



HAL
open science

Investigation of chain dynamics in poly(n-alkyl methacrylate)s by solid-state NMR: comparison with poly(n-alkyl acrylate)s

Marianne Gaborieau, Robert Graf, Hans Wolfgang Spiess

► **To cite this version:**

Marianne Gaborieau, Robert Graf, Hans Wolfgang Spiess. Investigation of chain dynamics in poly(n-alkyl methacrylate)s by solid-state NMR: comparison with poly(n-alkyl acrylate)s. *Macromolecular Chemistry and Physics*, 2008, 209 (20), pp.2078 - 2086. 10.1002/macp.200800314 . hal-04083164

HAL Id: hal-04083164

<https://hal.science/hal-04083164>

Submitted on 27 Apr 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Investigation of Chain Dynamics in Poly(*n*-alkyl methacrylates) by Solid-state NMR - Comparison with Poly(*n*-alkyl acrylates)

Marianne Gaborieau,*^a Robert Graf, Hans Wolfgang Spiess*

M. Gaborieau, R. Graf, H.W. Spiess

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Fax: +49 6131 379 320; E-mail: spiess@mpip-mainz.mpg.de

^a Current address: Centre for Nutrition and Food Sciences, Hartley Teakle building 83, University of

Queensland, Brisbane QLD 4072, Australia

Fax: +61 7 3365 1188; E-mail: m.gaborieau@uq.edu.au

Keywords

solid-state NMR, poly(*n*-alkyl methacrylates), molecular dynamics, true molar mass / molecular weight, poly(*n*-alkyl acrylates).

Summary

Poly(*n*-alkyl methacrylates), PnAMAs, exhibit a local nanophase separation, associated with intriguing chain dynamics features (*Macromol. Chem. Phys.* **2005**, 206, 142). PnAMAs of high molar mass, as determined by SEC and MHKS parameters, were investigated in the melt with a recently developed solid-state NMR method (NOE with dipolar filter; *Solid State Nucl. Magn. Res.* **2005**, 28, 160). The correlation times are assigned to the relaxation of the alkyl nanodomains, as coupled motions of the main chain and hindered local modes in the side chain. Comparison with poly(*n*-alkyl acrylates) shows a higher anisotropy of the main chain motions and a better organized local nanophase separation in PnAMAs.

Introduction

Quantifying chain relaxation in polymers is often an important step in the determination of comprehensive structure-property relations. Poly(*n*-alkyl methacrylates), PnAMAs, are industrially relevant samples as they are widely used in coatings. They are not crystalline, therefore have long been considered as completely disordered. However, X-ray scattering studies^[1] revealed the presence of some local order. Furthermore, their backbone dynamics exhibit intriguing features at the glass transition, linked to the above-mentioned local nanophase separation.^[2, 3] Advanced solid-state NMR^[4] and temperature-dependent X-ray investigations have recently revealed conformational memory and quantified a specific isotropization process.^[5-8]

We recently developed a new solid-state NMR method to quantify chain dynamics in polymers with weak dynamics contrast: the NOE experiment with dipolar filter.^[9] The principle of nuclear Overhauser effect (NOE) had been previously used differently in other solid-state NMR experiments to study miscibility in polymer blends^[10-12] and chain dynamics in polymer melts,^[13-15] or to differentiate chain length of branches in polyethylene.^[16] The comparatively simple NOE experiment with dipolar filter is a combination of a conventional exchange experiment^[4] with a dipolar filter, which selects according to local mobility, and is applicable to non-isotopically enriched samples. Originally validated on poly(ethyl methacrylate),^[9] it was then successfully applied to poly(*n*-alkyl acrylates), PnAAs.^[17] PnAMAs and PnAAs both consist of a polar more rigid backbone and apolar more flexible side chains. Therefore the PnAMAs are expected to exhibit an appropriate dynamic contrast to apply the NOE experiment with dipolar filter.

Therefore, the NOE experiment with dipolar filter is applied here to poly(*n*-butyl methacrylate) and poly(*n*-hexyl methacrylate). Both samples have sufficiently high molar masses to expect no influence of it on the relaxation processes studied. Actual molar masses have been determined with size-exclusion chromatography (SEC) using the Mark-Houwink-

Kuhn-Sakurada parameters.^[18] The dynamic processes quantified by the NOE experiment with dipolar filter are compared to relaxation data obtained earlier by independent solid-state NMR, dielectric and mechanical spectroscopy techniques.^[6, 7] Furthermore, they are interpreted together with the one detected previously in poly(ethyl methacrylate).^[9] Finally the PnAMA and the PnAA families are compared in terms of dynamics and local structure.

