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Water-Dependent Relaxation in Polymers. Study by the Thermally Stimulated Current Method

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ABSTRACT: The relaxation behavior of several polar polymers from 77 to 300 K was investigated as a function of moisture content by means of the thermally stimulated current method. The results were generally found in good agreement with published data obtained from dielectric and mechanical loss measurements. In all the polymers investigated, poly(methyl methacrylate), poly(ethyl methacrylate), polydiancarbonate, poly(ethylene terephthalate), polyamide 6–6, and aliphatic polycarbonates, the presence of water markedly affects the shape, amplitude, and maximum temperature of the relaxation peaks; as a general rule, water acts as a plasticizer for the motions involved but the variation in size of the corresponding peaks depends on the nature of the polymer and, in a given polymer, on the type of relaxation considered. New water-dependent relaxations also appear in certain polymers. These processes do not seem directly related to conformational motions but rather to breaking of hydrogen bonds of water–polymer complexes.

It is well established that water sorbed in hydrophilic polymers has a very pronounced effect on their relaxation behavior. Several dielectric and mechanical loss investigations, for example, have shown that the glass transition is always shifted to lower temperatures due to the plasticizing effect of water and that generally the secondary processes are markedly affected in size and position.[1-4] Additionally, a water-dependent new relaxation mechanism has been observed at low temperature in some polymers such as cellulose,[5] acetylated celluloses,[5] poly(methyl methacrylate),[6,7] polyimide,[8] polysulfone A,[4] and polyamides.[2] It seems that even in "dried" samples, residual water molecules could be mainly responsible for certain low-amplitude relaxations generally ascribed to local molecular motions of main chain or side groups. Such is probably the case, for example, for the β relaxation in poly(vinyl acetate), which is usually thought to arise from motions of the $OCOCH_3$ side group but strongly decreases in samples annealed under vacuum at temperatures higher than the glass transition temperature and can even become dielectrically undistinguishable.[9]

So far as we know, such water-dependent peaks have not been reported by the thermally stimulated current method (TSC). This method, based on the discharge current curves obtained during heating of dielectrics previously polarized at a high temperature with a dc field, is now currently used to study the relaxation properties in solid state.[10-12] Due to the very low equivalent frequency of this technique with regard to the dielectric loss method[10,13,14] the relaxation peaks are shifted to lower temperatures, which leads to a higher resolution of the spectrum. The

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TSC technique thus seems well suited to the study of complex or low-amplitude relaxations in polymers and can also be particularly useful to follow any variation in relaxation properties in the low-temperature region as a result of water sorption.

The present investigation is concerned with the influence of water on the TSC curves observed at low temperatures in polydiancarbonate (PDC), poly(ethylene terephthalate) (PET), polyamide 6-6 (N66), poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and a homologous series of aliphatic polycarbonates varying in monomeric unit size from four to twelve methylene groups (PC4, PC5, PC6, PC10, and PC12). When possible, the experimental results will be compared with published results of mechanical or dielectric loss measurements in order to look for new correlations between the two techniques.

Experimental Section

Commercial samples of polydiancarbonate, poly(ethylene terephthalate), polyamide 6-6, and poly(methyl methacrylate) were obtained from General Electric (Lexan), C.I.P.S.O. (Terphane and Ciponyl), and Röhm and Haas (Plexiglas), respectively. Poly(ethyl methacrylate) was prepared by radical polymerization in benzene with α-α′-bis(azoisobutyronitrile) as a catalyst. The aliphatic polycarbonates were obtained by transesterification of aliphatic dihydroxy compounds of the general formula $HO-(CH_2)_nOH$, where $n = 4, 5, 6, 10$, and 12 with equimolar amounts of carbonic acid diesters in the presence of metallic sodium. Their physical characteristics are reported elsewhere.[15]

The commercial samples were used in the form of sheets or films, 1-mm thick for PDC, N66, and PMMA and 0.1-mm thick for PET. The other polymers were compression molded into 1-mm thick plates at temperatures close to the melting points for the aliphatic polycarbonates (50 to 70 °C) and at 105 °C for PEMA.

