

¹H-NMRD Profiles of Polymers

A Preliminary Experimental Survey



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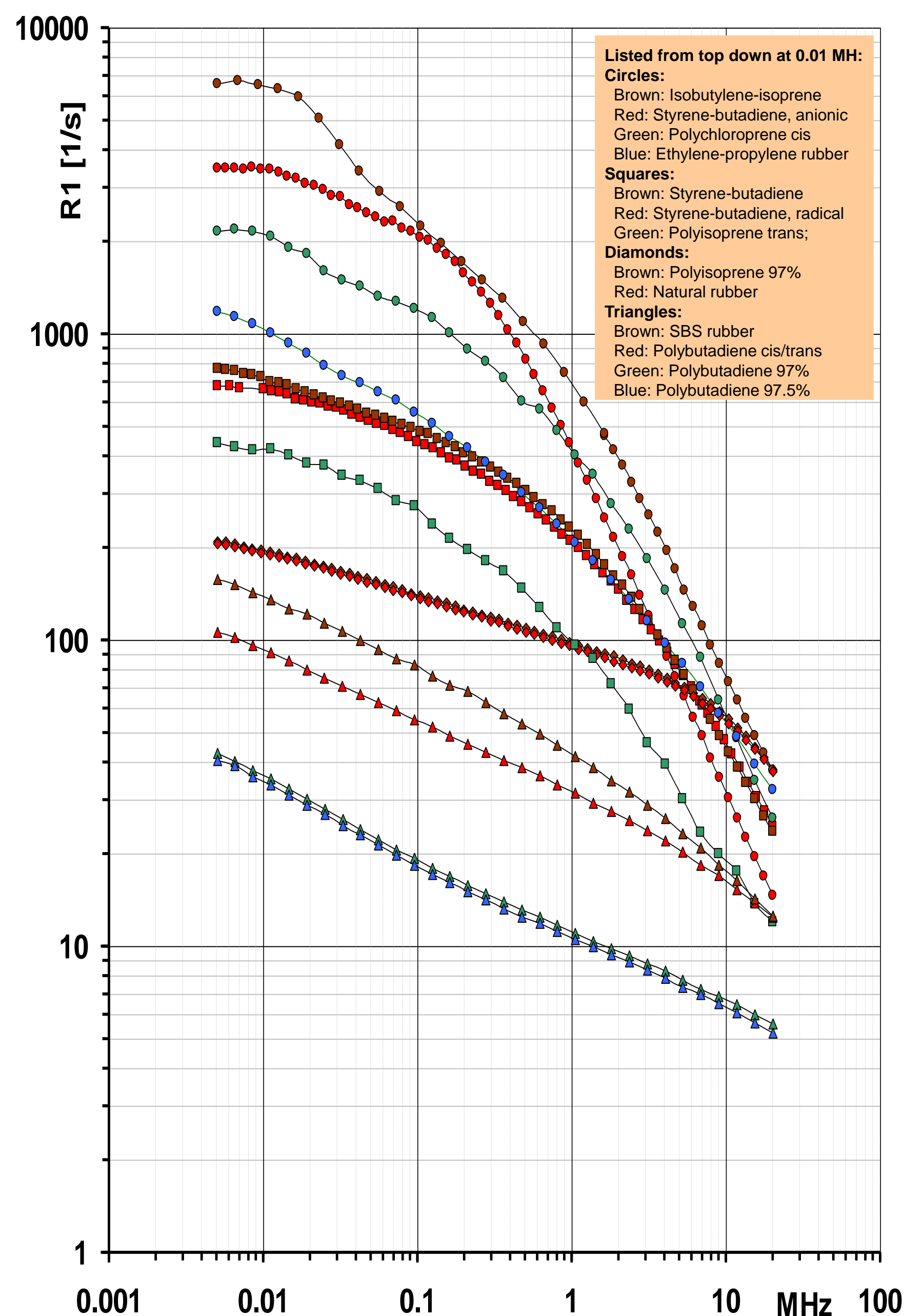
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We have undertaken a systematic exploration of proton dispersion profiles of several families of synthetic polymers. The ¹H NMRD profiles of solid samples were measured at 25°C over relaxation fields ranging from 5 kHz to 20 MHz (measured by ¹H Larmor frequency). So far, we have explored several classes of elastomers, styrenes, nylons and a polycarbonate. The survey, though still in a preliminary and phenomenological phase, allows us already to draw several experimental conclusions of considerable interest in view of the expected rapid growth of NMRD studies of molecular dynamics of bulk polymers.

