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Study of aliphatic polyurethanes by the low-field ^{1}H NMR relaxometry method with the inversion of the integral transformation

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In this paper, the distributions of the ^{1}H NMR spin-lattice and spin-spin relaxation times are used to characterize the mobility of different sections of macromolecules of aliphatic polyurethanes and the crosslinking density of polymer chains. The NMR relaxometry method with inversion of integral transformation is applied to study the effect of poly (ethylene glycol) (PEG) and glycerol phosphate calcium (GPCa) on polymer dynamics.

1 Introduction

Polyurethanes are an important class of industrial materials and are widely used as coatings, fabrics, resin binders and high performance elastomers. The structures of linear polyurethane elastomers has been intensively studied since the last century. It is well known that they consist of "rigid" and "soft" segments. Rigid domains plays the role of physical stitching between macromolecules, and soft domains provide good impact resistance and tensile strength for these materials [1]. Rigid domains in thermoplastic polyurethane elastomers generally form hydrogen bonds between rigid segments, which are easily destroyed at higher temperatures [2]. Thermoplastic PURs behave like crosslinked polymers and their mechanical properties deteriorate when the temperature approaches the point of softening of the material.

Polyurethanes (PUR) are among the most developed synthetic polymers for biomedical applications. The main advantage of PUR is the ease of modification of their physicochemical and mechanical properties, which can be changed by the proper choice of raw materials used for polymer synthesis. This is especially important in the field of materials that are used in regenerative medicine for the regeneration of tissues with the ability of these materials for subsequent biodegradation. These polymers represent a very large variety of materials with individual properties, with the evidence of the growing number of publications dedicated to PUR studies.

Methods for obtaining polyurethanes for biomedical applications were described in [3-5]. The obtained non-modified PUR and PUR modified with the help of salt of glycerol phosphate calcium (GPCa)

polyurethanes were studied by different methods [3]. GCPa is a drug for enhancing the regeneration of bone tissue on the implant. The purpose of modification of the PUR, used as an implant, is the integration of GPCa into the chains of PUR. Studies of hydrophilicity, mechanical properties, biocompatibility, etc. showed that the resulting modified polyurethane can be used for the manufacture of scaffolds.

Modification of the polyurethane with GPCa (PURs-M) results in a higher rate of degradation in acidic and alkaline environments compared to non-modified PUR. The modification increases the hardness of polyurethane and improves its biocompatibility, hydrophilicity, as well as the calcification of regenerated bone tissue.

NMR spectra of polymer solids, typically obtained by the Fourier transform of the free induction decay (FID) signal contain a lot of information about molecular dynamics. However, the lines of NMR spectra of solid samples are usually wide and are minimally informative due to the contribution of anisotropic interactions, for example, heteronuclear and homonuclear dipole-dipole interactions, which are usually averaged by rapid molecular motion in liquids. In solids, magic angle spinning is often used to make NMR lines narrow and to obtain high-resolution NMR spectra. In this work, however, we used the technique of relaxometry, because it is significantly more informative in the study of dynamic processes. The structure of the polymer system is usually quite complex. Protons of the polymer mesh, which are detected by the ^{1}H NMR method, can have many different nonequivalent positions in the macromolecule.

These protons having different environments contributing to the FID signal lose coherence due to the action of different relaxation mechanisms and at different relaxation rates, which are characterized by the spin-spin relaxation times (T_2). In practice, it is virtually impossible to directly measure the relaxation spectrum of T_2. The spectrum of T_2 means the distribution function of the transverse relaxation times $f(T_2)$. It can only be calculated by analyzing the experimental FID data, i.e. by solving the Fredholm integral equation of the first kind from the FID signal:

$$S(t) = \int_0^\infty f(T_2) e^{-\frac{t}{T_2}} dT_2 \,, \tag{1}$$

where S(t) is the magnitude of decaying echo signals in the Carr-Purcell-Meiboom-Gill method (CPMG).

