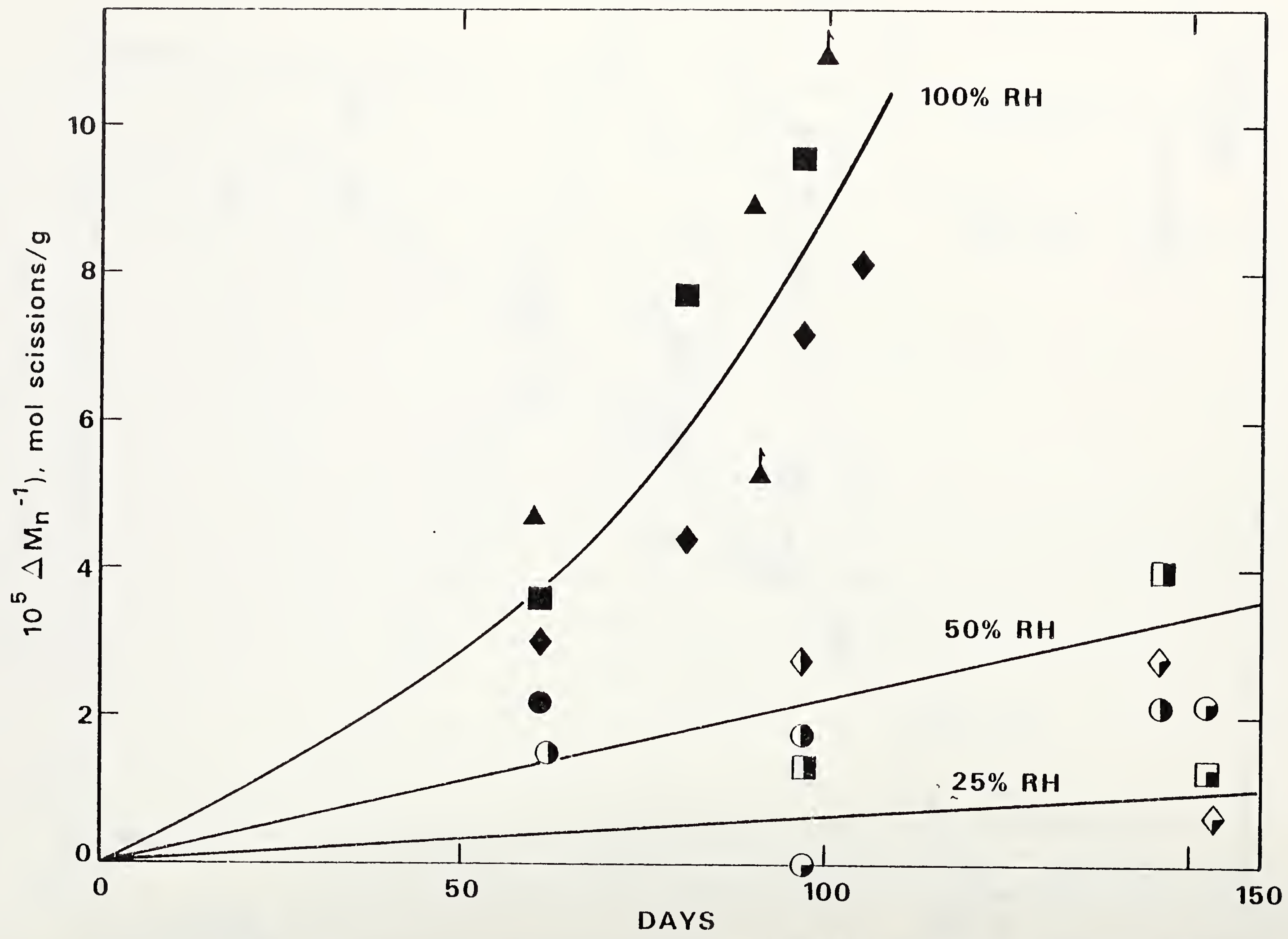

Fig. 8. Chain scissions versus aging time at 85 °C. ◔, ◑, ● uncoated electrographic film C; ◪, ◨, ■ coated electrographic film C; ▲ NBS 1470; ◇, ◈, ◆ encapsulating film. Shading and flags as in figure 1.

