

Relaxational Behavior of CR-39 Polycarbonate Used as Nuclear Track Detector

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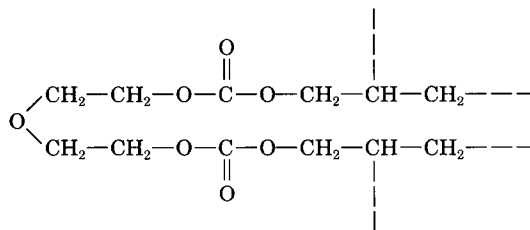
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SYNOPSIS

The relaxational behavior of CR-39 (poly allyl diglycol carbonate) nuclear track detectors was determined over a large temperature range (-100 to 125°C) including the glassy, glass transition, and ionic conduction regions by means of dynamic mechanical and dielectrical measurements, differential scanning calorimetry, linear coefficient of expansion, and especially thermally stimulated current methods owing to their high sensitivity and resolving power. This investigation was carried out as a first step aimed, on the one hand, at finding possible correlations between dosimetric performances, polymer morphology, and intrinsic or extrinsic relaxations and, on the other hand, at determining the origin of the inconsistent background and response properties, which are still a serious obstacle to the use of this material as a personnel dosimeter in spite of its high sensitivity and wide response range. Six distinct relaxation regions have been evidenced, most of which being to some extent dependent on the sample investigated and its thermal history. From higher to lower temperatures, these various relaxations have been ascribed to charge carrier migration over macroscopic distances (ρ), glass transition (α), nonequilibrium precursor motions of the glass transition (α'), and local mode motions of the diethylene-glycol dicarbonate links (β), diethylene glycol segments (γ), and carbonate groups (δ). In addition to these intrinsic relaxations, the as-received samples are also characterized by small-scale residual stresses that relax out irreversibly at temperatures lower than the glass transition temperature T_g . The systematic study of the influence exercised by the position of a specimen in a given sheet, and, for a given sample, by annealing, thermal cycling, and physical aging on relaxation properties shows that, besides spatially inhomogeneous internal stresses, cross-linking density, and cluster morphology, marked structural modifications and nonequilibrium processes can occur by heating the polymer above T_g . These phenomena deserve a great deal of consideration because they could be key points for identifying the sources of the troublesome fluctuations of dosimetric response. Relaxation studies thus appear as useful and sensitive tools for a deeper understanding of the performance of CR-39 polymer as a track recorder.

INTRODUCTION

CR-39 polymer is a highly cross-linked poly(allyl diglycol carbonate) whose structure can be schematized as follows:



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In the structure presented, the broken bonds represent continuation of the cross-linked three-dimensional network.

This polycarbonate is now well established as the most promising nuclear track detector for personnel dosimetry of fast neutrons because of its ability to detect recoil protons from tens of keV to the 10–20 MeV range, its high sensitivity and resolution, and its low cost.^{1–6} For routine measurements and operational applications, however, and in spite of the considerable effort spent to find the optimum polymerization conditions,^{7,8} a number of limitations remain, related to the reproducibility, background, aging, and fading properties of this material.⁹ The variability of background, in particular, which sets the lower limit for a detectable dose, is one of the more serious problems with CR-39.^{9,10} As a matter of fact, the background noise can markedly vary in sheets from different manufacturers, from one batch to another, from one part of a sheet to another part, and even from one side to the other of a given sample; in addition, it also generally increases with the age of the polymer and may be affected by the environmental conditions under which it is stored.^{9,11} Severe variations in the response of different commercial batches, as well as depth and spatial variations in sensitivity of a given batch, have also been evidenced by several investigators.^{9,12} Other sources of trouble are, on the one hand, the more or less rapid fall-off in sensitivity (fading) and increase in background noise during the time delay between irradiation and processing and, on the other hand, the pronounced changes in sensitivity and polymer properties by varying temperature in the range 0–80°C, i.e., the range within which dosimeters are used and processed.^{13–16}

All these troublesome effects and inconsistent properties of CR-39 are still far from being fully understood; since it appears that the performance of this material as a nuclear track detector is markedly influenced by its preparation,⁸ they have been tentatively related to variations and temporal dependencies of the composition and morphology of the polymer, possibly via cross-linking density and structure inhomogeneities or instabilities. For example, one possible explanation of the formation of irregular nodules appearing as background noise after chemical etching could be inhomogeneous cross-linking density, where densely cross-linked portions remain after etching.⁸ As far as the depth and spatial variations in track recording properties are concerned, the origin could possibly be found in inhomogeneous mechanical stresses present in the cast polymer and resulting from large internal temperature fluctuations and gradients (and even thermal runaway¹⁷) taking place during curing from the liquid monomer [diethylene glycol bis(allyl carbon-

ate)] as a consequence of the very exothermic nature of the process ($\Delta H \simeq 145 \text{ kJ mol}^{-1}$)¹⁸ and the relatively low thermal conductivity of the polymer¹⁹ (large variations in thermal conductivity and diffusivity have been measured during polymerization²⁰). Also, fading, which has been shown to be an intrinsic property of the polymer and not of the latent tracks, could be due to the existence of mechanical stresses (perhaps in conjunction with the excess carbon dioxide present in the material after manufacture).¹³ Finally, the thermally induced property changes may contribute to some of the inconsistencies. Heat treatment has been reported to alter the internal morphology of the polymer²¹ and possibly to induce the formation of a layer of enhanced bulk-etch rate, even in samples produced in a curing cycle designed to yield uniform polymerization with depth.¹² While published data on the effects of pre- or postirradiation annealing show considerable and complex variations (in this view, it should be noted that the high-temperature etching must be considered as a form of postirradiation annealing and should thus be taken into account in interpreting the results^{14,22}).

It thus appears that a deeper knowledge of the intrinsic and fundamental material characteristics and, in particular, of the temperature domains corresponding to specific molecular motions (i.e., the relaxational or transition behavior directly connected with molecular mobility) is essential for a better understanding of the performance of CR-39 as a track detector. It is well established that the relaxation temperatures in polymers may be of considerable technical importance in that they often determine what may be called the “working temperature range” of the glassy material.^{23,24} Not only is the glass transition important but also minor relaxations occurring at lower temperatures (local or secondary transitions) since it is often found that the macroscopic properties of a glass are determined by these relaxations (in particular, the mechanical properties are generally superior above the so-called β -transition temperature). It is also of particular interest for constant properties in the temperature range of use that energy-loss phenomena are small and constant over this range.²⁵ The determination of location and properties of all the transitions is also important because they are especially sensitive to the presence of intrinsic inhomogeneities and internal stresses and to the aging phenomenon. In fact, when a polymer is cooled and passes its glass transition temperature T_g , the cooperative motions of large parts of the main polymer chain are frozen in, but in a gradual way determined by the change in

free volume. So, below T_g , the vitrification process continues and the polymer is characterized by a more or less large excess of free volume that progressively decreases as a function of aging time. A glassy polymer is thus never in the equilibrium state and undergoes slow processes that attempt to recover this equilibrium, i.e., the material becomes stiffer and brittle and the diffusivity and transport properties decrease. This will manifest itself in relaxation measurements through a shift of the relaxation time spectrum of molecular motions to longer time scales.^{26,27}

So far, however, and surprisingly enough, no attention has been systematically paid to the problems of molecular mobility in CR-39. Only one research team^{8,28} has reported some dynamic mechanical results, showing that preparation from purified monomer leads to a polymer with improved background noise and sensitivity, having also higher overall modulus and higher transition temperatures compared to commercial materials (and thus probably higher cross-linking density), which seems to establish a possible relation between dosimetric performances and relaxation properties. In indirect connection with these properties, it should also be mentioned, on the one hand, the fact that the fading can be reduced at freezer temperatures (-20°C), which is probably a consequence of decreasing molecular mobility and, on the other hand, some experiments involving study of UV absorbance and track density as a function of annealing temperature, showing an unusual pattern of behavior with the appearance of marked minima and maxima attributed to compositional changes but possibly related to molecular transitions.¹⁴

In the framework of a general investigation aimed at determining the correlations between dosimetric performances, polymer morphology, and molecular transitions, we present in this paper the results of a systematic study of the relaxational behavior of unirradiated CR-39 polymer, carried out by means of dynamic mechanical and dielectrical measurements, differential scanning calorimetry, linear coefficient of expansion, and thermally stimulated current methods.