As a rule, the spin-spin relaxation time T_2 of a solid polymer is determined by several mechanisms. We analyzed the relaxation time of T_2 using the CPMG sequence [6]. This sequence reduces the influence of the inhomogeneity of the magnetic field and the diffusion contribution to the damping of the transverse magnetization. If the protons in the polymer system have high mobility, the dipole-dipole interactions between them are averaged by a rapid molecular motion. The FID in this case is determined mainly by the inhomogeneities of the constant magnetic field in which the nuclear spins are located. The influence of these inhomogeneities is usually several orders of magnitude smaller than the dipole-dipole interactions in rigid polymer systems [7]. Relaxation of the mobile component of the macromolecule is slow, because it is usually caused only by the inhomogeneities of the static field B_0, in which the nuclear spins are located. Homonuclear dipole-dipole interactions usually provide the dominant mechanism in ^{1}H-relaxation of slowly-moving (rigid) components, which leads to rapid spin-spin relaxation. Both mobile and slowly-moving (rigid) components can exist in a solid polymer.

In ref. [7], FIDs of solid polymers were represented using mixed Gaussian and exponential functions. The integration interval for the total T_2 spectrum was divided into two regions: a region of relaxation by the Gaussian function with shorter T_2 relaxation times and an exponential relaxation region with longer relaxation times. The relaxation of polymers was also examined in [8] with the Gaussian and exponential components taken into account.

Crosslinking of a polymer is the process of connection of the links of its molecules to a three-dimensional grid with wide cells, by forming transverse connections. This process can be considered as a transition of matter from an amorphous state to a crystalline one, while the ordered network structure of a crosslinked polymer can be compared to the crystal lattice of a solid. Studies of polymer degradation by the NMR relaxometry method with Laplace transform inversion are given in the paper [9].

^{1}H NMR high-resolution spectra of cycloaliphatic PUR with another modifier (ascorbic acid (AA)) are shown in [5], which allowed to determine the chemical structure of the polymer. These spectra for pure PUR and modified AA PUR are similar, and they confirm the presence of signals from both soft and solid segments of the polymer. ^{1}H NMR relaxometry was used to study the effect of water on crosslinked polyurethane coatings in ref. [10].

It is known that the width of the lines of static NMR spectra is an important source of information on molecular dynamics and interactions. However, the information about dynamics obtained from analyzing FID signals in the time domain is much more reliable for determining the real properties of the material.

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NMR relaxation times characterize the properties of polymeric materials, since they depend on cross-linking of macromolecules. The nature of the motion of sections of macromolecules of the polymer is complex and the decay of the transverse nuclear magnetization can not be described by a single relaxation time.

Obtaining the entire spectrum of relaxation times of biocompatible PURs is yet an unsolved problem. Solving this problem would allow us to judge on the nature of the motion of molecules and the distribution of the density of cross-links. Another problem is the determination of the effect of modifiers on the density of cross-linking of polymer chains, on the mobility characteristics of macromolecular sections, and on the quality of biocompatible polyurethanes.

The purpose of this work is to obtain spectra of the T_1 and T_2 relaxation times of biocompatible aliphatic polyurethanes by NMR relaxometry with an inversion of the integral transformation, and to determine the effect of modifying additives on the distribution of the density of crosslinks between macromolecules, and on the dynamic properties of molecular sections.

2 Experimental

Relaxation ^{1}H NMR experiments at 13.65 MHz were performed in a weak magnetic field (0.32 T) using a Tecmag Apollo spectrometer with the TNMR software. A permanent magnet was used with the size of the working region: diameter 5 mm, length 20 mm. The magnet consisted of two permanent magnets with the 60x80x100 mm size and a 25 mm gap between them, connected by a U-shaped magnetic core. Induction of the magnetic field in the gap was 320 mT. The inhomogeneity of the magnetic field at the location of the coil with a sample was 0.1 mT/cm. Inner diameter of the working coil of the sensor was 5.5 mm, length of the coil was 12 mm.

The procedure for obtaining the test samples of aliphatic polyurethanes is described in [3]. In the present work the following samples were studied:

1 – poly (ester ether urethane), modified by GPCa in the prepolymerization step, so that GPCa reacts with the NCO groups. Such a modified precursor polymer was then lengthened with BDO to produce PUR.

2 - poly (ester ether urethane), which was filled with GPCa, and the latter should not react with PUR, i.e. is asimply a filler.

3 - poly (ester ether urethane), unfilled and unmodified by GPCa. It is a control sample for samples 1 and 2.

4 - polyester urethane, which does not contain PEG and is not modified or filled with GPCa. Sample 4 is necessary to study the effect of the changes of the structure by the addition of poly (ethylene glycol) (PEG) to the system.