"Dry" samples were prepared by treatment under vacuum at temperatures higher than the glass-transition temperature for at least a week. Longer periods of heating showed no measurable decrease in weight. After TSC measurements, these reference samples were exposed at 20 °C to atmospheres of 100% relative humidity (r.h.) for various times and the percentage of water absorbed determined by weighing. The higher state of water sorption was obtained after exposure of the samples to water vapor for several weeks and therefore usually corresponds to equilibrium conditions (PDC, 0.35%; PET, 0.50%; PMMA, 1.8%; PEMA, 0.30%). Only for Nylon 6-6 was this condition not fulfilled for technical reasons (for samples containing more than 5% water, a partial fracture and peeling of electrodes occurs). After weighing, the samples were immediately transferred in the measuring TSC cell and quenched to −196 °C after electrical treatment.

The thermally stimulated currents were measured by the classical short-circuit technique[10,16] using either silver painted or vacuum evaporated aluminum electrodes.

Generally, when the complete relaxation spectrum of a polymer sample is wanted, the thermal cycles of polarization and depolarization consist essentially of the following steps: (1) heating to a temperature T_P higher than the glass-transition temperature T_g of the polymer investigated; (2) application of a dc electric field E_P for a time t_p long enough to obtain a saturated polarization of the dipolar processes at T_P; (3) rapid cooling in the field to a low temperature $T_0 << T_P$; and (4) cutting off the external field and linear heating of the short-circuited samples. For comparison of dried and "wet" samples, however, it is necessary to carry out the polarizing process at room temperature, i.e., the temperature of exposure of the samples to humidity, and to reduce the polarizing time to some minutes in order to avoid a significant water desorption. In practice, we have adopted $T_P = 20$ °C, $t_P = 10$ min, $E_P = 10$ to 30 kV/cm, and b(heating rate) = 5 °C/min. We have ascertained that this procedure does not affect the low-temperature part of the usual TSC spectra obtained by polarizing the samples at temperatures higher than T_g.[13]

The reproducibility of the TSC spectra observed with different, identically conditioned, samples was satisfactory; in the range −180 to −20 °C, the differences in the position of the peaks were at worst 2 °C and the relative error in integrated curves was lower than 5%.

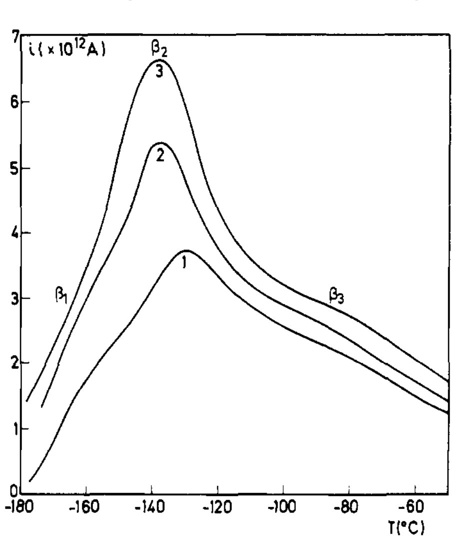

Figure 1. The water dependence of the TSC spectrum of polydiancarbonate in the β range: (1) 0% H_2O; (2) 0.14% H_2O; (3) 0.35% H_2O.

Results

1. Polydiancarbonate. The low-temperature TSC spectrum of dry, amorphous PDC is essentially composed of three overlapping, poorly resolved peaks (labeled β_1, β_2, and β_3 in order of increasing temperatures), centered at about −130 °C (Figure 1, curve 1). These data are in good agreement with previously reported dielectric and mechanical results on this polymer. As a matter of fact, several authors have observed a clearly asymmetrical β loss peak and deduced the existence of two[17,18] or three[19] different processes. We have shown elsewhere that the analysis of the TSC peak by special techniques such as partial and fractional polarization allows one to demonstrate unambiguously the existence of a three-peak structure.[13]

It seems likely that this β relaxation results from local reorientation motions of the carbonate groups, probably coupled with motions of the phenylene units, but the detailed mechanism is still obscure and remains the subject of numerous discussions in the literature. Chung and Sauer, for example, have contested the pure molecular origin of the high-temperature component (β_3) and ascribed it to the presence of water in the samples.[20]