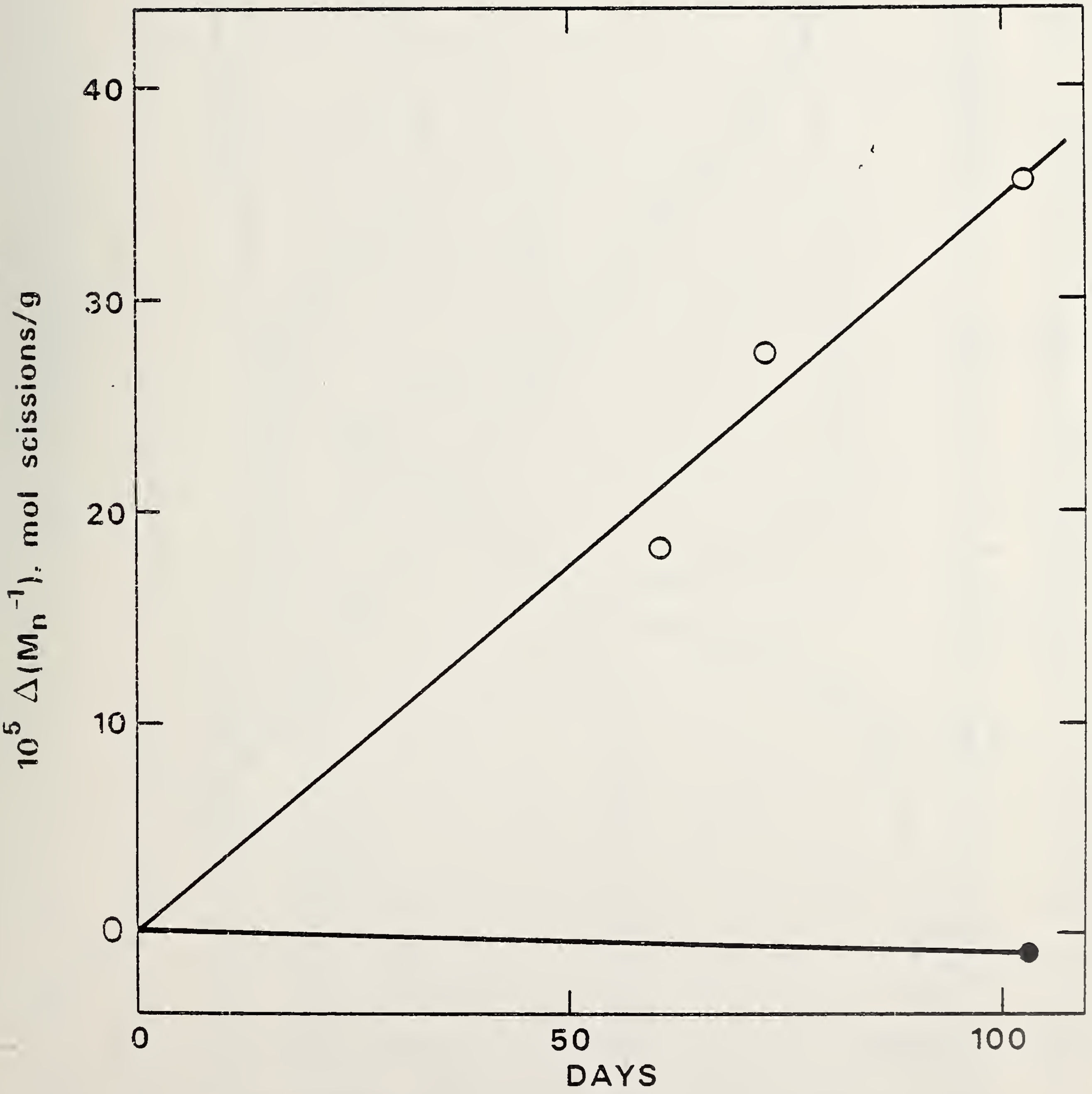

Fig.9. Chain scissions in glassy PET made from NBS 1470. O, 85 °C, 100% RH; ●, 55 °C, 100% RH.