Thus, samples 1 and 2 are the same polyurethanes. However, in the first sample GPCa was added to the precursor polymer and thereby contacted the NCO groups present there, i.e., a modification of the GPCa prepolymer was performed here, and then the polyurethane, extending the modified pre-polymer with BDO. Sample 2 is a pre-polymer, butanediol-extended (BDO), with CPCa added as a filler. CPCa does not react with the pre-polymer, since there were no reactive groups for it in the system when it was added to the system.

Samples before the measurements were crushed and placed in glass ampoules. To measure the T_1 relaxation times, both the inverse-recovery and saturation pulse sequences were used. The CPMG sequence was used to measure the spin-spin relaxation times T_2. For realization of inverse integral transformation, the RILT [11] script was used, executed in the MatLab environment. The regularized inversion algorithm for the Laplace transform (RILT) is based on the *fminsearch* function of the MatLab package, which finds the minimum of the scalar function of several variables, starting with some initial estimate. The array of distributions of relaxation times is the inverse integral transformation of the array of experimental data *y(t)* and is calculated by the method of regularized least squares. To obtain smooth and regular output data, the algorithm provides a selection of the regularization parameter. The regularizor is represented as: $REG = \alpha^2 \sum_i \left(r_i - R_{ij} g_j\right)^2$, where α is the regularization parameter, g_j is the relaxation time distribution vector, r_i is the second derivative of g_j, R_{ij} is the matrix determining the form of regularizor [11, 12].

3 Results and discussion

The polymer under study is a chain of high- and low-molecular polymer blocks connected by urethane groups. High molecular weight polymers are oligomeric α, ω-dihydroxy (ethylene-butylene

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adipate) (dHEBA) and poly (ethylene glycol) (PEG). Low molecular weight polymers are 1,6-hexamethylene diisocyanate (HDI). 4-butanediol (BDO) is used as a chain extender. In modified polyurethane, calcium glycerol phosphate (GPCa) is used to stimulate the regeneration of bone tissue.

The nature of the rigid block has the greatest influence on the physical properties of polyurethanes. The change in the density of urethane groups in macromolecules changes the characteristics of PURs.

PUR consist of alternating soft and hard (rigid) segments (Fig. 1). The segmented structure of PUR affects the physicochemical and thermomechanical properties of these materials. Soft segments form dHEBA and polyethylene glycol PEG, rigid segments are HDI diisocyanate, a low molecular weight BDO extension, and a GPCa modifier. Soft segments provide the elastomeric nature of PUR, and the rigid segments provide good mechanical strength due to the hydrogen bonds formed between the urethane groups.

It is assumed in [3] that GPCa is included in the PUR structure through covalent bonds during the synthesis. And it is noted that PUR-M, apparently, has a large number of hydrogen bonds of urethane in comparison with PUR. This is confirmed by the performed analysis using Fourier-transform infrared spectroscopy (FTIR) [13, 14]. FTIR-spectra of PUR-M showed that it has a higher level of hydrogen bonds between hard segments than in PUR chains. This indicates that a large amount of the GPCa modifier used is incorporated into the PUR structure via a covalent bond, which is confirmed in addition of FTIR and Raman spectroscopy [3].

A polymer in a glassy state, or a crosslinked polymer with a high crosslink density, will give a peak at very short T_2 values at a map of relaxation time distribution. Peaks at long T_2 values can be attributed to very mobile macromolecules of polymers - for example, to free broken ends, to non-overlapping segments of the polymer chain, etc. It should be noted that most of the information on very rapidly falling relaxation components T_2 can be lost because of the dead time of the receiver.

The distribution of the NMR spin-spin relaxation times of the proton for the polyurethanes under study is illustrated in Fig. 2. All distributions are bimodal. The bimodal character of the distribution of the relaxation times T_2 is observed, as a rule, in weakly crosslinked elastomers. In this case, the groups of spins of the macromolecule are weakly related to each other and have different dipole-dipole interactions.

If there is a bimodal distribution of the relaxation times, the short-time component is caused by protons located on sections of the macromolecules between the transverse bonds, while protons at the free ends of the macromolecules make the main contribution to the long time component [15]. For the bimodal T_2 distribution, the short and long-time components of the transverse relaxation time are a measure of the molecular mobility and the density of the sample crosslinks. The higher the value of T_2, the lower the crosslinking density in the polymer.