EXPERIMENTAL

Sample Preparation

All samples used in this study were cut by means of a diamond-saw from the same commercial sheet of Bristol CR-39, approximately $800\ \mu\text{m}$ thick. They

were obtained in the form of squares $2.5 \times 2.5\ \text{cm}^2$ (for electrical measurements) or $0.2 \times 0.2\ \text{cm}^2$ (for DSC measurements) or rectangles $1 \times 4\ \text{cm}^2$ (for mechanical and expansion measurements). Powdered specimens for DSC measurements were also prepared by scraping sheets with a stainless-steel rasp.

The samples for electrical measurements were silver-coated with two measuring electrodes and a guard ring (area of the guarded electrode $2.01\ \text{cm}^2$) in order to prevent surface leakage currents, and they were then short-circuited until as the measurements were started. All samples were kept over phosphorus pentoxide at the freezer temperature (-20°C).

Mechanical Measurements

The dynamic mechanical spectra were determined by the method of forced oscillations in torsion with a Rheometrics mechanical spectrometer model 800 (rectangular sample geometry). Measurements were taken by heating the samples at a heating rate of $1^\circ\text{C}\ \text{min}^{-1}$ in the temperature range between -40 and 110°C using $1\ \text{Hz}$ frequency of torsional vibrations. The results are presented in terms of real shear modulus G' and loss factor $\tan \delta = G''/G'$. During the measurements, the sample ends were maintained under a small, constant normal force and the changes in length of the sample were recorded, allowing the calculation of the evolution of the linear coefficient of expansion.

DSC Measurements

The DSC measurements were carried out at a heating rate of $20^\circ\text{C}\ \text{min}^{-1}$ in the temperature range between -40 and 110°C using a Perkin-Elmer-4 calorimeter. The samples were always placed in identical positions in sealed aluminum pans.

Electrical Measurements

The measurements were performed at a heating rate of $1^\circ\text{C}\ \text{min}^{-1}$ (dielectric measurements) or $6^\circ\text{C}\ \text{min}^{-1}$ (thermally stimulated current measurements) in the temperature range between -100 and 125°C with a three-terminal electrode system under a controlled nitrogen flow ($25\ \text{cm}^3\ \text{min}^{-1}$) in a modified dielectric test cell of a relaxation spectrometer (Unirelax, Tetrahedron) where the heating and cooling rates were controlled by an automatic temperature programming system (Wizard 1501, Tetrahedron). The electrical connections between the

metal-coated samples and the electrodes of the cell were established via silver-pasted thin copper wires so that the samples were maintained freely in the cell and no pressure was exerted on them during the measurement. This procedure was found necessary to obtain reproducible results and to avoid the presence of spurious or exceedingly noisy currents, often accompanying the volumic variations of the samples during heating.

For dynamic dielectrical measurements, the spectrometer was provided with a General Radio bridge (type 1615-A) together with an oscillator-detector (General Radio, type 1232-A), allowing the determination of the complex dielectric constant in the frequency range from 10^{-2} to 10^2 kHz. The results are presented in terms of the imaginary part of the dielectric constant (ϵ'') as a function of temperature.

For thermally stimulated current (TSC) measurements, the spectrometer was provided with a stabilized dc generator (VG Electronics) and a current detector (Keithley electrometer, type 616). The thermal cycles of polarization and depolarization consisted of the following steps:

1. Cooling the samples to a temperature $T_0 = -100^\circ\text{C}$ at a rate $b_c = 10^\circ\text{C min}^{-1}$ in short-circuit conditions.
2. Application of a dc field F_p ranging from 2.5 to $12.5 \times 10^5 \text{ Vm}^{-1}$ and linear heating at a rate $b_h = 6^\circ\text{C min}^{-1}$ up to various maximum polarization temperatures T_p . The current recorded during this step is the thermally stimulated polarization current (TSPC).
3. Cooling in the field to the temperature T_0 at the rate b_c .
4. Disconnecting the dc supply and linear heating of the short-circuited samples at the rate b_h . The current recorded during this step is the thermally stimulated depolarization current (TSDC).

To test the possible presence of a spontaneous polarization in the specimens, some experiments have also been performed by heating as-received samples short-circuited through the electrometer, that is, without any external voltage being previously applied. The current recorded is a particular case of TSDC, which is designated by "TSDC under zero bias voltage" or thermally stimulated spontaneous current (TSSC).

For all types of experiments, physical aging and annealing at various temperatures were always achieved entirely in the measuring cell.

RESULTS AND DISCUSSION

Thermally Stimulated Spontaneous Currents (TSSC) and Differential Scanning Calorimetry (DSC)

Figure 1 shows the temperature dependence of short-circuit currents observed during the course of a spontaneous depolarization carried out from room temperature (RT) to 110°C on a series of samples cut from the same CR-39 as-received sheet (first heating cycle). In each case, significant TSSC currents have been obtained, thus reflecting the initial existence of a nonnegligible internal polarization. Their polarity depends on the configuration of the specimens relative to the electrodes, but, for convenience of comparison, they are all plotted in the same conventional direction. In all but one case, the main feature of these curves is the presence of a single current peak extending in a range from RT to approximately 90°C with a maximum temperature T_M at $70 \pm 5^\circ\text{C}$. Most generally, the maximum current amplitude is of the order of $4 \cdot 10^{-13}$ to $6 \cdot 10^{-13}$ A, with a corresponding polarization of $4 \cdot 10^{-9}$ to $8 \cdot 10^{-9} \text{ C cm}^{-2}$. Some samples show a more particular behavior, however, being characterized either by spectacularly larger current and polarization (Fig. 1, curve $-\cdot-\cdot-$) or by a current reversal occurring near 70°C (Fig. 1, curve $- -$). In principle, such a reversal could result from the existence of two competing processes or, more probably, of an important inhomogeneity of charge distribution in the sample volume.

In DSC thermograms, a well-defined endothermal

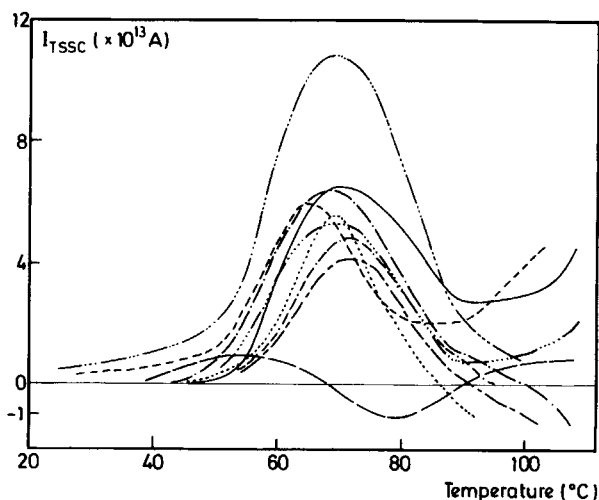


Figure 1 Thermally stimulated spontaneous currents obtained from various as-received CR-39 samples.

peak characterized by significant variations in amplitude and shape from sample to sample also always appears in a similar temperature range during the first heating stage (Fig. 2) and is also present, often with a higher magnitude, in powdered samples (Fig. 3).