Experimental Part

Materials

The samples investigated in the present articles are poly(ethyl methacrylate), poly(*n*-butyl methacrylate) and poly(*n*-hexyl methacrylate) samples, abbreviated respectively PEMA, PBMA and PHMA (Figure 1). The suffixes 13C, DSG and DMC refer to a 20 % random ¹³C labeling of the carbonyl group, a complete ²H labeling of the alkyl side group and a complete ²H labeling of the main chain respectively.

The synthesis of the non-commercial ¹³C or ²H labeled monomers and the free-radical polymerizations in solution at 60°C in toluene or chlorobenzene were reported earlier.^[7, 19-22] From ¹H or ¹³C NMR measurements in CDCl₃, all samples have a high tendency to syndiotacticity (65 ± 7 % of syndiotactic triads).^[7, 20-22] The glass transition temperatures T_g are shown in Supporting Information. The apparent average molar masses were obtained from size-exclusion chromatography (SEC, also commonly named gel-permeation chromatography, GPC) in tetrahydrofuran (THF) with poly(methyl methacrylate) (PMMA) standards.^[7, 20-22]

Actual molar masses by SEC

SEC separates samples according to hydrodynamic volume and not according to molar mass. Thus a conventional calibration with standards of a different chemical nature to the studied samples yields apparent molar masses, which can significantly differ from the true

ones.^[18] This is known, but often underestimated.^[18] Even if no standard of same chemical nature are available, it is possible to obtain true molar masses by using the universal calibration from narrow standards and the Mark-Houwink-Kuhn-Sakurada (MHKS) parameters of both the standards and the analyzed sample. The universal calibration equation of Benoît (Equation (1))^[23-25] is combined with the Mark-Houwink-Kuhn-Sakurada (MHKS) empirical relation (Equation (2))^[26] to obtain Equation (3):

$$[\eta]_{\text{PMMA}} \cdot M_{\text{PMMA}} = [\eta]_{\text{X}} \cdot M_{\text{X}} \quad (1)$$

$$[\eta] = K \cdot M^{\alpha} \quad (2)$$

$$M_{\text{X}} = \left(\frac{K_{\text{PMMA}}}{K_{\text{X}}} M_{\text{PMMA}}^{\alpha_{\text{PMMA}}+1} \right)^{\frac{1}{\alpha_{\text{X}}+1}} \quad (3)$$

where $[\eta]$ is the intrinsic viscosity, M is the molar mass, K and α are the MHKS parameters which can be found in the literature, X and PMMA subscripts indicate the analyzed sample and PMMA standards respectively. Equation (3) allows calculating the true molar mass M_{X} of polymer X from the apparent molar mass M_{PMMA} determined for polymer X using PMMA conventional calibration.

The MHKS parameters K and α are collected in Table 1 for the investigated PnAMAs. It should be noted that the parameters given for PMMA, PEMA and PBMA are recommended by the IUPAC working party on “modeling of polymerization kinetics and processes”,^[27] and thus critically selected among different literature values. Contrary to that, the parameters given for PHMA are extracted from a single literature source.^[28]

Using Equation (3), the true number- and weight average molar masses M_{n} and M_{w} were calculated from the apparent ones previously determined using conventional calibration with PMMA standards. Apparent and true molar masses are compared in Table 2. It is observed that the difference between the apparent and true molar masses is insignificant for PEMA (lower than 2 %); it is lower than the experimental error coming from the SEC analysis itself, evaluated at roughly 5 to 10 % for M_{w} and 15 to 20 % for M_{n} .^[29] It should be

noted that a difference in tacticity could lead to an additional 20 % error in the case of PEMA.^[30] In our study, however, the PMMA standards and the investigated PEMA samples had a similar syndiotactic content. Then, the use of the molar masses determined using PMMA calibration introduces a negligible error. It is not the case of the PBMA samples, for which the introduced error is approximately as high as the experimental error, and can not be neglected any more. However, the order of magnitude of the measured value is still valid. Contrary to that, for the PHMA sample the molar masses determined using a PMMA calibration are totally erroneous. An error larger than 60 % is found with respect to average of the two molar masses, which corresponds to an error of 100 % with respect to the true molar masses. Therefore, in the case of PHMA samples, it is necessary to consider the universal calibration and recalculate the true molar masses. The difference in behavior of model PnAMAs might be attributed to a different solubility in THF at 30 °C. Furthermore, it should be noted that the molar masses are high enough to have no influence on the local chain dynamics investigated below.