Comparison of the T_2 distributions for the modified GPCa polyurethane (curve 1) and for unmodified (curve 3) allows us to conclude that the former are less mobile due to the presence of rigid GPCa blocks in chains. These blocks increase the concentration of the cross-links and shift the peaks of T_2 to a region of smaller relaxation times compared to sample 3. The mobility of polyurethane chains reduces even in the presence of GPCa used as a filler (curve 2). The absence of elastic PEG segments in polyurethane chains (sample 4) also reduces the mobility of molecular fragments due to the increase in the cross-link density as compared to control sample 3. The long-time component of T_2 refers to the terminal regions of the molecules or the inner sections of the elastic blocks (Fig. 2, 3), and the short-time component corresponds to the regions of the molecules between the meshes and crosslinks, where their density is high.

The presence of two peaks in the T_2 distribution (curve 5) for GPCa powder is due to the protons of the C-H and OH-groups. The peak in the long-time region is caused by the protons of the OH- groups, which have a higher mobility.

Since the area of the peak in the T_2 spectra is proportional to the density of the corresponding type of spins in the sample, the areas of individual peaks can give quantitative information on the ratio of the spin concentrations at the corresponding positions.

The distribution of the T_1 relaxation times is practically unimodal for all the samples studied (Fig. 3). The peak for modified polyurethane (curve 1) is shifted to a shorter relaxation time region as compared to the unmodified samples 2 and 3. This is due to the fact that the T_1 relaxation times are due to the same factors as the T_2 times. The practically unimodal distribution of the spin-lattice relaxation is probably due to the fact that it is due to small-scale motions of the tail and central parts of the molecules and to the fact that these motions differ little from each other. It should be noted that the spin-lattice relaxation times are much longer than the transverse relaxation times. Therefore, spin diffusion leads to an alignment of the T_1

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relaxation times for protons in the tail and central parts of macromolecules. We are talking about the transfer of magnetization in the presence of a magnetization gradient, at which mass transfer is absent.

Modified and unmodified PURs were slowly heated for one hour to a temperature of 110 ℃, then were cooled in air and held for seven days in order to detect changes occurring with the polymers. The distributions of the T_1 and T_2 relaxation times for both polymers after such a treatment are shown in Fig. 4 and 5. As can be seen from Figs. 4 and 5, both peaks in the distribution of the T_2 times for the modified PUR under the heat treatment described above are shifted towards smaller values, whereas the peak in the T_1 distribution shifts towards longer values. A much larger shift of the peaks along the T_2 axis towards short times occurs for an unmodified PUR, while the peaks do not shift along the T_1 axis.

The changes in the position of the peaks in T_1 and T_2 distributions can be explained, assuming that the increase in the concentration of crosslinks and hooks of polymer chains occurs with the heating-cooling described above, which is accompanied by a decrease in the elasticity of the samples. The weak peaks seen in Fig. 5 are apparently due to the terminal parts of the macromolecules of the polymer. The nature of the motion of the tail parts of macromolecules differs from the patterns of the motion of the central parts.

4 Conclusion

Thus, in this paper, the distributions of the ^{1}H NMR relaxation times are used to characterize the mobility of segments of macromolecules of aliphatic polyurethanes, the density of cross-linking of polymer chains, and their changes when polymer is modified with GPCa. The relaxation technique used here allows us to establish a relationship between the structure, dynamics, and properties of polymers.

The outlined researches allows us to come to the conclusion about smaller mobility of macromolecules of polyurethane modified by GPCa, which is caused by the presence of rigid GPCa blocks in chains. The presence of rigid blocks corresponds to an increase in the cross-link concentration, which results in shifts of T_2 peaks to the region of smaller relaxation times for the modified GPCa compared to the un-modified polyurethane. The absence of elastic segments of PEG in polyurethane chains also reduces the mobility of molecular fragments due to the increase in the cross-link density as compared to the control sample.

The following regularity is observed: the higher the cross-link density, the higher the hardness of the samples and the shorter the T_2 relaxation time. Interpretation of ^{1}H NMR relaxation data in terms of the T_2 relaxation spectrum makes it possible to separate the protons of the polymer system into distinct species characterized by different molecular dynamics. The studies implemented in this work make an important contribution to the development of the science of polymers, which will eventually solve important applied problems.

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Figure 1. High-molecular weight elastic blocks (a) and low-molecular-weight rigid blocks (b).