Both TSSC peaks and DSC endotherms are very sensitive to preannealing and aging treatments. If performed at temperatures lower than T_M , they give rise to a progressive shifting to higher temperature and decrease in amplitude of the peak, these effects being larger as the annealing temperature and time are higher (Figs. 4 and 5). As far as thermally stimulated experiments are concerned, these results are similar to those observed by applying the partial heating technique to TSDC peaks and can be ascribed to a gradual depolarization of the sample involving a large distribution of relaxation times.^{29,30} For higher annealing temperatures and whatever the annealing time, these peaks are no more visible on a second TSSC or DSC run carried out in the same conditions on the same specimens, even if rapid cooling was used ($10\text{--}50^\circ\text{C min}^{-1}$) between the heating cycles. This proves not only their nonreversible nature, but also shows that the underlying process cannot be related to a nonequilibrium relaxation directly resulting from cooling through T_g (located in the vicinity of 90°C , see following section). In addition, the TSSC peaks and DSC endotherms cannot be correlated to any known intrinsic transition of the polymer (no relaxation peak can be situated in this temperature region, see following section), to a thermal detrapping of charge carriers possibly injected during manipulation of the samples (which could not explain the DSC results), or to a disorientation of chain segments from some previous aligned configuration possibly frozen in

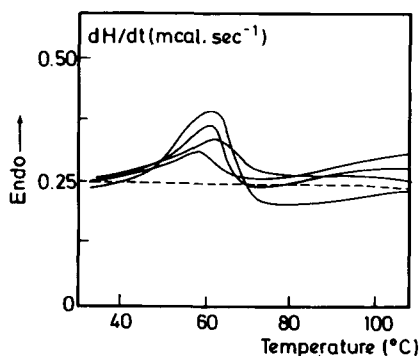


Figure 2 DSC thermograms of various CR-39 samples in sheet form. First heating (—) and second heating (---).

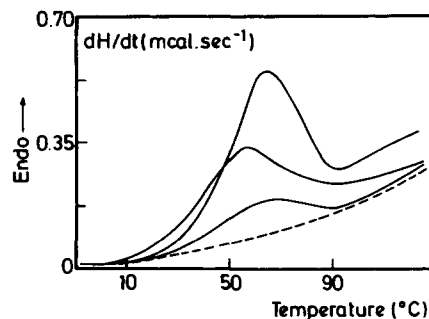


Figure 3 DSC thermograms of various CR-39 powdered samples. First heating (—) and second heating (---).

during the casting process (which could not explain the DSC endotherms observed with powdered specimens).

Of course, some kind of nonequilibrium mechanism must be advocated. The most plausible is the presence, in as-received samples, of plastic instabilities and unrelaxed small-scale stresses that could be direct consequences of the large internal temperature fluctuations and gradients taking place during curing and already postulated for interpreting the depth and spatial variation in track recording properties.^{17,20} If such is the case, the TSSC and DSC methods could become very useful and sensitive tools for evidencing internal stresses too small to be found by birefringence measurements and for quantifying them at various places of a given sheet. The exact molecular mechanism involved, however, remains unclear. The relaxation of residual stresses must obviously be related to some increase in molecular mobility and could result from localized motions of

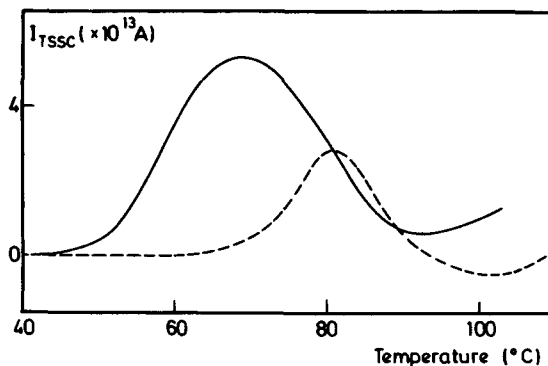


Figure 4 Effect of preannealing treatment on TSSC of CR-39 sheets. The solid line refer to a typical spectrum obtained from as-received samples. The dashed curve was observed after previous annealing at 60°C during 2 h.

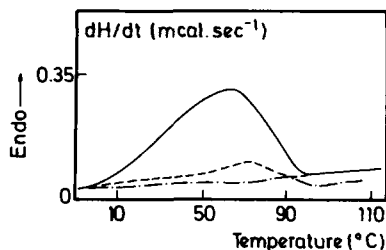


Figure 5 Effect of preannealing treatments on DSC thermograms of CR-39 powdered specimens. As-received sample (—), annealing at 40°C during 1 h (---), and annealing at 75°C during 30 min (— · —).

main-chain segments precursor of the glass transition (i.e., corresponding to the lowest relaxation times of the distribution associated with the glass transition).

Besides the peak or current reversal occurring in the vicinity of 70°C, the TSSC spectra are also characterized in the high-temperature range by a steadily increasing current of polarity similar or opposite to that of the main peak, depending on the considered sample. This is a purely electrical effect and a common feature to most polymers. The perfect explanation of its generation is still obscure. It does not arise from stored charges but could result from internally created charge gradients along the thickness direction of the film, thermal degradation, thermoelectric effects, contact electrification, or small electrochemical potential differences between the two electrodes.^{30,31}

Thermally Stimulated Depolarization and Polarization Currents (TSDC and TSPC)

The TSDC method was used as the first step aimed at determining the intrinsic molecular mobility and transport properties in CR-39 because this technique is now considered as a very sensitive probe of kinetic transitions, molecular relaxation processes, ionic migration, and/or carrier release of traps in polymers. As far as dipolar phenomena are concerned, a TSDC spectrum is somewhat similar to the more conventional dielectric loss curves plotted as a function of temperature (ϵ'' or $\tan \delta$ -T measurements). The TSDC method is, however, inherently more sensitive, and owing to its low equivalent frequency (10^{-2} – 10^{-4} Hz), the resolution is usually much better.^{29,30} On the other hand, it also has some disadvantages associated to the variety and complexity of interfering mechanisms and to the fact that the smallest internal motions can be evidenced only at

very low temperatures. Most of the time, it has, thus, to be cross-checked and complemented by other methods in order to obtain a complete picture of the temperature-dependent relaxations.³⁰

The TSPC method, consisting of registering the charging instead of discharging current as a function of temperature, provides a first useful complement to the TSDC method, allowing, in particular, one to distinguish between dipolar and ionic migration processes, but it is subject to additional difficulties resulting from the possible superposition of internal conduction or injection currents.³⁰

Figure 6 shows typical TSDC and TSPC spectra observed from -80 to 140°C in a CR-39 sample polarized at 125°C in a dc field of strength $F_p = 6.2 \times 10^5$ V m⁻¹ during a time of 10 min (for the sake of comparison, they are both reported in the same conventional direction, although their polarities are obviously opposite). The TSDC spectrum is characterized by at least six distinct peaks that have been labeled ρ , α , α' , β_2 , β_1 , and γ in order of decreasing temperatures. There is no general agreement in peak designation for polymers presenting several transitions, and this is a source of some confusion in the literature. In dielectric and mechanical loss measurements, the peaks are often labeled from higher to lower temperatures with the successive letters of the Greek alphabet α , β , γ , and so on, but there is a marked trend for designating the glass transition by α and the highest intrinsic secondary relaxation by β .²³ So, when other types of peak occur in certain circumstances, we find it more advisable to use a complementary terminology. This is the case here for the ρ peak, appearing only by the TSDC method, and the α' peak, which is probably a non-equilibrium relaxation not typical of the polymeric structure (see below). In addition, the large peak located below 0°C appears unique in some samples (β type) but structured in others (case represented in Fig. 6), so it was found advisable to designate the two components, when present, by β_1 and β_2 .