Curves 2 and 3 in Figure 1 illustrate the effect of water content on the TSC curves in the β-relaxation range. The entire spectrum increases in intensity and in breadth but apparently only the main β_2 peak is really affected. The variation in amplitude of the high-temperature shoulder, in particular, principally appears as a simple consequence of overlapping and it thus seems unlikely that water is the main factor involved in the β_3 relaxation as suggested by Chung and Sauer. A general increase in β-relaxation losses by sorbed water has also been observed by Allen et al. from dielectric and mechanical studies.[4]

The TSC peak position in the wet samples seems independent of the water content in the range investigated, yet it is different from the position in the dry state (Figure 1). This fact is also in agreement with the results of Allen et al. but the shift observed by these authors occurs in the opposite direction; in TSC experiments, water "plasticizes" the β relaxation while it acts as an "antiplasticizer" in dynamic loss measurements. The reason for this discordance is not clear but a decrease in maximum temperature seems more likely in view of published results on

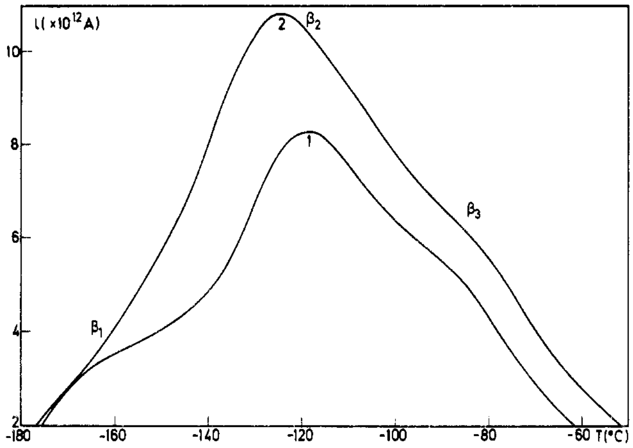

Figure 2. The water dependence of the TSC spectrum of poly(ethylene terephthalate) in the β range: (1) 0% H_2O; (2) 0.5% H_2O.

several other polymers.[1,2,5,21]

2. **Poly(ethylene terephthalate).** The low-temperature TSC spectrum of dry, amorphous PET is represented in Figure 2 (curve 1). It is essentially similar to the spectrum of PDC and also results from the overlapping of three separate relaxation processes (β_1, β_2, and β_3). The same conclusion has been drawn from mechanical and dielectric loss data, in particular by Illers and Breuer[22] and Armeniades and Baer,[23] and confirmed by dilatometric[24] and infrared absorption measurements.[25]

The molecular mechanisms generally postulated are local conformational motions involving the COO groups, possibly associated with the gauche or trans conformations of the polymer chain. As for PDC, however, they are still subject to controversy.[26]

When water is sorbed in the samples, the behavior of this complex β relaxation is strictly identical to that observed in PDC (Figure 2, curve 2), i.e., slight shifting to lower temperatures and general increase in amplitude, mainly due to the variation in central peak intensity (β_2).

A significant increase in the height of the dielectric loss maximum and the amount of the permittivity increment associated with the β process has also been observed in wet samples by Reddish.[27] No variation of peak position was noted but a direct comparison with the TSC results is difficult since Reddish's data were obtained isothermally (O °C) over a large frequency range.

3. **Polyamide 6–6.** The low-temperature TSC spectrum of dry samples of Nylon 6–6 show two distinct maxima at ca. -80 and -140 °C, labeled β and γ, respectively (Figure 3). On account of the low equivalent frequency of the TSC method,[10,13] they correspond well to the β and γ relaxations observed at about -40 and -110 °C by dynamic loss measurements (100 Hz).[26]

It is generally considered that these two processes originate from molecular motions in amorphous domains but the particular mechanisms involved are still much debated. The γ relaxation could result from local motions involving methylene sequences[28] or amid groups[29] or both[2] while the β relaxation has been ascribed to terminal groups,[30] water–polymer complexes,[31] or polar groups together with water–polymer complex units.[2]

As shown by curve 2 in Figure 3, the effect of sorbed water on the TSC spectrum is complex. The γ and β peaks are characterized by a decrease in amplitude together with a depression of their maximum temperatures while a new peak, larger than the two others, occurs at about -25 °C.