Figure 2. Distribution of relaxation times T_2 in different samples of polyurethane. The following notation here and in Fig. 3 is adopted: 1-poly (ester ether urethane), modified GPCa, 2-poly (ester ether urethane) with GPCa filler, 3-poly (ester ether urethane), unmodified and without filler, 4-polyester urethane, not containing PEG and not modified, 5 - glycerol phosphate calcium salt.

Figure 3. Distribution of spin-spin relaxation times T_1 in aliphatic polyurethanes.
GPCa (curve 5) is given for comparison.

Figure 4. The distributions of relaxation times T_2 for sample 1 (polyurethane modified by GPCa) and sample 4 (polyurethane, unmodified) are represented by curves ***a*** and ***c***. Curves ***b*** and ***d*** are, respectively, distributions for the same samples subject to heating to 110 ℃ and with subsequent exposure for 7 days at room temperature.

Figure 5. The same as in Fig. 4, but for relaxation times T_1.

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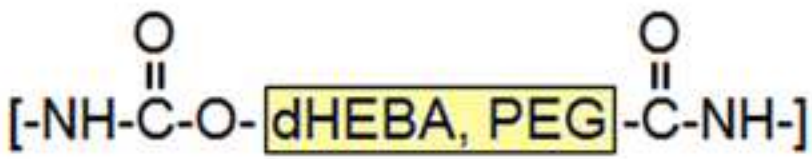

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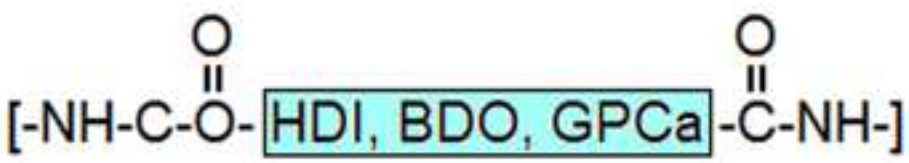

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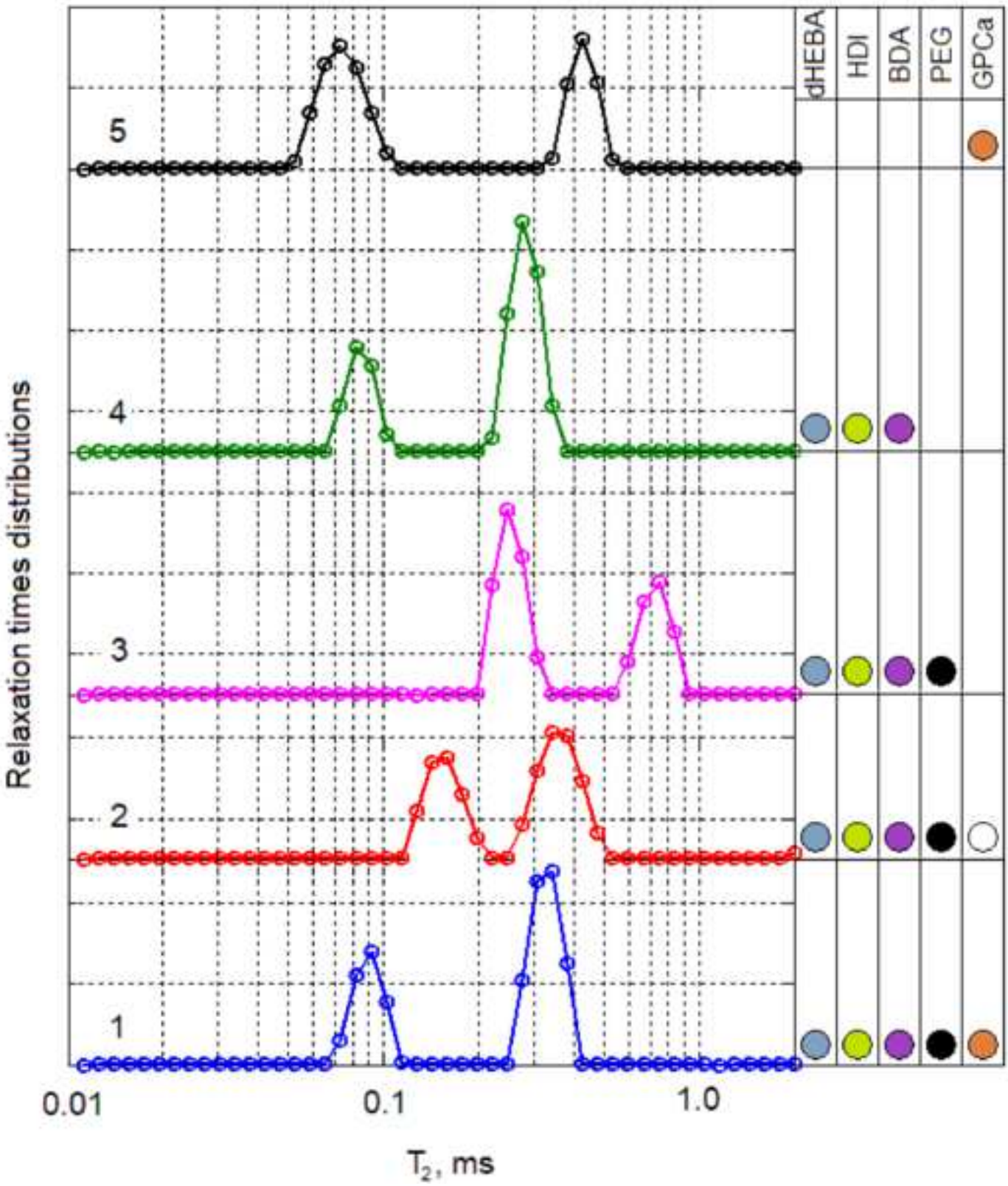
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Relaxation times distributions
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Figure