In many individual profiles, the R₁ values range over more than three orders of magnitude. In virtually all cases, the variation continues down to the lowest measured frequencies, following curves which deviate sharply from the simple BPP model and which rarely exhibit any plateau, be it at high or at low frequencies (only in a few cases there seems to be a plateau below 10 kHz). This implies a wide spectrum of correlation times and dynamic models much more complex than what might appear from relaxation studies carried out at high fields and fixed frequencies. This presentation does not attempt any theoretical interpretation of the collected data in terms of molecular dynamics (a task which is the central part of an ongoing but far from complete effort).



<<< The elastomers

comprise at least four different types of relaxation behaviour.

The “circles” group reaches R₁ values of well over 1000 at low fields and features bimodal τ_c distributions. In each case there is a main dispersion region around a few MHz and a clear hint of a secondary dispersion region around a few tens of kHz.

The slower-relaxing “squares” group comes closest to what might appear as a BPP-like profile. However, the slope at high fields is far from what it should be (around -1 on the log-log scale rather than the -2 required by BPP), indicating a rather wide (though probably mono-modal) distribution of τ_c's.

The two samples in the “diamonds” group have essentially identical profiles even though the samples are different. Their most striking feature is the broad region of frequencies (three-orders of magnitude) where the profile is linear on the log-log scale with a well-defined derivative of just about -0.15.