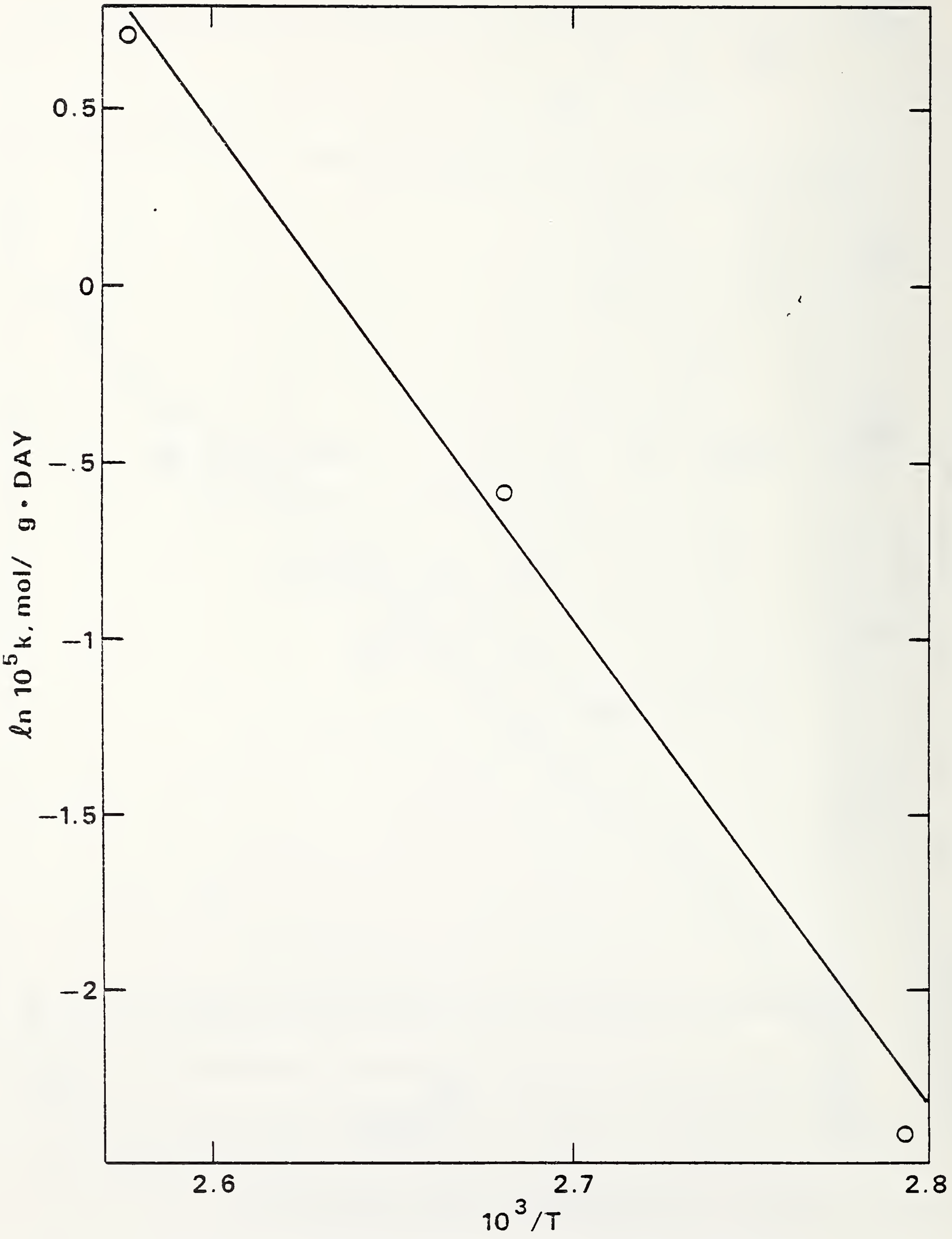

Fig. 10. Arrhenius plot of scission rate at 100% RH.