Solid-state NMR methods

The solid-state NMR measurements were carried out on a Bruker DSX spectrometer at Larmor frequencies of 300.13 MHz for ¹H and 75.47 MHz for ¹³C using commercial 7.5 mm static and 4 mm magic angle spinning (MAS) double resonance probes from Bruker BioSpin GmbH. For the measurements done under static conditions, the actual sample temperature was calibrated using lead nitrate and a few melting points.^[31]

Static ¹H spectra were recorded using a 4 μs 90 ° pulse, 16 transients and 5 s recycle delay. MAS was avoided in order to prevent interference between different homodipolar averaging mechanisms. Temperatures ranged from ca T_g-50 K (where the full width at half maximum of the lines, fwhm, levels off) to ca T_g+125 K (where a low fwhm is obtained, due to motional averaging).

Lee-Goldburg cross-polarization (CP) MAS spectra were recorded at 3 kHz MAS spinning frequency using 4 mm rotors. In the ^1H channel the RF power level was set to a nutation frequency of 83 kHz (corresponding to a 90° pulse length of 3 μs) for excitation as well as for ^1H continuous wave decoupling during acquisition. A relaxation delay of 3 s was chosen for these experiments. The Lee-Goldburg irradiation^[32] for the CP was adjusted on the ^1H nuclei by first calculating the corresponding irradiation offset frequency for the chosen RF power level and then finely adjusting the irradiation power by optimizing the resolution of ^{13}C multiplets under Lee-Goldburg decoupling conditions. The following series of experiments was conducted: first a simple LG-CP spectrum, second a LG-CP spectrum recorded immediately after a dipolar filter, third a LG-CP spectrum recorded after a dipolar filter with the same experimental settings and a subsequent mixing time (see Supporting Information and ref. ^[9] for pulse schemes). The experiments were conducted on PBMA at ca 370 K (ca T_g+70 K) with a CP contact time of 500 μs , a filter with 15 μs delay and 1 cycle, mixing times of 5 and 50 ms, and 1024, 5120, 10240, 15360 transients for the four spectra, respectively.

The principle of the nuclear Overhauser effect (NOE) experiment with dipolar filter was presented in detail previously (see ref. ^[9] and Figure 2 for pulse scheme). Schematically, the filter leaves magnetization only to the more mobile ^1H nuclei of the sample, then the magnetization is transferred to their neighboring groups during the mixing time τ_m , and finally the evolved magnetization is recorded; the experiment is repeated for several τ_m values, and the evolution of the magnetization of the more mobile ^1H nuclei is analyzed as a function of the mixing time. 62.5 kHz RF nutation frequency and 5 s recycle delay have been used. The delay between pulses in the dipolar filter has been varied from 10 to 20 μs , and the number n of cycles in the dipolar filter from 1 to 12, depending on the sample and the temperature. For each sample at each temperature, an average of the correlation times obtained with different filter parameters has been determined. The measurements were carried out at temperatures

ranging from T_g+45 K to T_g+130 K on sample PBMA, at T_g+77 K on sample PBMA13C, and from T_g+55 K to T_g+115 K on sample PHMA13C.

A poly(ethyl acrylate) sample^[17] was investigated in the melt by ^{13}C NMR for comparison purposes. ^{13}C spectra were recorded with single pulse excitation and Hahn echo under static conditions on a Tecmag spectrometer operating at a ^{13}C Larmor frequency of 75.47 MHz, at temperatures ranging from T_g+23 to T_g+57 K.

Results and Discussion

Mechanism of NOE experiment with dipolar filter

The NOE experiment with dipolar filter^[9, 17] applies a dipolar filter to select the magnetization in the more mobile parts of the sample, followed by a mixing time to allow magnetization transfer in the sample by a cross-relaxation (or NOE) mechanism (see ^[9] for pulse scheme). The ^1H static spectra of poly(*n*-alkyl methacrylates) exhibit an apparent single line over the temperature range investigated here (see Figure 3 for sample PBMA and Supporting Information for all samples). At the end of the dipolar filter, the ^1H spectrum shows an apparent single line, which is narrower than the one observed without dipolar filter, and becomes broader for increasing mixing times τ_m , until it reaches the line width observed without dipolar filter. Before conducting any chain dynamics quantification with this experiment, it must be checked (i) if there is a dynamic contrast inside the sample, (ii) what selection the dipolar filter actually does and (iii) if the magnetization transfer during the mixing time actually occurs via a cross-relaxation mechanism.^[9, 17] This was previously verified for poly(ethyl methacrylate) samples^[9] and will be checked below for PBMA.