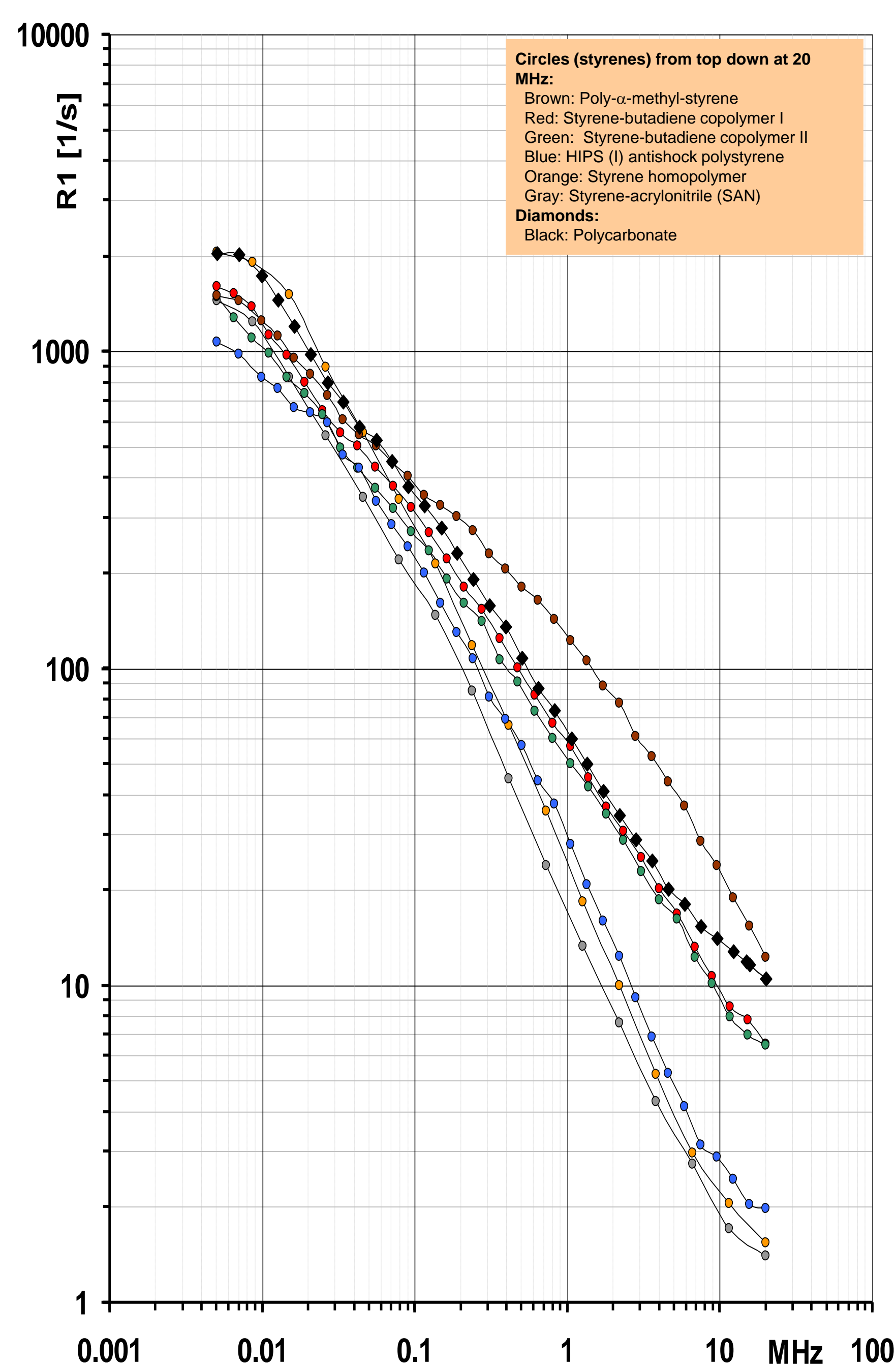
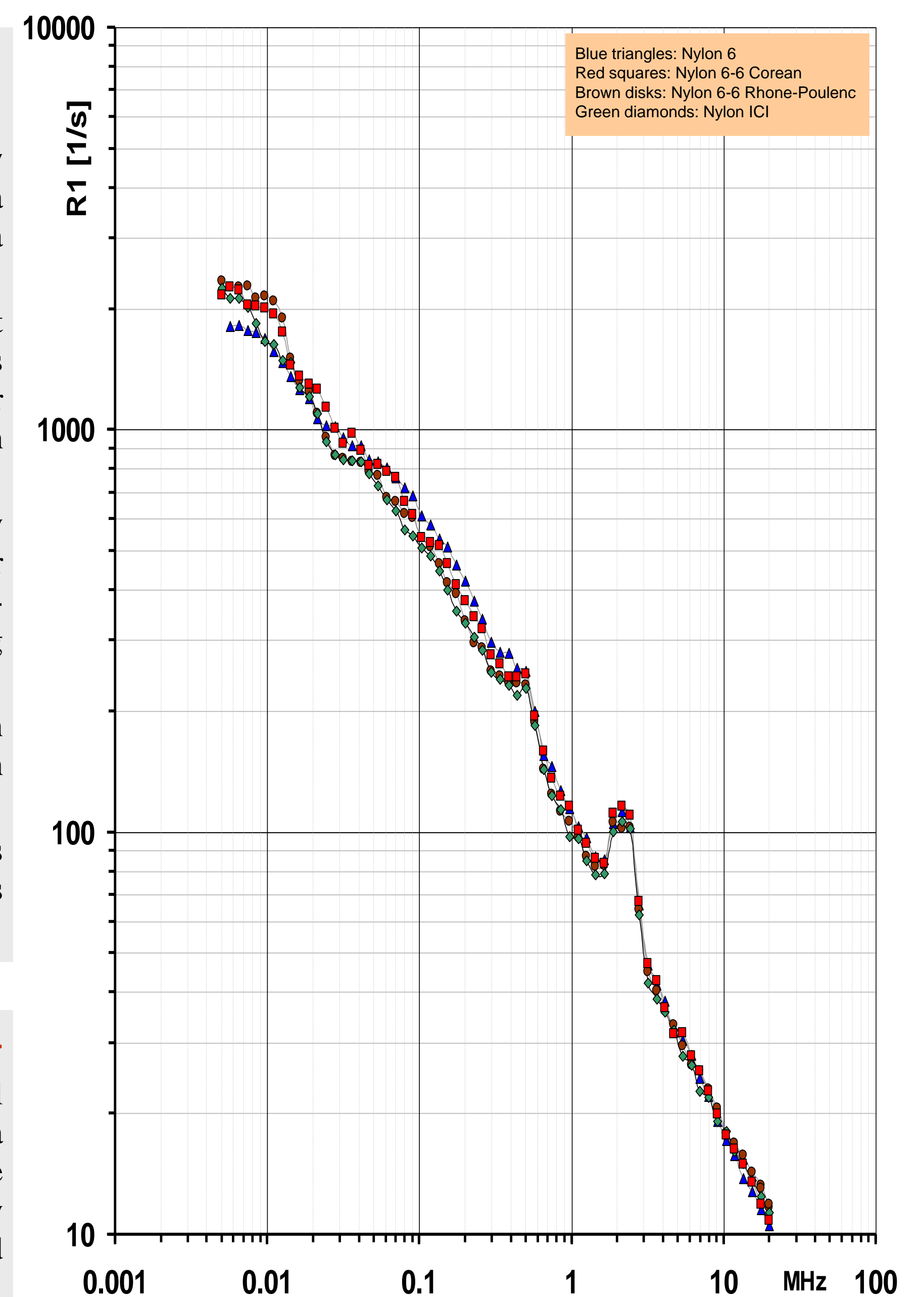
The slowest relaxing “triangles” group comprises samples with approximately linear log-log dependences whose slopes fall in these cases between -0.25 and -0.30.