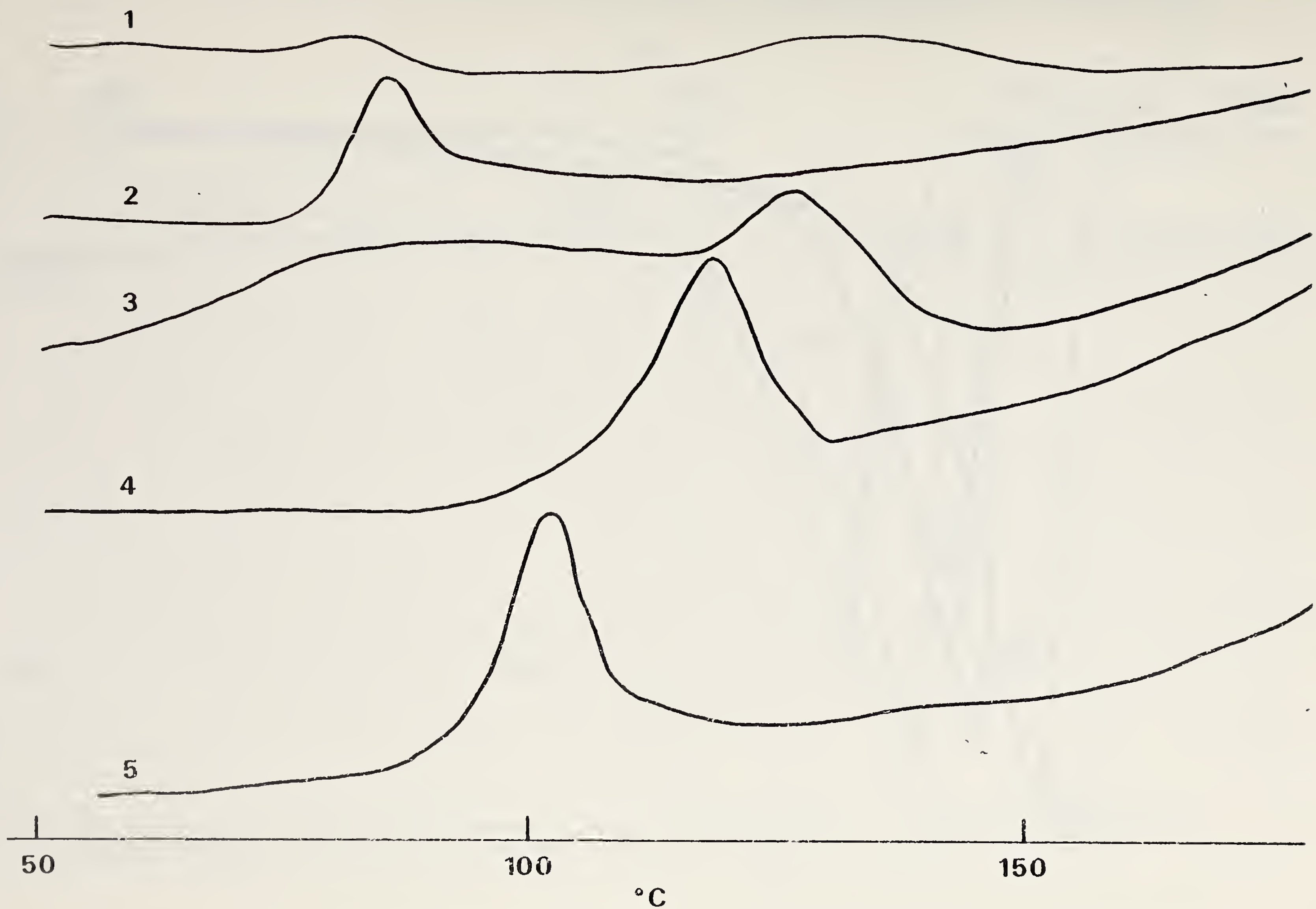

Fig. 11. Differential scanning calorimeter curves. 1, unaged film base; 2, unaged uncoated electrographic film C; 3, film base aged 85 °C, 100% RH, 105 days, 4, film base aged 85 °C, 25% RH, 154 days; 5 , film base aged 55 °C, 100% RH, 163 days.