A 2D-WISE spectrum of sample PEMA13C showed the following order for decreasing mobility: side chain CH_3 , then main chain CH_3 , then CH_2 groups.^[9] It is therefore expected

that for PBMA and PHMA there is a gradient of mobility along the side chain, starting from the more mobile CH₃ end group. It is indeed indirectly verified by independent LG-CP experiments, in which the selected ¹H signal was transferred to ¹³C nuclei via Lee-Goldburg cross-polarization and acquired in the ¹³C channel under MAS to gain chemical shift resolution.^[9] All the chemical sites of the monomeric unit of PBMA are resolved in the ¹³C LG-CP spectrum (Figure 4(a)). The dipolar filter actually selects the CH₃ end group of the side chain and partly the next two CH₂ groups and the main chain CH₃ group (Figure 4 (b)), whereas the OCH₂ group and the quaternary carbon are suppressed. The spectra recorded without dipolar filter and with 50 ms mixing time are identical (Figure 4 (a) and (d)), indicating a return to equilibrium within 50 ms after the application of the dipolar filter. Furthermore, spectra recorded after 5 ms or 50 ms mixing time are virtually identical (Figure 4 (c,d)). This will be further discussed below.

Monitoring the intensity of the more mobile parts of the sample as a function of the mixing time during the exchange experiment with dipolar filter, allows to investigate the mechanism of the magnetization transfer involved.^[9] The two possible mechanisms indeed result in a different dependency of the intensity decay upon mixing time: (i) linear intensity decay with the square of the mixing time for a coherent magnetization transfer via residual dipolar couplings,^[33] and (ii) logarithmic intensity decay with the mixing time for a non coherent magnetization transfer via cross-relaxation (or NOE).^[9] The corresponding plots were done for all samples at all temperatures and a representative example of PBMA at T_g+100 K is shown on Figure 5. The recorded intensity decays exponentially with mixing time, in agreement with a NOE mechanism, while the evolution of recorded intensity with the square of the mixing time is clearly not linear, indicating a negligible contribution of coherent magnetization transfer. Therefore the magnetization transfer occurs predominantly via a non-coherent mechanism during the mixing time (although a small contribution of coherent

magnetization transfer can not be excluded). A cross-relaxation formalism was thus used to treat and interpret the recorded data for all samples at all temperatures.

Note that a biexponential decay is observed for the recorded magnetization for sample PBMA below T_g+90 K, as found previously for sample PEMA below T_g+60 K.^[9] This could hardly be due to an improper correction for T_1 relaxation, since a well defined plateau is observed after the end of the second decay. As extensively discussed for PEMA,^[9] the evolution of the recorded intensity with mixing time does not allow to discriminate between a superposition of two NOE processes, and a coherent spin diffusion process. However, the fit of experimental data as a superposition of NOE processes yields a slow motion component (fast magnetization decay) which follows the same Arrhenius behavior as the single NOE process observed at higher temperatures. Thus the interpretation of the biexponential decay as arising from a superposition of NOE processes was favored. Furthermore, the LG-CP spectrum measured at the end of the fast decay (after 5 ms mixing time) was identical in line shape to the one measured after the end of the slow decay (after 50 ms, Figure 4). Thus the two NOE processes are not occurring in different parts of the monomeric unit, but rather in the same part of the monomeric unit but at different rates. This behavior is observed for poly(ethyl methacrylate) and poly(*n*-butyl methacrylate) over the range from ca T_g+40 K to ca T_g+60 K and T_g+90 K respectively. This corresponds to the temperature range where the strong anisotropy of the molecular motion due to the local structure has been reported (from ca T_g+30 K to ca T_g+80 K on the NMR time scale).^[5, 6] Therefore it is concluded that the NOE measurement detects the local structure. The NOE experiment with dipolar filter is thus able to detect the faster involved molecular motion involved (though without allowing a precise quantification). This detection is obtained without isotope labeling, using rather simple NMR techniques: a classical exchange experiment combined with the dipolar filter.