The elastomer samples are very easy to measure since their FID's have a considerable duration and - even at 20 MHz - their T₁'s are quite short so that polarization times are short either.

The nylons >>>

The four nylon samples shown on the right have almost identical profiles characterized by a roughly linear log-log slope with a derivative of about -0.75. Superimposed on this background are the nitrogen glitches at positions where ¹H Larmor frequency crosses the ¹⁴N NQR-NMR transitions (for these samples around 2.1 MHz and 500 kHz).

The nylon samples had very short FID's (< 35 μs) so that their measurement required solid-state class probe and parameters.



<<< The polystyrenes and a polycarbonate

The polystyrene polymers and copolymers on the left also exhibit nearly linear log-log profiles with slopes varying between -0.5 and -1.2. In general, the slopes of copolymers are not as steep as those of homopolymers, indicating a broader spectrum of internal motions. The markedly different behaviour of the poly-α-methylstyrene is almost certainly related to the internal rotation of the methyl group.

The styrene samples have the shortest FID's (< 30 μs). Combined with long high-field T₁ values, this makes them at least 10 times more difficult to measure than the elastomers.

Conclusions

Though there are marked differences between individual profiles, the survey as a whole exhibits a surprising internal coherence, making it possible to group the polymers into families according to the shapes of their profiles (it is comforting that such classification correlates with the known chemical composition of the samples).

It is beyond any doubt, however, that **the internal coherence of the survey would be completely lost if it were not possible to measure reliable R₁ values in the range from 100 to almost 10000 s⁻¹**. Indeed, while most of the studied polymers exhibit quite low R₁ values at 20 MHz (in some cases close to 1, often around 10 and always below 100), the situation changes dramatically at fields around 1 MHz and lower. Without the R₁ values lying in the two decades above 100 s⁻¹, FFC relaxometry of bulk polymers would be seriously handicapped.

Experimental

All samples shown here were measured in untreated bulk using the automated profile-acquisition procedure with NP/S and PP/S sequences. The following parameters were common for all the samples:

Sample temperature (TEMP): 25°C,
Polarization field (BPOL): 15MHz,
Switching times (SWT): 1 ms,
Acquisition field (BACQ) & frequency (SF): 9.15 MHz,
90-degree pulse width (PW90): 6.5 μs,
Receiver inhibit time (RINH): 8 μs,
Block size (BS): 32,
Number of scans (NS): 4, no dummy scans (DS=0),
Number of tau-blocks (NBLK): 32, in some cases 64,
Evaluation window (PINI-PEND): 1-16.

For the elastomers, we have used used:

Sweep width (SW): 200 kHz,
Filter width (FLTR): 90 kHz,
Acquisition delay (ACQD): 11 μs.

For all other samples, we used instead:

Sweep width (SW): 2 MHz,
Filter width (FLTR): 600 kHz,
Acquisition delay (ACQD): 1.6 μs,

Statistical analysis of the mono-exponential fitting residues has passed all the measured relaxation decay curves as mono-exponential with a single exception (the trans polyisoprene) where a slight non-exponentiality has been detected (we report the R₁ values of the slower of the two components present).

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