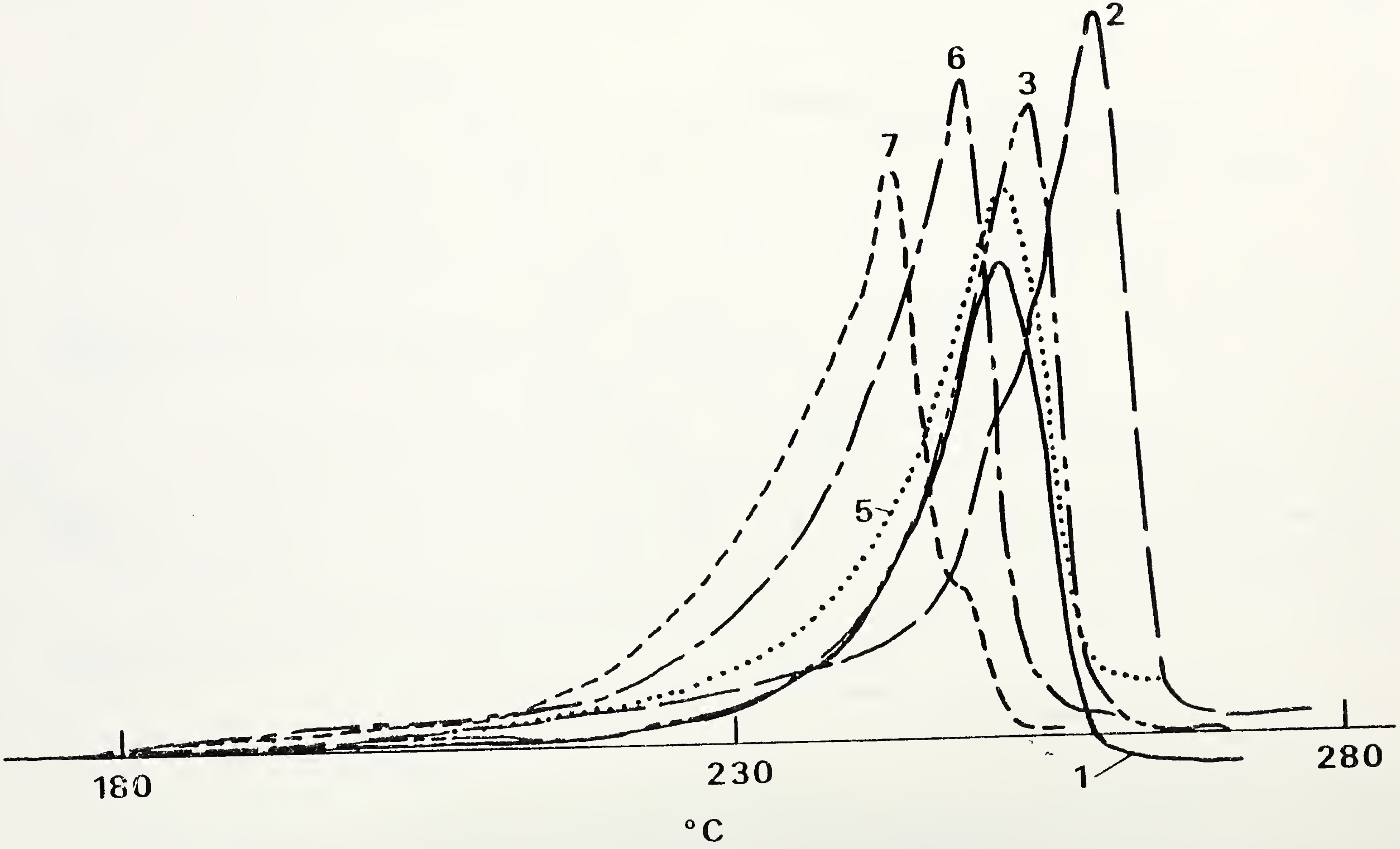

Fig. 12. Differential scanning calorimeter curves. 1), unaged film base; 2, unaged clear electrographic film C; 3, film base aged 85 °C, 100% RH, 105 days; 5, film base aged 55 °C, 100% RH, 163 days; 6, NBS 1470 film, aged 100 °C, 100% RH, 39 days; 7, NBS 1470 film, aged 115 °C, 100% RH, 13 days.