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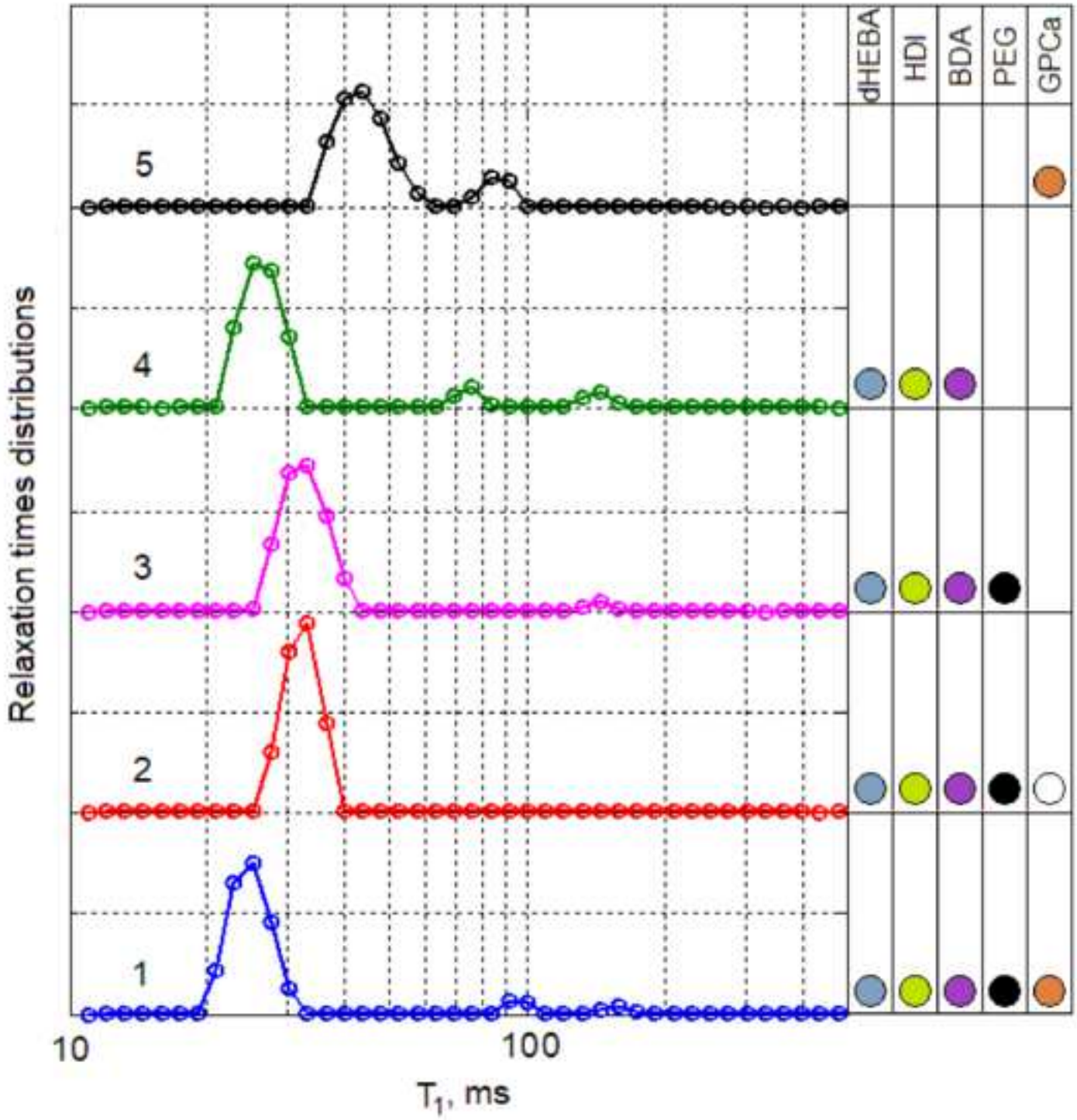