As shown in Figure 7, nonnegligible variations in shape, position, amplitude, and structuration of the TSDC peaks can be observed in different samples, but the most significant of them occur in the ρ and α' regions.

The ρ TSDC peak usually appears with a distinct maximum (ranging from 105 to 125°C) only for polarization temperatures T_p higher than 125°C (Fig. 8). For T_p higher than 130°C, it gradually shifts toward higher temperatures and markedly increases in amplitude, becoming rapidly predominant with respect to the α peak, which, consequently, is only visible as a small shoulder in its initial part (there-

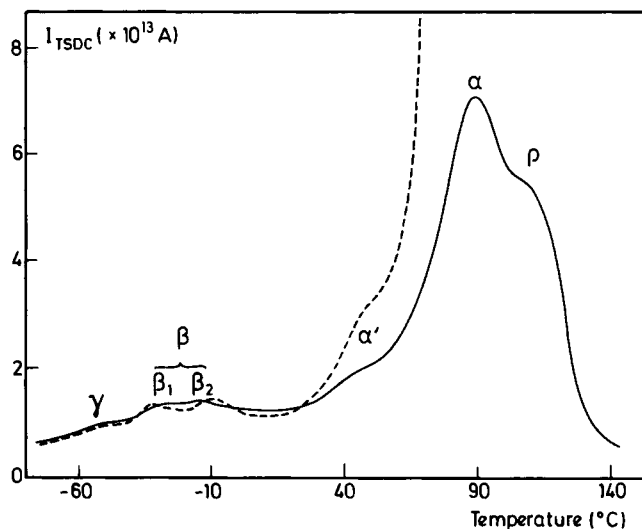


Figure 6 Typical TSDC (—) and TSPC (---) spectra of CR-39. For convenience of comparison, both are reported in the same conventional direction.

fore a 10°C increase of T_p gives rise to an intensity increase of more than one order of magnitude). Qualitatively, these properties are typical of ionic processes, which is confirmed by the fact that the ρ peak has no equivalent in the TSPC spectra (where a steadily increasing conduction current is observed instead) or in dielectric or mechanical measurements (see following sections). There is thus no doubt that it results essentially from a polarization process involving charge carrier migration over macroscopic distances (space charge polarization due to the unavoidable presence of small amounts of ionic impurities in the matrix). In fact, the pres-

ence of such a ρ peak in TSDC curves is a common feature of practically all polymers,^{29,30} but its very high sensitivity to polarization conditions such as found in CR-39 is rather unusual and has no obvious explanation. In particular, its rapidly increasing amplitude as a function of T_p can be ascribed neither to an abrupt increase in molecular mobility in the corresponding temperature range (which cannot be evidenced by mechanical measurements, e.g.) nor to a marked increase in the number of charge carriers involved (due to degradative processes) because there is no corresponding spectacular increase in ohmic conductivity.

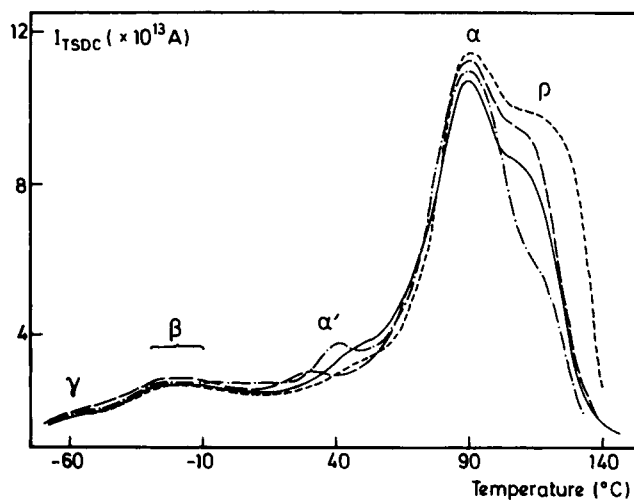


Figure 7 Typical variations observed in the TSDC spectra recorded from various CR-39 samples. $F_p = 12.5 \times 10^5 \text{ V/m}$, $T_p = 125^\circ\text{C}$, $t_p = 10 \text{ min}$.

As seen in Figure 9, which gives an Arrhenius plot in which the logarithm of conductivity is plotted as a function of the reciprocal of temperature, the ρ region is, instead, characterized by a progressive decrease in slope at high temperatures. At this stage, we think that this phenomenon could reflect morphological variations of the matrix, inducing new structural defects that may play a major role in electrical transport properties by supplying new trapping sites and thus increasing the charge storage capacity. This is not to say that degradation is not also implied, but more experimental evidence is needed for complete understanding.

The α TSDC peak can be well resolved by using polarization temperatures a little bit lower than 125°C and polarization times lower than 15 min, for which it is only slightly deformed in its low- and high-temperature parts by the α' and ρ peaks, respectively (Fig. 8). A complete elimination of the ρ small shoulder would be possible by lowering T_p , but, under these conditions, a partial truncation of the α distributed relaxation would occur and the observed maximum would no more correspond to the exact location of the transition.^{29,30} Unless otherwise specified, the polarization conditions used throughout for studying the properties of the α peak were $T_p = 124^\circ\text{C}$ and $t_p = 10$ min.

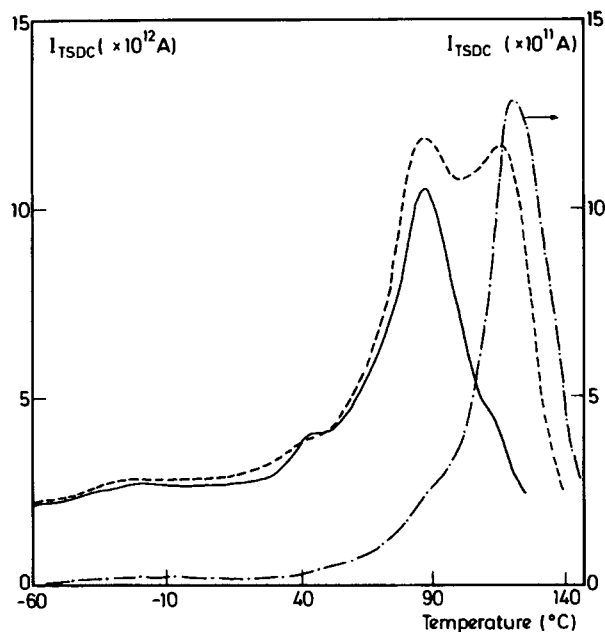


Figure 8 Influence of polarization temperature on the TSDC spectra of CR-39. $F_p = 12.5 \times 10^5$ V/m, $t_p = 10$ min, $T_p = 124^\circ\text{C}$ (—), 126°C (---), and 134°C (- · -).

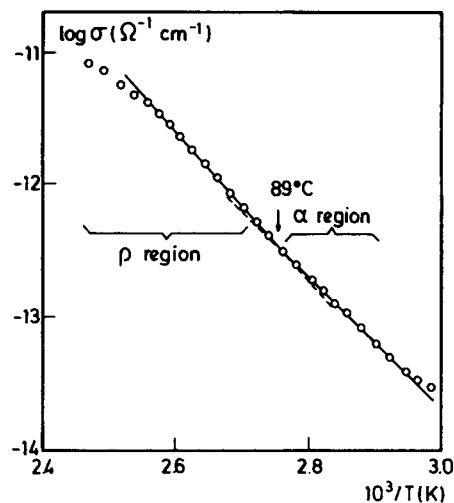


Figure 9 Arrhenius plot of apparent conductivity (as determined from TSPC measurements) of a CR-39 sample in the α and ρ regions.