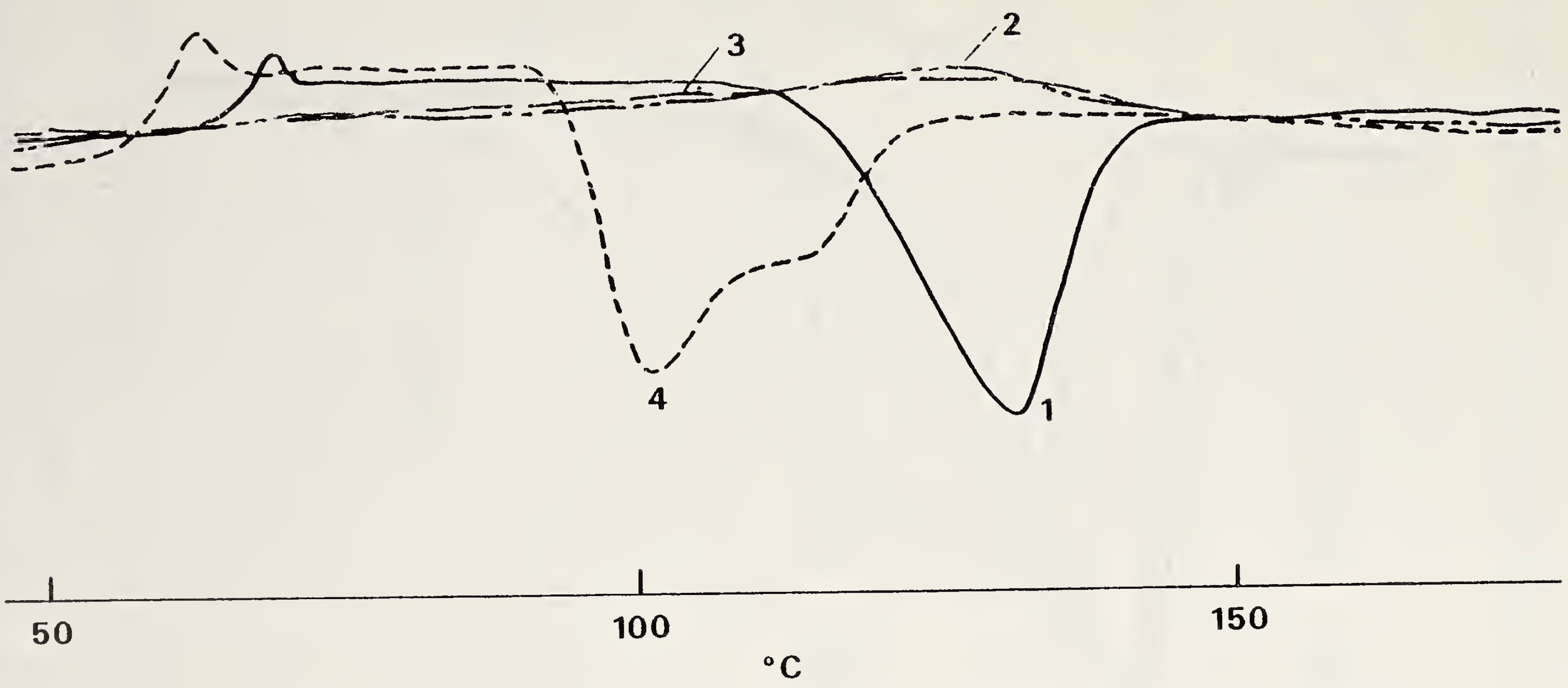

Fig. 13. Differential scanning calorimeter curves for glassy polymer. 1) Unaged; 2) Aged 85 °C, 100% RH, 61 days; 3) Aged 85 °C, 100% RH, 103 days; 4) Aged 55 °C, 100% RH, 103 days.