The effect of water on the mechanical and dielectric relaxation behavior of polyamides has been extensively studied and the complex nature of the phenomenon often reported.[2,26] The decrease in γ-peak intensity and its shifting to lower temperatures are in agreement with dynamic loss results.[2] For the β relaxation, a decrease in maximum temperature is also observed by loss methods; on the other hand, the magnitude of the loss peak reaches a maximum for a moisture content of about 1% but remains always larger than in dry samples.[2] These last data are consistent with the TSC results only if our reference sample still contained small amounts of water. Systematic studies are needed to obtain more detailed information on this problem.

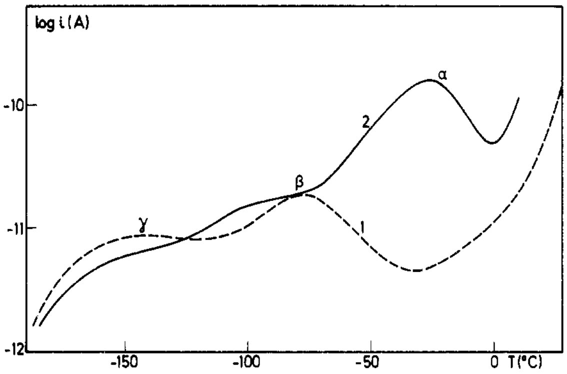

Figure 3. The water dependence of the TSC spectrum of Nylon 6–6 in the low-temperature range: (1) 0% H_2O; (2) 5% H_2O.

The appearance of a large peak at a temperature lower than 0 °C has also been reported from mechanical and dielectric loss measurements for moisture content higher than 2%.[2] In fact, this is not a new relaxation but the α process (glass transition) appearing normally at about 50 °C (1 Hz) and shifted to lower temperatures as a consequence of the important plasticizing effect of water in this polymer.[2]

4. **Poly(methyl methacrylate) and Poly(ethyl methacrylate).** Figure 4 (curves 1 and 1′) shows the low-temperature TSC spectra of dry samples of PMMA and PEMA. They are characterized by a broad β peak at about -35 and -50 °C, respectively, and a weak shoulder, labeled β', centered at about -115 and -125 °C, respectively.

The comparison of the β peaks with the dielectric and mechanical β relaxations has been investigated by several authors and their equivalence seems now well established, at least in PMMA.[10,13,32] The molecular mechanism involved is generally thought to arise from the hindered rotation of the ester side group around the C–C bond.

As seen in PDC and PET and in accordance with dielectric results on PMMA,[6] the β relaxation is markedly enhanced by sorbed water and slightly shifted to lower temperature (Figure 4, curves 2, 3, and 2′).

A most significant feature in these polymers is the way in which the β' peak is affected by changes in the water content (Figure 4). Appearing only as a very weak shoulder in water-free samples, this peak is well resolved in the wet polymers. From dynamic loss measurements in PMMA, such an additional relaxation region due to water has also been observed by some authors near -100 °C (1 Hz)[6,7] and the maximum temperature of the corresponding loss peak is also a decreasing function of the water content. On account of the difference in frequency measurements, it correlates well with the β' TSC peak.

As shown in Figure 5, introducing to the polymer another low molecular weight diluent, i.e., benzene, also significantly affects the relaxation behavior in this β' range. A higher concentration is however necessary to observe a