Chain dynamics in PBMA and PHMA by NOE

As detailed in a previous article,^[9] the magnetization intensity recorded in the present one-dimensional NOE experiment with dipolar filter follows the same time evolution as the diagonal line intensity in a 2D NOE experiment for a homonuclear CH₃-CH₂ system in the slow motion limit, derived from general equations given by Macura and Ernst^[34]:

$$I(\tau_m) = K \cdot [3 + 2 \exp(-5q\tau_c\tau_m)] \quad (6)$$

where $I(\tau_m)$ is the monitored line intensity, K is a constant, q is the coupling strength, τ_c is the correlation time of the molecular motion giving rise to the cross-relaxation, and τ_m is the mixing time. The q parameter was independently measured through the second moment of the ¹H line recorded below T_g under static conditions^[9] to be 11.7 kHz² for PBMA, 8.3 kHz² for PBMA13C and 11.7 kHz² for PHMA13C (data not shown^[31]).

It is observed in both cases that the dependence on inverse temperature is nearly linear over the studied temperature range. Linear regressions of the extracted correlation times yielded activation energies of 30 and 17 kJ·mol⁻¹ for the samples PBMA (together with PBMA13C), and PHMA13C respectively. It has then been discussed previously^[9] that the CH₃-CH₂ model used to fit the NOE data is rigorously valid only for the partially deuterated poly(ethyl methacrylate) sample PEMADMC. However, to our knowledge, no analytical equation is available for moieties larger than two groups of equivalent nuclei. Therefore, the correlations times extracted for samples PBMA, PBMA13C and PHMA13C should be interpreted with care.

Interpretation for all poly(*n*-alkyl methacrylates)

The correlation times τ_c measured by NOE are plotted together with literature ones^[7] obtained by NMR, dielectric and mechanical relaxation for both samples (Figure 6, all numerical values are given in Supporting Information). Note that the ¹³C labeling on 20 % of the carbonyl groups do not have a significant influence on the NOE experiment, as shown for samples PBMA and PBMA13C. A linear dependence of the determined correlation time upon

inverse temperature is observed for all samples in the temperature range studied. This should not, however, be taken as evidence for a simple local Arrhenius-type relaxation. Linear regressions of all concerned correlation and relaxation times as a function of temperature were done, and the results are detailed in supporting information, including the poly(ethyl methacrylate) samples measured previously.^[9]

In poly(*n*-alkyl methacrylates), the presence of local order gives rise to highly anisotropic motions in the melt; the isotropization relaxation process, detected by independent advanced solid-state NMR methods, was defined as the time scale on which the highly anisotropic motion of the main chain linked to local order and conformational memory are averaged.^[5-8] It was previously observed that the slow process quantified by NOE for PEMA occurs on the time scale of the isotropization of the main chain.^[9] Furthermore, the dipolar filter mostly selects the CH₃ end group of the alkyl side group, thus the NOE experiments detects local motions of that CH₃ end group together with the next CH₂ groups(s), i.e. local reorientation in the side groups. From Figure 3 of ref. ^[6] and Figure 9 of ref. ^[9] it is clear that in PEMA the isotropization process is considerably slower than both the conventional α - and $\alpha\beta$ -relaxations detected by conventional relaxation spectroscopy. Moreover, in the temperature range where the NOE experiment is applied, i.e. about 60 to 110 K above T_g , the quasi linear dependence of correlation time of isotropization on inverse temperature coincides with the extrapolated values for the β -relaxation. Indeed, the apparent activation energy of the slow process detected by NOE, 27 kJ·mol⁻¹, is similar to that of the β -relaxation (27 kJ·mol⁻¹ to 31 kJ·mol⁻¹). Therefore, the process detected by NOE is assigned to reorientations of parts of the side chains following the isotropization of the main chain. This indicates that the local nanodomains restrict the motion of the side chains being part of it. They then reorient or reorganize together with the nanodomain. It is remarkable that the NOE with dipolar filter method can detect such a collective process, involving distinct polymer chains.

For the PBMA and PHMA samples, a similar argumentation can be conducted. The main difference is that the slow process detected by NOE experiment moves away from the collective isotropization relaxation process with increasing side chain length (the respective activation energies are ca 30 kJ·mol⁻¹ and 50 kJ·mol⁻¹ for PBMA samples, 17 and ca 50 kJ·mol⁻¹ for PHMA samples). This is in agreement with the arguments developed above, considering that the NOE would detect both local reorientations within alkyl side chains, and collective motions of distinct polymer chains involved in the reorganization of nanodomains. Indeed, with increasing side chain length, the number of local modes exhibiting a lower activation energy than the isotropization of the main chain increases, thus decreasing the correlation time and activation energy of the slow process detected by NOE. Finally, for PHMA samples only one process is detected, which is in accordance with the very similar correlation times of the $\alpha\beta$ -relaxation and of the isotropization processes.