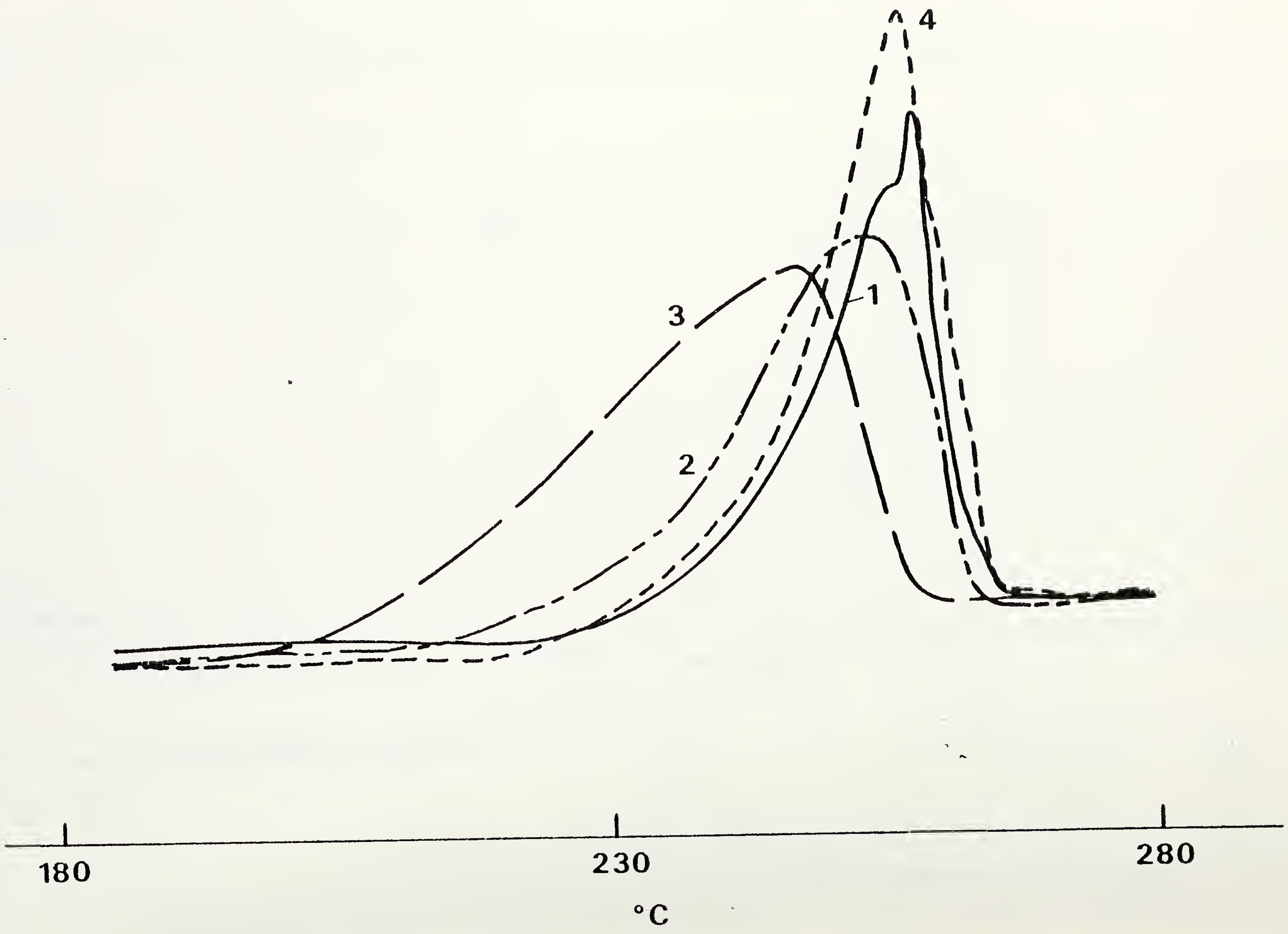

Fig. 14. Differential scanning calorimeter curves for glassy polymer. Same curve designations as in Figure 13.