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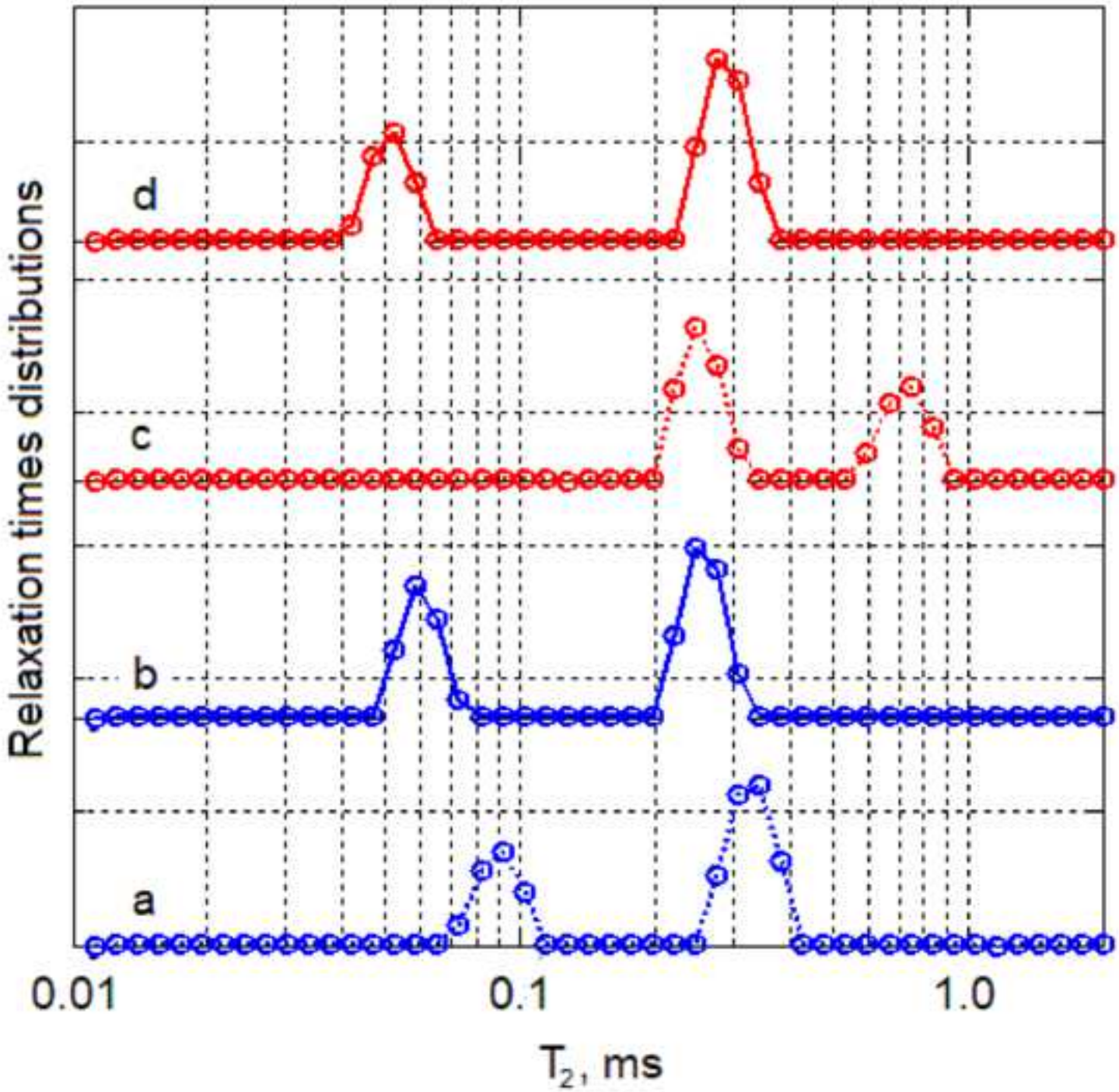