Note that there might be a connection between the slow process observed by NOE here and the α_{PE} relaxation process observed by Beiner *et al.*,^[2, 35] since both are linked to the presence of nanodomains. However, the α_{PE} process occurs in the glassy state while the one observed by NOE occurs in the melt.

Comparison of poly(*n*-alkyl methacrylates) with poly(*n*-alkyl acrylates)

As a similar study was previously conducted in polyacrylate samples,^[17] it is relevant to compare here the findings obtained on those chemically similar families of polymers. Above $T_g + 20$ K, the poly(*n*-alkyl acrylates), PnAAs, are more mobile than the poly(*n*-alkyl methacrylates), PnAMAs. This is indicated first by a lower full width at half maximum of ¹H static spectra as a function of temperature distance to T_g ,^[31] due to the broader glass transition in PnAMAs.

It is also indicated by the line shape of the C=O signal in ¹³C static spectra. A large axial-symmetric C=O tensor in the case of poly(ethyl methacrylate) (PEMA) below $T_g + 100$

K indicates a highly anisotropic motion of the main chain.^[5] It has been assigned to conformational memory^[6] and its averaging was assigned to the isotropization process. In fact, the temperature dependent line shapes were successfully fitted assuming random angular jumps with a single correlation time. The decrease in correlation time for the PnAAs is reflected in the motional narrowing of the CSA tensor. Figure 7 shows the evolution of the static C=O tensor line shape with temperature for poly(ethyl acrylate) (PEA): a narrower, nearly isotropic symmetric tensor line is observed above $T_g + 30$ K. Thus the motional narrowing occurs at temperature difference from T_g significantly lower for PEA than for the PEMA, indicating a lower anisotropy of the main chain motions at the same distance to T_g . This indicates stronger constraints in the PEMA structure.

The similarities and differences between PnAMAs and PnAAs, observed in terms of structure by X-ray scattering and in terms of dynamics by solid-state NMR, are summarized in Table 3. They show that similar local structures are present in PnAAs and PnAMAs, with a better organization in PnAMAs (more regular and less flexible structure), associated with stronger anisotropy of motions. It is expected that PnAMAs are better organized than PnAAs for three reasons. First, their tacticity is different: PnAAs are atactic while PnAMAs are highly syndiotactic when produced by free-radical polymerization. The higher tacticity of PnAMAs (65 ± 7 % of syndiotactic triads) should lead to a higher tendency to order. Second, the PnAAs exhibit chain branching (a few percents of the monomeric units^[31]), while chain branching has never been reported in PnAMAs. Order should be disturbed around the branching points. Third, the PnAMA backbone contains a CH_3 group where the PnAA backbone contains a less bulky hydrogen. Therefore, the PnAA backbone is much more flexible than the PnAMA one.

An idealized structure can be proposed for the PnAAs and PnAMAs^[8] (Figure 8), inspired by the packing of model hairy rods.^[36] The shown slices must be repeated to obtain a local structure, with alternating layers of side chains and main chains^[8, 20] or with

nanodomains of side chains separated by main chains.^[37] We emphasize here that these structures are idealized, in reality the order is much lower.^[8] Moreover, this structure is valid only for a few monomeric units long along the backbone.^[7]

Finally, an interesting property was observed for the relaxation process measured by NOE. Although the measured correlation times depend on the alkyl side chain length, they become sample-independent for the PnAMAs when plotted as a function of the temperature difference to the T_c (where T_c is the crossover temperature at which the α - and β -relaxation processes merge, see supporting information for values), not as a function of the temperature difference to the T_g (Figure 9). For the PnAAs, they became sample-independent when plotted as a function of the temperature difference to the T_g .^[9] The reason for this is not understood yet.

Conclusion

Poly(*n*-alkyl methacrylates) of high molar mass, as determined by SEC and Mark-Houwink-Kuhn-Sakurada parameters, were investigated with a recently developed solid-state NMR method (NOE with dipolar filter),^[9] in the melt. The selection achieved by the dipolar filter is based on mobility, and the following magnetization transfer occurs via non coherent cross-relaxation or NOE. The correlation times of the processes detected by the NOE experiment were interpreted in the context of local nanophase separation in PnAMAs. The correlation times of the slow process quantified by the NOE measurements in the present work has been assigned to the relaxation of the alkyl nanodomains, as coupled motions of the main chain and of hindered local modes in the side chain. Furthermore, the above described NOE experiment may indirectly detect the nanophase separation in PnAMAs via a biexponential behavior of the recorded magnetization decay, on the temperature range where the nanophase separation results in strong anisotropic chain motions.