During a first heating cycle, the α peak can be situated at $90 \pm 1^\circ\text{C}$ for all the samples investigated, i.e., close to the glass transition temperature as specified by manufacturers of similar polymers (85°C).³² Its relation with the glass transition is confirmed by the following facts: (1) its high amplitude and asymmetrical shape are typical of this kind of transition as seen in TSDC measurements³⁰; (2) its position and amplitude are only slightly sensitive to slight variations in the polarization conditions; (3) it corresponds closely to the beginning of the conduction current observed in the TSPC curves (Fig. 6) and thus to a temperature region characterized by a high molecular mobility (necessary for charge carrier transport); (4) it is revealed in TSPC measurements by a break in slope in the Arrhenius plot $\log \sigma = f(1/T)$ (Fig. 9); and, finally, (5) it has its equivalent in dielectrical and mechanical loss measurements (see following section) but not in DSC thermograms, which are not sensitive enough for detecting glass transition in highly cross-linked materials.

There is thus no doubt that the α TSDC peak is associated with micro-Brownian motions of chain segments, but a systematic study of the field dependence and of the influence of thermal history shows that some other mechanisms are probably involved. As seen in Figure 10, the maximum intensity of the α peak increases less than linearly with increasing field strength. This behavior is more typical of an ionic migration process (for which the gradual accumulation of carriers near the electrodes rapidly

decreases the effective directing field) than of an uniform volume dipolar polarization (for which a strict proportionality to the field strength is expected).^{29,30} Moreover, repeated cooling–heating sequences on a given sample induce a gradual decrease in peak intensity and shift of its position toward lower temperatures, so that, during a fourth heating cycle, the maximum temperature can be situated at $81 \pm 1^\circ\text{C}$, i.e., approximately 10°C less than during the first cycle (Fig. 11). This is confirmed in TSPC curves where the break in slope in the conductivity Arrhenius plots undergoes a similar shift (Fig. 12).

It must also be noted from this figure that important changes in the absolute values of conductivity are observed during successive cycles. This complex behavior cannot be ascribed to a progressive degradation of the material (e.g., decrease in cross-linking density) since this phenomenon should unavoidably cause an important increase in ohmic conductivity from cycle to cycle, when a significant decrease from third to fourth cycles is observed instead. More probably, it must be related to a gradual change in the polymer morphology. It has been postulated³³ and confirmed by us³⁴ that even in a fully polymerized CR-39 material some difference in the network structure between the original microgel particles and the polymer in the interstitial space can survive, such inhomogeneities being perhaps one of the reasons for anomalous etching and response fluctuations. In this view, the progressive shift of T_g toward lower temperatures and the de-

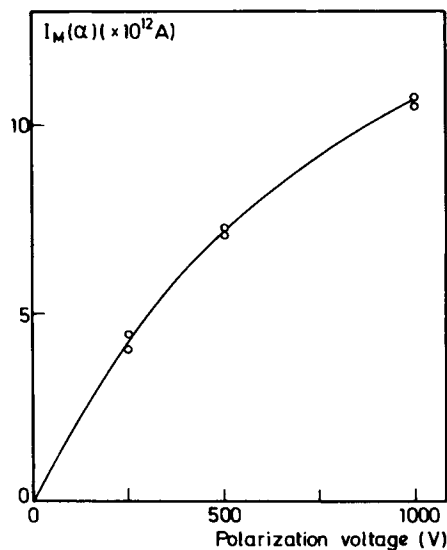


Figure 10 Influence of polarization voltage on the maximum intensity of the α TSDC peak of CR-39.

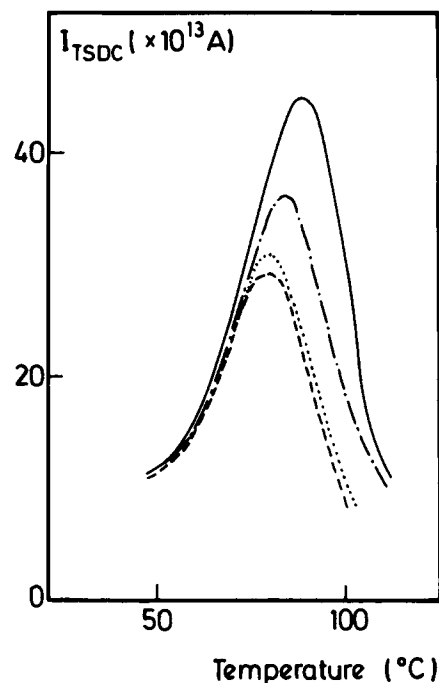


Figure 11 Influence of repeated thermal cycles on the TSDC α regions of CR-39.

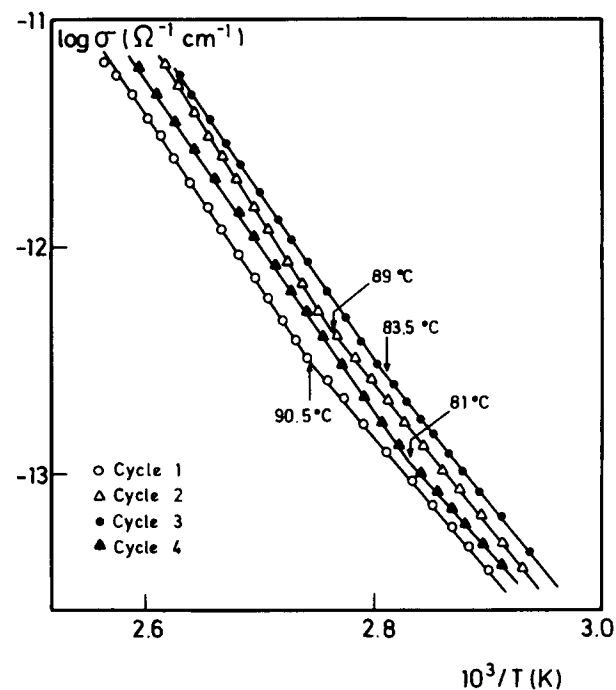


Figure 12 Influence of repeated thermal cycles on the Arrhenius plots of apparent conductivity (as determined from TSPC measurements) of a CR-39 sample in the α and ρ regions. The arrows show the gradual shift of the slope break corresponding to T_g .

crease in amplitude of the α' TSDC peak in successive heating cycles could suggest that the polymer gradually gains a more homogeneous structure (decrease in the interfacial component of the α' peak³⁰). It should also be mentioned that this α' transition could be correlated with the minima observed by Ipe and Ziemer¹⁴ in the 60–80°C range in their curves of net track density and UV-absorbance as a function of annealing temperature.