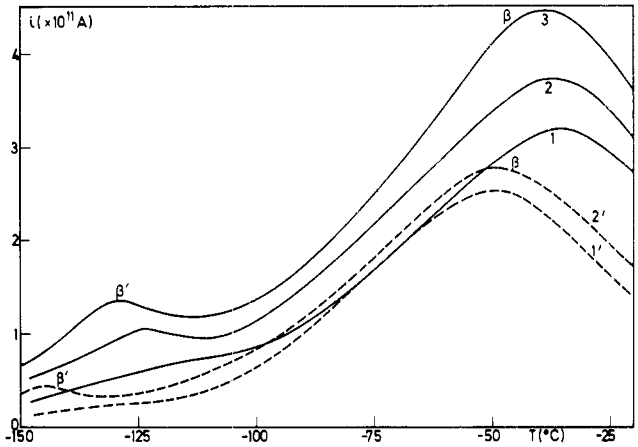

Figure 4. The water dependence of the TSC spectra of PMMA (—) and PEMA (- - -) in the low-temperature range: (1) 0% H_2O; (2) 0.5% H_2O; (3) 1.8% H_2O; (1′) 0% H_2O; (2′) 0.3% H_2O.

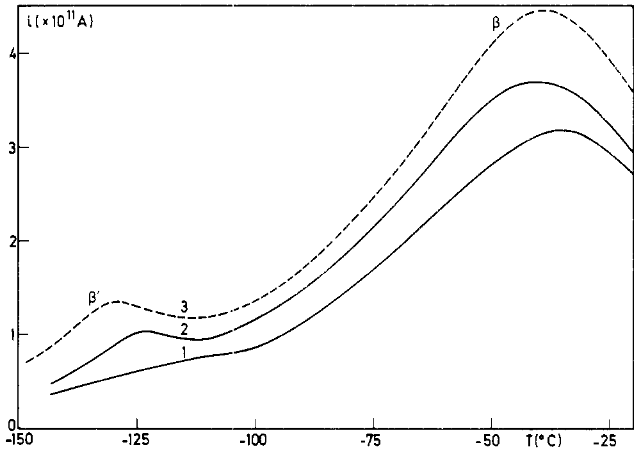

Figure 5. Comparison of water (curve 3) and benzene (curve 2) dependence of the TSC spectrum of PMMA in the low-temperature range: (1) 0% H_2O and C_6H_6; (2) 3.75% C_6H_6; (3) 1.8% H_2O.

TSC peak with a magnitude similar to the wet polymer, probably due to the nonpolar character of the benzene molecule. Thus, contrary to the generally accepted hypothesis, the β′ loss peak does not seem really specific to water.

5. Aliphatic Polycarbonates. The TSC spectra of some aliphatic polycarbonates are represented in Figures 6 to 9. For dry samples, they are essentially composed of two well-separated peaks appearing at about −120 °C (β peak) and −30 °C (α peak). They have been analyzed in a previous paper and respectively attributed to a local crankshaft motion involving the carbonate groups and to the conformational motions of chain segments related to the glass transition.[15] To our knowledge, no dielectric or mechanical result has been reported about the relaxation properties of these polymers.

As shown in Figures 6–9, the spectra are strongly affected by water sorbed in the samples. The α peaks markedly increase in amplitude while a new peak, labeled β′, appears on the high-temperature side of the β peak and becomes prominent at high moisture levels. Simultaneously, the β peak decreases in intensity. This last phenomenon is particularly apparent in PC4 and PC12 but, due to the important overlapping of the β and β′ peaks, the exact evolution cannot be precisely followed; in PC5, for example, the β peak is rapidly masked by the increasing β′ peak.

On the other hand, increasing water content shifts the three peaks slightly to lower temperatures.

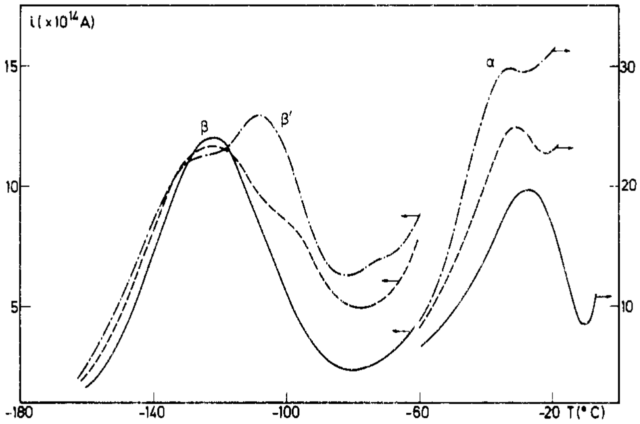

Figure 6. The water dependence of the TSC spectrum of PC4 in the low-temperature range: (—) 0% H_2O (sample dried under vacuum and over P_2O_5 for a week); (- - -) sample stored in room atmosphere for a week (~55% rh); (-·-) sample stored at 100% rh for a week.