Comparison with poly(*n*-alkyl acrylates) showed a higher anisotropy of the main chain motions at the same distance to T_g , associated with a better organized local nanophase

separation in the poly(*n*-alkyl methacrylates). More order is expected in the methacrylate family as a result of higher tacticity, absence of branching and more flexible backbone. An idealized local structure is proposed.

Acknowledgements

M.G. thanks the Arkema company (Total group) for financial support and Dr Patrice Castignolles for discussions about molar mass determination. We thank Uta Pawelzik for samples synthesis (in particular the synthesis of selectively labeled monomers), Dr Michael Wind and Dr Mario Beiner for sample characterizations and for fruitful discussions, Manfred Hehn and Hans-Peter Raich for technical help with the NMR spectrometers.

References

- [1] R. L. Miller, R. F. Boyer, J. Heijboer, *J. Polym. Sci. B Polym. Phys.* **1984**, *22*, 2021.
- [2] M. Beiner, H. Huth, *Nature Mater.* **2003**, *2*, 595.
- [3] K. L. Ngai, T. R. Gopalakrishnan, M. Beiner, *Polymer* **2006**, *47*, 7222.
- [4] K. Schmidt-Rohr, H. W. Spiess, "*Multidimensional solid-state NMR and polymers*", 1st ed., Academic Press Ltd, San Diego, USA, 1994, p. 496.
- [5] M. Wind, L. Brombacher, A. Heuer, R. Graf, H. W. Spiess, *Solid State Nucl. Mag. Reson.* **2005**, *27*, 132.
- [6] M. Wind, R. Graf, A. Heuer, H. W. Spiess, *Phys. Rev. Lett.* **2003**, *91*, 1557021.
- [7] M. Wind, R. Graf, S. Renker, H. W. Spiess, *Macromol. Chem. Phys.* **2005**, *206*, 142.
- [8] M. Wind, R. Graf, S. Renker, H. W. Spiess, W. Steffen, *J. Chem. Phys.* **2005**, *122*, 0149061.
- [9] M. Gaborieau, R. Graf, H. W. Spiess, *Solid State Nucl. Magn. Reson.* **2005**, *28*, 160.
- [10] J. L. White, P. Mirau, *Macromolecules* **1993**, *26*, 3049.
- [11] P. A. Mirau, H. Tanaka, F. A. Bovey, *Macromolecules* **1988**, *21*, 2929.
- [12] S. S. Hou, R. Graf, H. W. Spiess, P. L. Kuo, *Macromol. Rapid Commun.* **2001**, *22*, 1386.
- [13] K. Schmidt-Rohr, H. W. Spiess, *Macromolecules* **1991**, *24*, 5288.
- [14] X. H. Qiu, N. E. Moe, M. D. Ediger, L. J. Fetters, *J. Chem. Phys.* **2000**, *113*, 2918.
- [15] T. Fritzmann, S. Hafner, D. E. Demco, H. W. Spiess, F. H. Laukien, *J. Magn. Reson.* **1998**, *134*, 355.
- [16] M. Pollard, K. Klimke, R. Graf, H. W. Spiess, M. Wilhelm, O. Sperber, C. Piel, W. Kaminsky, *Macromolecules* **2004**, *37*, 813.
- [17] M. Gaborieau, R. Graf, S. Kahle, T. Pakula, H. W. Spiess, *Macromolecules* **2007**, *40*, 6249.
- [18] Y. Guillaneuf, P. Castignolles, *J. Polym. Sci. A Polym. Chem.* **2008**, *46*, 897.
- [19] S. C. Kuebler, "*Molekulare Dynamik und Anisotropie polymerer und flüssigkristalliner Materialien*", Ph.D. thesis, Johannes Gutenberg University, Mainz, Germany, 1996,
- [20] M. Wind, "*Festkörper NMR Spektroskopie: Anisotrope Dynamik polymerer Schmelzen und dendritischer Systeme*", Ph.D. thesis, Johannes Gutenberg University, Mainz, Germany, 2001,
- [21] A. S. Kulik, H. W. Beckham, K. Schmidt-Rohr, D. Radloff, U. Pawelzik, C. Boeffel, H. W. Spiess, *Macromolecules* **1994**, *27*, 4746.
- [22] S. C. Kuebler, D. J. Schaefer, C. Boeffel, U. Pawelzik, H. W. Spiess, *Macromolecules* **1997**, *30*, 6597.
- [23] H. Benoit, Z. Grubisic, P. Rempp, D. Decker, J. G. Zilliox, *Journal De Chimie Physique* **1966**, *63*, 1507.
- [24] Z. Grubisic, P. Rempp, H. Benoit, *J. Polym. Sci. B Polym. Lett.* **1967**, *5*, 753.
- [25] Z. Grubisic, P. Rempp, H. Benoit, *J. Polym. Sci. B Polym. Phys.* **1996**, *34*, 1707.
- [26] Y. Guillaneuf, D. Bertin, P. Castignolles, B. Charleux, *Macromolecules* **2005**, *38*, 4638.
- [27] S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, A. Kajiwara, B. Klumperman, G. T. Russell, *Macromol. Chem. Phys.* **2000**, *201*, 1355.
- [28] S. Aqeel, D. Lath, E. Lathova, J. Pavlinec, I. Lacik, *Polym. Bull.* **2002**, *47*, 563.
- [29] R. J. Bruessau, *Macromol. Symp.* **1996**, *110*, 15.
- [30] D. Cho, I. Park, T. Chang, K. Ute, I. Fukuda, T. Kitayama, *Macromolecules* **2002**, *35*, 6067.
- [31] M. Gaborieau, "*Solid-state NMR investigation of spatial and dynamic heterogeneity in acrylic pressure sensitive adhesives (PSAs) compared to model poly(n-alkyl acrylates) and poly(n-alkyl methacrylates)*", PhD thesis, University Louis Pasteur, Strasbourg, France, 2005, <http://eprints-scd-ulp.u-strasbg.fr:8080/301/>.
- [32] M. Lee, W. I. Goldberg, *Phys. Rev.* **1965**, *140*, A1261.