The α' peak always appears in thermally stimulated current curves in the form of a more or less well-individualized shoulder on the low-temperature side of the α relaxation. Its characteristics of amplitude, shape, and position vary markedly from sample to sample (Figs. 7 and 13), depend on the type (TSDC or TSPC) of measuring technique (Fig. 13), and, for a given specimen, are also highly sensitive to the thermal history but in an apparently unpredictable way. By using repeated heating-cooling sequences, in particular, the α' peak can grow from the first to the second cycle and then gradually decrease (Fig. 14) or, alternatively, it can undergo no significant variation during the first cycles and then decrease or increase depending on the sample investigated. By using various field strengths during the successive cycles, similar types of evolution are observed, sometimes accompanied by shift and structuration of the peak (Fig. 15). All these experimental facts seem to indicate that these apparently erratic variations cannot be attributed only to

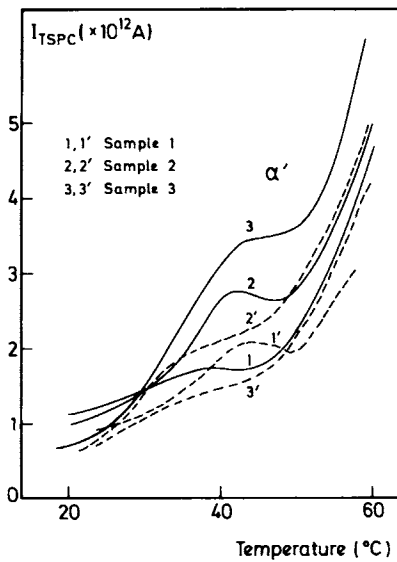


Figure 13 Typical α' peaks observed in the TSDC (---) and TSPC (—) spectra of three different CR-39 samples. $F_p = 6.2 \times 10^5$ V/m, $T_p = 124^\circ\text{C}$, $t_p = 10$ min.

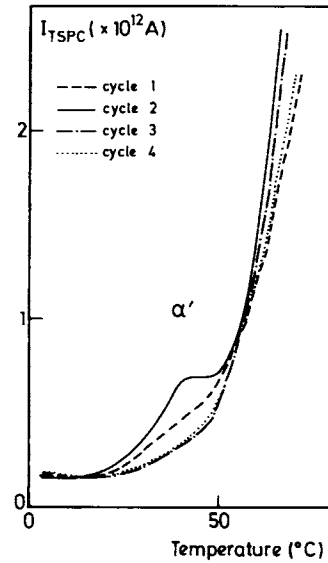


Figure 14 Influence of repeated thermal cycles on the α' TSPC region of a CR-39 sample. $F_p = 2.5 \times 10^6$ V/m, maximum temperature reached after each cycle = 124°C .

the possible structural modifications and that the α' relaxation is, in fact, not characteristic of the equilibrium state of the polymer. It is very probable that it has to be related to the so-called “intermediate” relaxations that have been reported to appear in a number of polymers as nonequilibrium shoulders on the dissipation curves over the temperature range of 40–80°C for low-frequency measurements.^{23,35–37} Generally speaking, this kind of intermediate relaxation could be considered as a more or less proximate

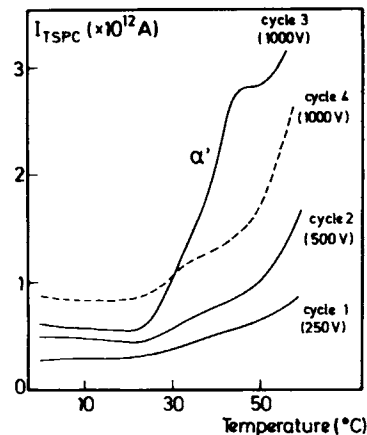


Figure 15 Influence of repeated thermal cycles performed with various applied voltages on the α' TSPC region of a CR-39 sample. The maximum temperature reached after each cycle was 124°C .

nonequilibrium precursor of the glass transition resulting from the motion of several repeat units of the polymer chain, made possible by the increase in free volume and molecular mobility consecutive to the cooling through T_g . However, little is known about its detailed molecular mechanism and it remains unclear why an erratic evolution is observed in a given sample from cycle to cycle, even though the cooling process is well controlled and always identical in all experiments.

The β peak, widely spread between -40 and 20°C , appears usually composed of two overlapping, poorly resolved peaks (β_1 and β_2 in order of increasing temperatures). Occasionally, however, a one-peak structure is found in some samples, whereas, for a given specimen, the complex nature of the β region is always better evidenced in TSPC than in TSDC measurements (Fig. 6). On the other hand, annealing experiments carried out at temperatures lower than 125°C or successive heatings performed up to temperatures not exceeding 125°C do not lead to significant variations in the properties of the TSDC or TSPC β peaks, and it is thus probable that they correspond to an intrinsic, complex local mode relaxation of the polymer. Their temperature range is too high for assigning them to local reorientation motions of the carbonate groups alone, since, in most polymers containing such groups, the corresponding TSDC peak occurs at temperatures lower than -100°C (-130°C in polydiacarbonate,³⁸ e.g.). More probably, they result from motions involving the entire diethylene glycol dicarbonate (DEGDC) links, perhaps with some cooperation of the main polyallyl chains. This could explain the complex nature of the β relaxation since some of these DEGDC entities may exist in a cyclized form or may be terminated at one end by residual allyl groups.^{8,39} In this hypothesis, the variations observed from sample to sample could be a good and sensitive probe of the spatial variations in cross-linking density and homogeneity.

The γ peak invariably appears as a small shoulder on the low-temperature side of the β peak and can be approximately located near -60°C (Fig. 6). It is well reproducible from sample to sample and is insensitive to thermal history. Since its temperature range is still too high for relating it to carbonate groups, it is probable, if the hypothesis about the origin of the β relaxation is correct, that the γ relaxation involves motions of smaller segments of the DEGDC links, for example, crankshaft-type motions of diethylene glycol groups, but more experimental evidence would be needed for a final attribution.

Dielectric Measurements

The temperature dependence of the imaginary part ϵ'' of the dielectric constant at four frequencies ranging from $5 \cdot 10^{-1}$ to 10 kHz is shown in Figure 16. Two well-individualized loss maxima are observed: a small α peak at temperatures higher than 100°C and a large δ peak at temperatures lower than -20°C . For the lower frequencies used, a small shoulder is also obtained in the intermediate temperature range. As expected, the entire spectrum shifts to higher temperatures with increasing frequency but the effect is less and less pronounced from low to high temperatures, so that the resolution gradually decreases. In particular, the intermediate shoulder seems to undergo a gradual suppression and ultimately disappears at the highest frequencies, which obviously results from its progressive merging with the α peak.

In the range investigated, the maximum temperature of the α peak varies only slightly with measuring frequency (from 104 to 114°C in the example shown), which corresponds to a high apparent activation energy of several eV, typical of a glass transition process. Clearly, this dielectric loss peak corresponds to the α TSDC peak, the difference in position resulting logically from the low equivalent frequency of the TSDC method (approximately 10^{-3} Hz for the heating rate used of 6°C min^{-1}). A direct comparison is, however, not possible by extrapolation of the dielectric results at the equivalent frequency of TSDC, because in this temperature range, the log frequency vs. $1/T$ plot exhibits a curvature more or less consistent with an equation of the WLF form.

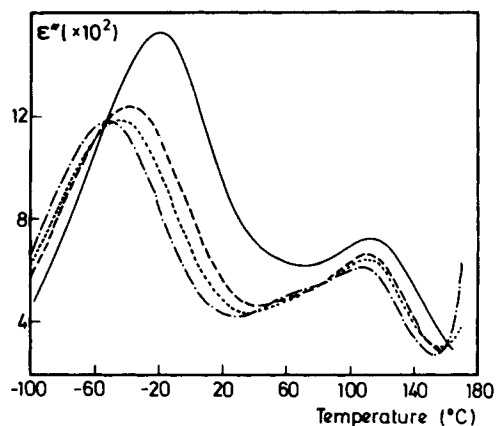


Figure 16 Temperature dependence of dielectric losses of CR-39 at 0.5 kHz ($-\cdot-$), 1 kHz (\dots), 2 kHz ($----$), and 10 kHz ($—$).