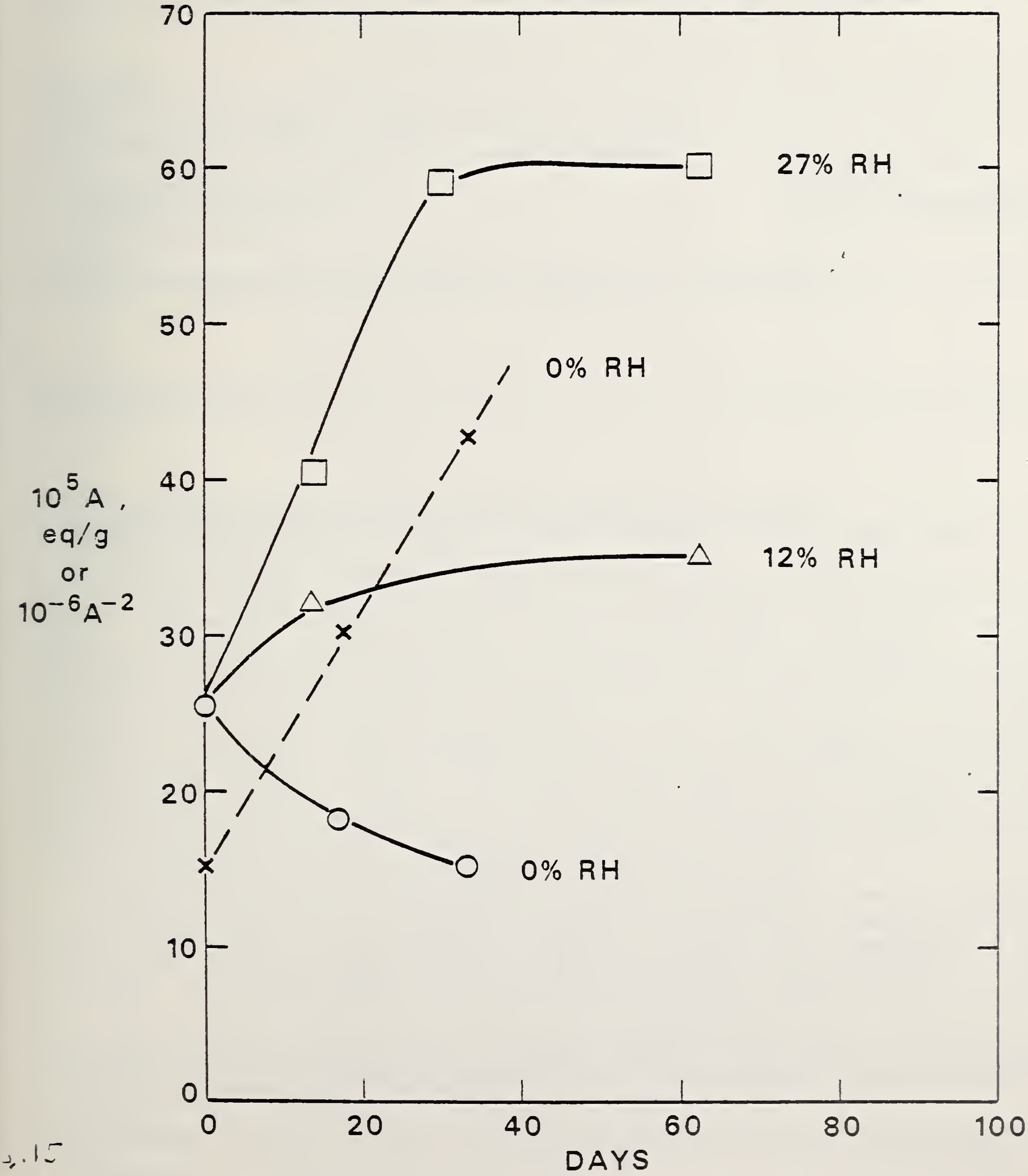

Fig.15

Re-aging of preaged polycaprolactone polyurethane elastomer. Preaging, 85 °C, 100% RH. Re-aging 85 °C, RH as indicated. [A]: □, 27% RH; △, 12% RH; O, 0% RH; X, $[A^{-2}]$ (Dashed line).

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The stability of poly(ethylene terephthalate) is being studied in order to predict its long term behavior as the base of the film and tape used to record archival information. This report contains results of the first year's work. Film base, with and without photographic and other coatings, was aged at several temperatures and humidities. Mechanical and calorimetric properties and molecular weights were measured at intervals. Degradation was relatively rapid at temperatures of 115, 100, and 85°C at 100% relative humidity. The scission rate at 85°C was about 10^{-6} mol scission/g-day and the activation energy was 113 k J/mol. Rates decreased strongly with relative humidity, becoming negligible in dry air and nitrogen. At 55°C and 100% relative humidity degradation was not significant in 163 days. Samples are seriously embrittled by the introduction of about one scission per molecule--about 10^{-4} mol scission /g. Differential scanning calorimetry showed little change in melting behavior of semicrystalline samples aged at 55 and 85°C. Glassy samples crystallized during aging at 85°C but not at 55°C.

Magnetic tapes based on poly(ethylene terephthatate) usually have a polyester polyurethane binder that holds the magnetic particles. The binder is thought to be more sensitive to hydrolysis than the tape base. Results obtained with a thermoplastic polyester polyurethane imply that there may be an equilibrium extent of degradation for any storage condition. It is anticipated that the study will go on for four more years.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

degradation; film base; hydrolysis; photographic film; polyester; poly(ethylene terephthalate); recording media; stability

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