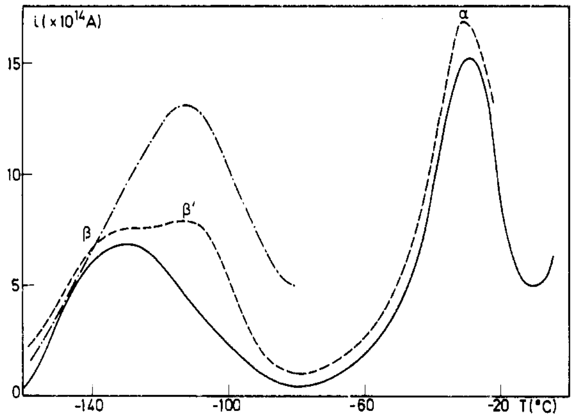

Figure 7. The water dependence of the TSC spectrum of PC5 in the low-temperature range: (—) 0% H_2O (sample dried under vacuum and over P_2O_5 for a week); (- - -) sample stored in room atmosphere for a week (~55% rh); (-·-) sample stored at 100% rh for a week.

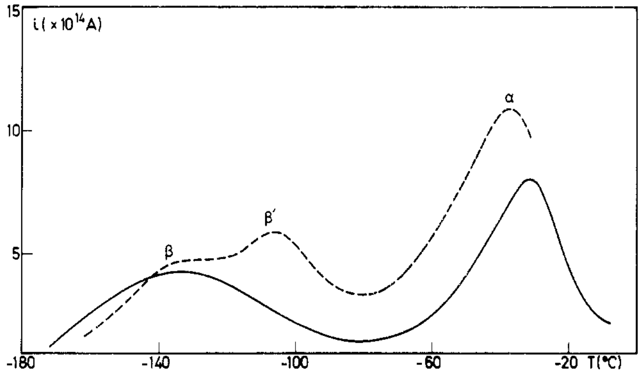

Figure 8. The water dependence of the TSC spectrum of PC10 in the low-temperature range: (—) 0% H_2O (sample dried under vacuum and over P_2O_5 for a week); (- - -) sample stored at 100% rh for a week.

It is also important to note that the β′ peak occurs at about the same temperature (−110 to −120 °C) in all the polycarbonates.

Discussion

The TSC data relating to the influence of water on the relaxation behavior of the various polymers investigated are in good agreement with the published results of dielectric and mechanical loss studies. The variations in amplitude and the shifting of the preexisting peaks are

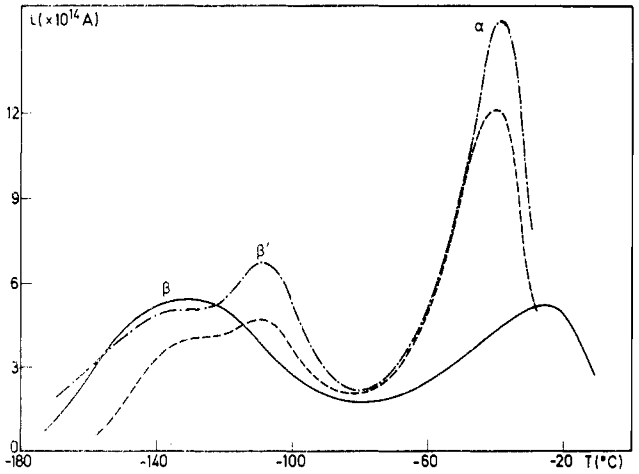

Figure 9. The water dependence of the TSC spectrum of PC12 in the low-temperature range: (—) 0% H_2O (sample dried under vacuum and over P_2O_5 for a week); (- - -) sample stored in room atmosphere for a week (~55% rh); (-·-) sample stored at 100% rh for a week.

generally similar and the specific water-dependent loss peaks appearing in certain wet polymers are also observed by the TSC technique. In addition, this technique is usually characterized by a higher sensitivity and a better resolution, allowing us to follow accurately the separate evolution of the components of the complex peaks as appearing in PDC or PET.