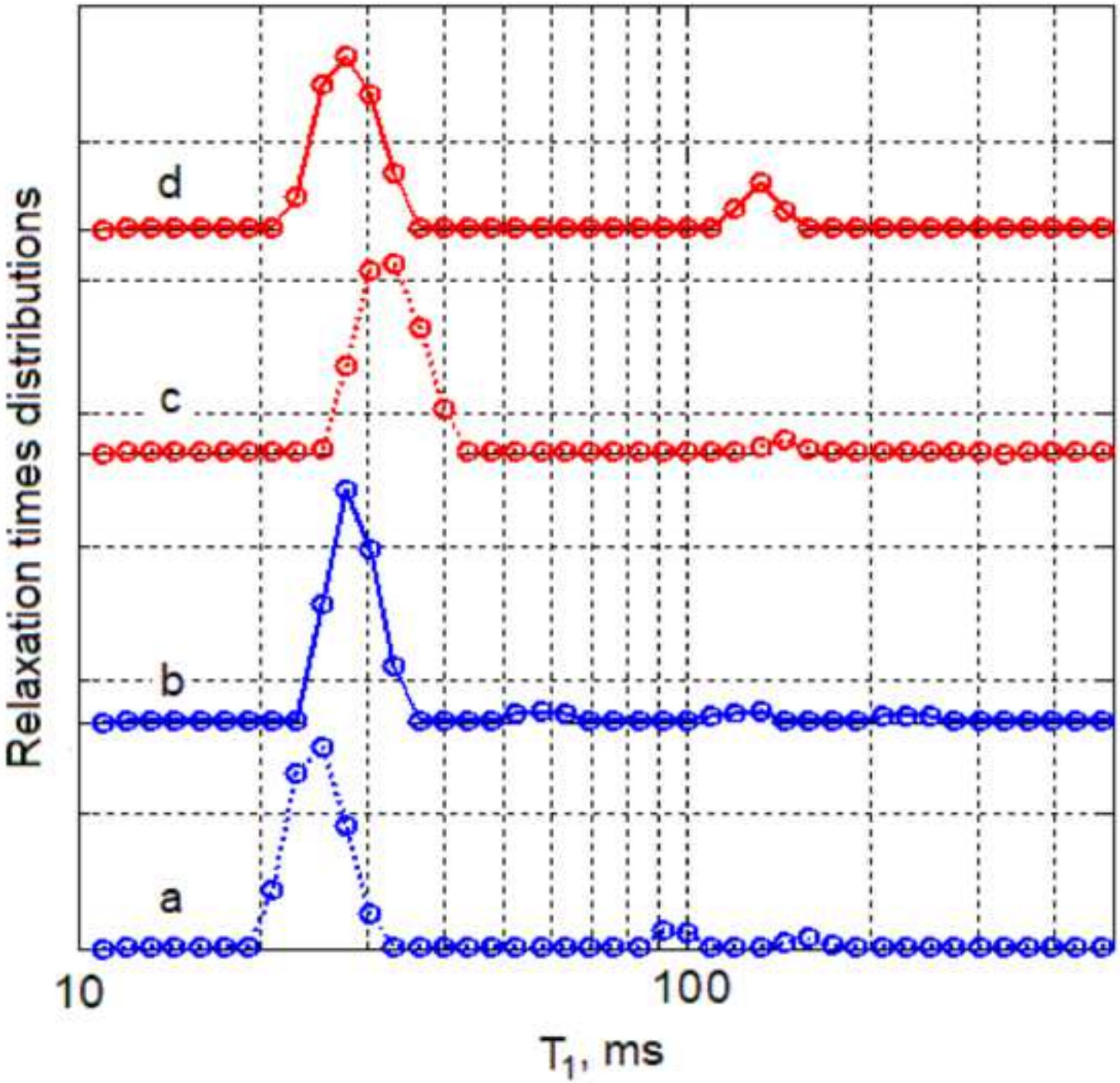
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