The δ peak is characterized by a maximum temperature varying markedly with measuring frequency (from -50°C to -22°C for frequencies ranging from $5 \cdot 10^{-1}$ to 10 kHz). Figure 17 gives the corresponding log frequency vs. $1/T$ plot (the thick part of the line indicates the region of the measurements, whereas the thin part is extrapolation), showing a linear dependence typical of a thermally activated Arrhenius process with an activation energy of about 0.5 eV. The extrapolated curve shows clearly that the δ peak cannot be associated with any of the low-temperature relaxations observed in TSDC measurements since maximum temperatures lower than -100°C would be expected for measuring frequencies of the order of the TSDC equivalent frequency. In fact, the extrapolated value at 1 Hz (-93°C) is compatible with the maximum temperatures of the local mode relaxation processes observed by mechanical and dielectric measurements at a similar frequency in several polycarbonates (-90 to -110°C) such as polydian carbonate, poly(bis-ortho-cresol A carbonate), or poly(bis-

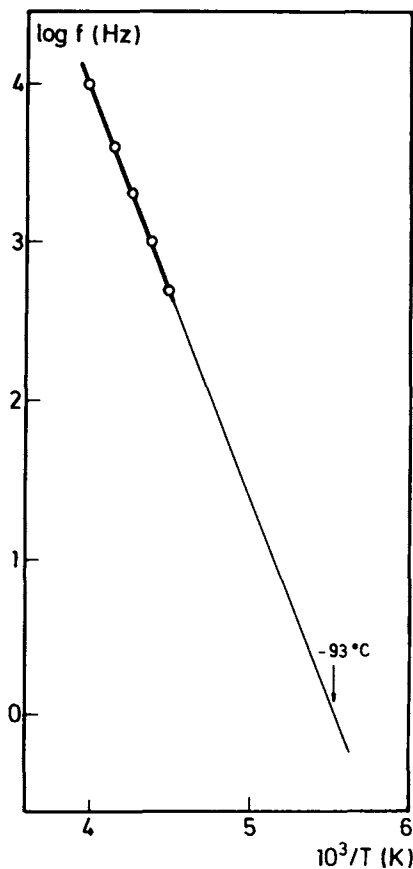


Figure 17 Frequency-temperature Arrhenius plot of the δ dielectric loss maxima of CR-39.

phenol acetophenone carbonate)^{40,41} and the extrapolated value at 10^{-3} Hz (about -135°C) is in good agreement with the maximum temperature of the low-temperature TSDC peak obtained in polydian carbonate (-130°C).³⁸ It thus seems reasonable to postulate the same origin for the δ loss peak of CR-39, i.e., local motions of the carbonate groups.²³

The intermediate relaxation appearing as a small shoulder in the increasing part of the α peak can probably be related, at least in part, to the α' non-equilibrium relaxation because its properties are markedly dependent on the sample investigated and, for a given sample, on the thermal history. However, on account of its temperature range, it is likely that some contribution of the β relaxation evidenced in TSDC measurements is involved, this complex structure resulting from the merging of the two processes at the frequencies used. As far as the small γ relaxation is concerned, it is expected from equivalent frequency estimation to appear near 0°C (1 kHz) and is thus probably masked by the high-temperature part of the δ peak.

Mechanical and Thermal Expansion Measurements

The results of isochronal measurements of dynamic mechanical spectra for various samples are shown in Figure 18. On account of the measuring frequency (1 Hz) and their temperature range, the peaks observed in the loss factor vs. temperature curves can be easily correlated with the TSDC and dielectric relaxations. The broad loss peak at low temperatures (centered at about 10°C) reflects the complex β relaxation process, the important peak with a maximum temperature of about 95°C is the manifestation of the glass transition (α process), and the shoulder approximately located between 50 and 70°C corresponds to the nonequilibrium α' relaxation. As expected, each loss peak is accompanied by a drop in the corresponding real shear modulus (G') curve, but, surprisingly enough, the most intense effect is obtained in the α' region, unambiguously showing the important role played by nonequilibrium effects in the properties of this material. In the T_g range, the variations in shear modulus are faint and the damping peak is broad, which confirms that the polymer is characterized by a high degree of cross-linking.^{24,42,43} Occasionally, however, an unusual behavior was observed in some samples, showing a sudden sharp increase of the shear modulus by approaching T_g (Fig. 19). This is probably an indication that these samples were not fully cured and

that a cross-linking reaction occurred during the tests.²⁴

Figure 20 shows the temperature dependence of the length of various CR-39 samples, expressed in terms of the linear coefficient of expansion α_D defined by dL/LdT , where L is the current length of the specimen. All the curves have the same general shape, being characterized by an apparently well-defined peak in the vicinity of 55°C, i.e., in the α' relaxation range. Taking into account the nonequilibrium nature of this relaxation, the peak could, in fact, be a consequence of the existence, besides the normal reversible thermal expansion effect, of an entropic contraction component leading to a temporary fall of α_D in the corresponding limited temperature region (55–80°C).

Further experimental evidence of the nonequilibrium character of the α' relaxation is given by annealing and aging experiments carried out at temperatures lower than the glass transition temperature. As shown in Figures 21 and 22, as a matter of

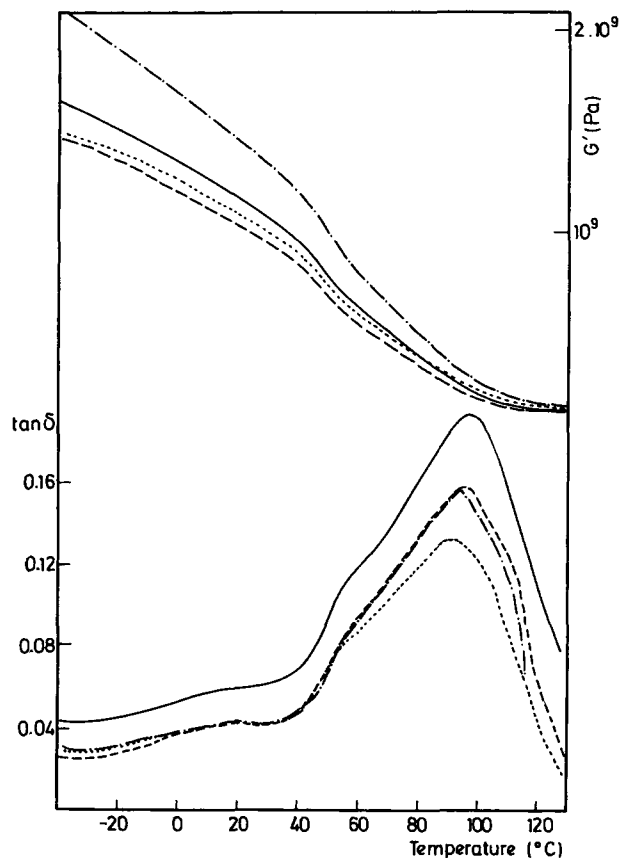


Figure 18 Temperature dependence of real part of shear modulus (G') and loss factor ($\tan \delta$) for various CR-39 samples. The identically symbolized curves in the two types of measurements refer to same samples.

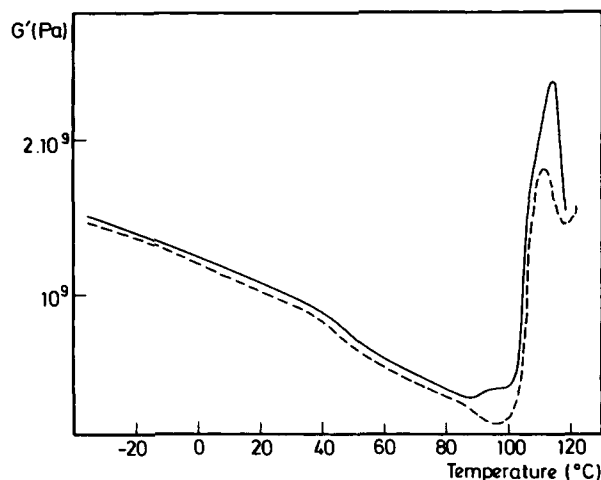


Figure 19 Temperature dependence of real part of shear modulus G' observed for two CR-39 samples probably not fully cured.

fact, annealing a sample at 75°C during 2 h gives rise to pronounced changes in the α' range; the G' and α_D vs. T curves are markedly smoothed and the shoulder in the $\tan \delta$ vs. T curve almost completely disappears.