We may summarize as follows the main general features found from the TSC study: (1) in all the polymers investigated, the low-temperature relaxation properties are significantly affected by the presence of water; (2) as a general rule, increasing water content results in a shifting of the peaks to lower temperatures; (3) the variation in size of the peaks depends on the nature of the polymer and, in a given polymer, on the type of relaxation considered; the main β-relaxation increases in intensity with the water content in PDC, PET, PMMA, and PEMA and decreases in aliphatic PC and N66; the γ relaxation is also reduced in this last polymer while the β_3 process appearing in PDC and PET seems little affected; (4) new water-dependent β' relaxations appear at least in PMMA, PEMA, and aliphatic PC; in PMMA, however, swelling with benzene is also capable of inducing this process which is thus not specifically indicative of a water–polymer complex.

Due to the extensive overlapping of the different relaxation processes, we cannot exclude the possibility that such β' peaks also occur in the other polymers. With this in view, we are presently undertaking a detailed analysis of the spectra by means of partial heatings or fractional polarization techniques.[14]

In any way, it thus appears that the effect of water on the relaxational behavior of polymers is quite complex and presumably results from several different competitive mechanisms involving various physical states of the water sorbed. From dielectric, mechanical, and NMR data on a number of water–polymer systems, it seems reasonable to distinguish between at least two forms of sorbed water: the first is attached firmly to specific polar sites and produces little perturbation of the matrix while the second results from clustering or association of the water molecules and may involve some variation in free volume. Obviously, the relative influence of these two types of water on macromolecular motions depends on the amount of water sorbed and on the measuring temperature. When an increase in the β-relaxation amplitude is observed, there is little doubt that the polar water molecules are directly participating in the molecular process, probably by forming hydrogen bonds with the polar macromolecular units, and the plasticizing effect may then correspond to a decrease in the activation energy due to the weakening of intermolecular attractions. The opposite phenomenon, i.e., the decrease in relaxation amplitude by sorbed water, is more difficult to explain; as a matter of fact, since a decrease in peak temperature simultaneously occurs it cannot be ascribed only to the presence of immobile water hindering polymer chain mobility. Additional studies are needed to obtain more detailed information regarding this problem.

The fact that residual water molecules could be responsible for certain low-amplitude relaxations observed in dry samples is debatable. This is probably the case for the β' processes in PMMA, which is highly water sensitive, but not for the β_3 processes in PDC and PET, which are practically unaffected by the moisture content.

However, the possibility of obtaining new TSC relaxations in the presence of water is unambiguously proved in the case of aliphatic polycarbonates. As shown in a previous paper,[15] the β relaxation occurring in dry samples cannot be resolved into discrete components and the β' relaxation is thus specific to wet samples. As postulated in particular by Kapur et al.[33] from dynamic loss measurements and in agreement with the fact that they always appear in about the same temperature range, such processes could simply involve the breaking of hydrogen bonds in water–polymer complexes rather than new conformational motions. They could then be related to the dielectric transition occurring in ice at ca. −70 °C (1 Hz) and believed to arise from the diffusion of intersticial water involving the breaking of hydrogen bonds.

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Nuclear Spin Diffusion between Polyurethane Microphases

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ABSTRACT: The rate at which nuclear spin energy diffuses from one spin population to another in a polyurethane was measured by a technique based on the Goldman–Shen experiment. Determination of the spin diffusion constant permitted the diffusion path length to be calculated. The agreement between these results and the interdomain spacing determined by small-angle X-ray diffraction gives strong support to the hypothesis that the two components of a polyurethane's free induction decay correspond to the material's two microphases. Variation of the soft-phase spin–spin relaxation time with pulse spacing showed that the mobility of soft-phase segments depends on their proximity to the interface region.