CONCLUSIONS

As a first step of a study aimed at determining, on the one hand, the origin of background and sensitivity fluctuations of CR-39 nuclear track detectors and, on the other hand, the existence of possible structure-dosimetric response correlations, the relaxational behavior of this material has been investigated over a temperature range sufficient to include the glassy, glass transition, and ionic migration regions and by using various complementary methods, most efforts having been concentrated on the ther-

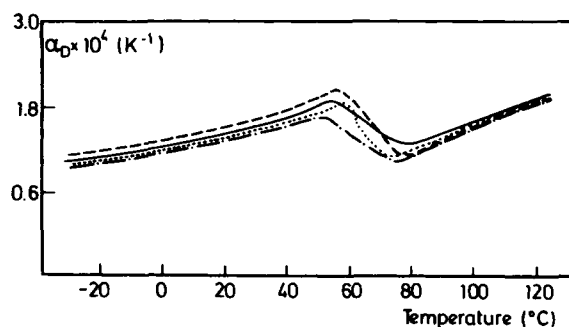


Figure 20 Temperature dependence of expansion coefficient of various CR-39 samples.

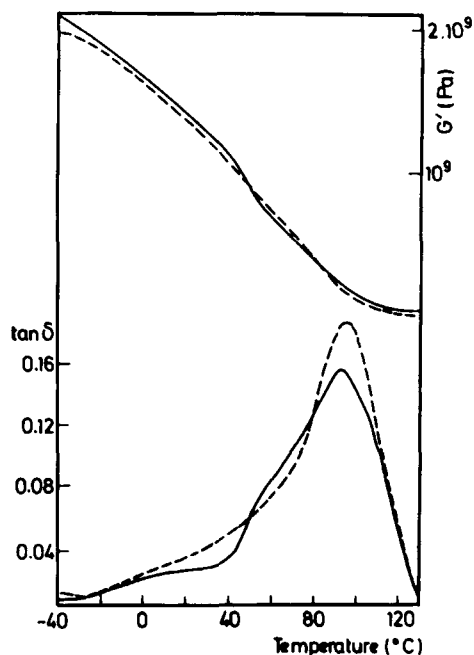


Figure 21 Effect of preannealing treatment on the temperature dependence of real part of shear modulus (G') and loss factor ($\tan \delta$) of CR-39. Curves obtained before (—) and after (---) annealing at 75°C during 2 h.

mally stimulated methods owing to their high sensitivity and high resolving power consecutive to the low equivalent measuring frequency involved ($\approx 10^{-3}$ Hz).

From the thermally stimulated spontaneous currents (TSSC) and DSC experiments, it has been shown that small-scale residual stresses are always present in the as-received samples, probably resulting from internal temperature variations and gradients produced during the curing process. The nonequilibrium stresses, which relax out irreversibly at temperatures below T_g , show considerable differences in samples cut from the same original sheet and could contribute significantly to the depth and spatial variations observed in track recording properties.

In samples from which the stresses were previously eliminated, six distinct relaxation regions, labeled ρ , α , α' , β , γ , and δ from higher to lower temperatures, have been evidenced by means of thermally stimulated currents, dynamic dielectrical, and dynamic mechanical measurements.

The ρ relaxation, typical of the TSDC spectrum, results from a polarization process involving charge carrier migration over macroscopic distances (space charge polarization). The unexpectedly large vari-

ations observed as a function of the polarization conditions lead to the conclusion that, at temperatures higher than 125°C , important morphological changes occur in the matrix, giving rise to new structural defects and, thus, increasing the charge storage capacity.

The α relaxation undoubtedly reflects the glass transition of the polymer, i.e., cooperative motions of large parts of the main chain. Its position obviously depends on the method used via the measuring frequency, but from quasi-static TSDC measurements, T_g can be situated at about 90°C , at least during a first heating cycle. Repeated cooling-heating sequences gradually induce a decrease of this T_g value and a decrease in amplitude of the relaxation, which has been attributed to the progressive disappearance of previous inhomogeneities due to separation of cross-linked polymeric clusters.

The intermediate α' relaxation is a nonequilibrium relaxation, very sensitive to thermal history and physical aging effects in a rather erratic manner. It should be considered as a more or less proximate nonequilibrium precursor of the glass transition involving motion of several repeat units of the polymer chain, made possible by the increase in free volume and molecular mobility consecutive to the cooling through T_g . The exact molecular mechanism, however, is not still fully understood.

The low-temperature β , γ , and δ relaxations are local mode molecular transitions taking place in the glassy region and resulting from more or less limited motions of smaller groups. The β relaxation is a complex one that can be probably ascribed to motions of the diethylene glycol dicarbonate entities that can exist under various forms in the polymeric network (inter- and intrachain links, side chains

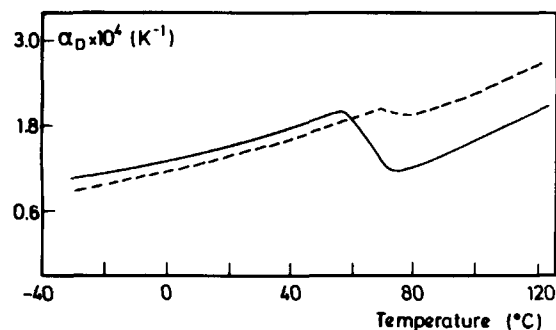


Figure 22 Effect of preannealing treatment on the temperature dependence of expansion coefficient of CR-39. Curves obtained before (—) and after (---) annealing at 75°C during 2 h.

ended by residual allyl groups). The weak γ relaxation, only seen in TSDC measurements, has been tentatively attributed to more local motions of the diethylene glycol segments in the same entities, whereas the large δ relaxation, only evidenced in dynamic dielectric measurements, seems related to motions of the carbonate groups.

Even in stress-free materials, most of these relaxations are to some extent dependent on the sample investigated, probably as a result of spatially inhomogeneous cross-linking density and cluster morphology, i.e., structural variations that could also contribute to some of the inconsistencies encountered in the dosimetric applications. In addition, the relaxational behavior of a given sample is also very sensitive to annealing, thermal cycling, and physical aging processes even at the low-temperature level, showing, on the one hand, that nonequilibrium effects can play an important role in the material properties and, on the other hand, that heating above T_g can induce, besides possible degradation and compositional changes, marked morphological modifications of the matrix, consisting in a first step ($T < 125^\circ\text{C}$) of a gradual homogenization of the network structure, leveling the differences between the original microgel particles and the interstitial polymer, and in a second step ($T > 125^\circ\text{C}$), of a structural reorganization producing new structural defects. These structural variations could explain the complex influence exercised by annealing procedures on the background track recording and fading properties of CR-39 as well as the irregular tracks appearing as background noise after chemical etching (because etching must be considered as an instance of postirradiation annealing). Generally speaking, the relaxational methods thus appear as useful and sensitive tools for evidencing and characterizing the possible sources of dosimetric response fluctuations, i.e., internal stresses, structural defects, and inhomogeneities, plastic instabilities leading to nonequilibrium effects, and thermally induced morphological modifications.

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