I. Introduction

Recent studies[1,2] have shown that several polyurethanes exhibit a two-component NMR free-induction decay (FID). In the past such behavior by a polymer was associated with the presence of both crystalline and amorphous phases.[3,4] These systems, however, show no evidence of a crystalline phase by wide-angle X-ray diffraction. The two components were interpreted to correspond to the hard and soft domains of a system which had undergone microphase separation. The rigid segments comprising the hard domains give rise to a fast decay while the flexible segments comprising the soft domains give rise to a slow exponential decay. Before confidence can be placed in this interpretation, other explanations for a two-component decay must be carefully considered.

The most probable alternative explanation for a two-component decay is that proposed by Resing in his studies of molecules adsorbed on surfaces.[5] He discusses how a very broad distribution of correlation times can give rise to a two-component decay without the system existing in two distinct phases. Another explanation is that cross correlation effects in a segment moving anisotropically can cause a nonexponential decay.[6,7] To eliminate these two alternatives we have performed a Goldman–Shen[8] experiment first suggested for this purpose by Resing.

If two distinct spin populations have different spin temperatures, they will tend to approach a common spin temperature by the mechanism of spin diffusion. The Goldman–Shen experiment is a technique to put the separate spin systems at different temperatures and then sample them as a function of time so that their approach to equilibrium can be followed. By measuring the diffusion time and calculating the diffusion constant from relaxation data, the diffusion path length can be determined. Of course, for a system with a broad distribution of correlation times or one exhibiting cross-correlation effects, there is only one spin population so the equilibration time is much faster. Experiments reported in this study show that the spin populations having different relaxation rates are separated in space by a distance compatible with previous measurements of interdomain spacing made by the small-angle X-ray scattering technique (SAXS).

The effects of spin diffusion have been seen before in polymeric systems by measurements of the spin–lattice relaxation time in the rotating frame[9] and in biological and polymeric systems by spin–lattice relaxation time (T_1) measurements.[10-13] The time scale for diffusion in each of these experiments was fixed by the corresponding relaxation parameter. The advantage of the Goldman–Shen experiment is that the time for spin diffusion can be arbitrarily varied, and if this time is much less than T_1, the analysis is straightforward.

II. Experimental Section

a. Instrumentation and Signal Analysis. The FID measurements were made on a Bruker SXP broad-band spectrometer operating at 90 MHz in the phase-sensitive detection mode. The external field was that imposed by a Varian V-3800-1 high-resolution magnet equipped with a flux stabilizer. The FID signals were captured by a Biomation 610 transient recorder and stored by a Digital Equipment Corp. PDP-11/10 computer. Several decays, each containing 256 data points, were averaged and then decomposed by means of nonlinear least-squares regression into a fast Gaussian or exponential component and a slow exponential component associated with the rigid and mobile phases, respectively. Care was taken to minimize the effects of field inhomogeneities and field drift. All measurements were performed at 25 °C.

b. Materials. EN-4, EN-7, and EN-8 are cross-linked polyurethanes manufactured by Conap Co. Each has polybutadiene soft segments, 2,4-toluene diisocyanate based hard segments with 2-ethyl-1,3-hexanediol, and bis(2-hydroxypropyl)aniline curing agents. EN-4 uses a mercury oleate catalyst while EN-7 and EN-8 use varying amounts of ferric acetylacetonate as a catalyst. The formulation of these compounds has been discussed in the literature.[14] The other type of polyurethane investigated is designated Adiprene L-100/MOCA. It is made from a 2,4-toluene diisocyanate end-capped ether (polyoxy-1,4-butylene) with methylenebis(*o*-chloroaniline) (MOCA) as a curing agent. Samples of Adiprene L-100/MOCA cured at 298 and 347 K were investigated.

The EN series gives the cleanest decomposition into fast and slow components of any polyurethane we have investigated while Adiprene L-100/MOCA gives a FID which, as measured by the square root of the mean squared deviation, is the most difficult to fit accurately. It is interesting to note that the SAXS maximum is more distinct for the EN series than for the Adiprene L-100/MOCA. The ease of the FID decomposition and the sharpness of the SAXS maximum both suggest that the domains of the EN series are more sharply defined. A Gaussian/exponential fit is superior to an exponential/exponential fit for the EN series while an exponential/exponential fit is slightly better

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