- [33] D. E. Demco, S. Hafner, C. Fulber, R. Graf, H. W. Spiess, *J. Chem. Phys.* **1996**, *105*, 11285.
- [34] S. Macura, R. R. Ernst, *Mol. Phys.* **2002**, *100*, 135.
- [35] K. L. Ngai, M. Beiner, *Macromolecules* **2004**, *37*, 8123.
- [36] A. Adam, H. W. Spiess, *Makromol. Chem. Rapid Commun.* **1990**, *11*, 249.
- [37] M. Beiner, *Macromol. Rapid Commun.* **2001**, *22*, 869.

Tables, Figures, Schemes, Formulas

Table 1. Mark-Houwink-Kuhn-Sakurada (MHKS) parameters for investigated PnAMAs in THF at 30 °C. [27, 28]

Sample	$K \cdot 10^5$ ($\text{dL} \cdot \text{g}^{-1}$)	α
PMMA	9.44	0.719
PEMA	9.70	0.714
PBMA	14.8	0.664
PHMA	1.94	0.76

Table 2. Molar masses of the model PnAMAs in $\text{g} \cdot \text{mol}^{-1}$; the error is calculated with respect to the average of the two values.

Sample	Apparent molar masses from PMMA calibration: ^[19, 20]			True molar masses from Equation (3):			Difference (%) on:	
	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	M_n	M_w
PEMA	112 900	153 300	1.36	115 000	156 200	1.36	1.8	1.9
PEMA13C	54 500	120 000	2.20	55 400	122 200	2.21	1.6	1.8
PEMADSG	117 100	170 000	1.46	119 300	173 300	1.45	1.8	1.9
PEMADMC	76 400	105 700	1.38	77 700	107 600	1.38	1.7	1.8
PBMA	44 600	80 400	1.80	48 500	89 100	1.84	8.7	9.8
PBMA13C	125 700	203 300	1.83	141 400	232 400	1.64	11.8	13.4
PHMA13C	129 800	278 800	2.15	65 500	138 300	2.11	-65.8	-76.4

Table 3. Comparison of the structural and dynamic features detected respectively with wide-angle X-ray scattering (WAXS) and solid-state NMR in static conditions, for poly(*n*-alkyl methacrylates), PnAMAs (this work and ref. ^[2, 5, 7-9]), and poly(*n*-alkyl acrylates), PnAAs (this work and ref. ^[1, 17, 31]).

Method	Feature	PnAMAs	PnAAs
WAXS	nanostructure	yes	yes
WAXS	correlation between side chains in their domains	yes	no
¹³ C NMR	anisotropic main chain motion	high	low
¹ H NMR	mobility above T_g+20 K	lower	higher

Figure 1. Non isotope labeled poly(*n*-alkyl methacrylates): PEMA (x=2), PBMA (x=4), PHMA (x=6).

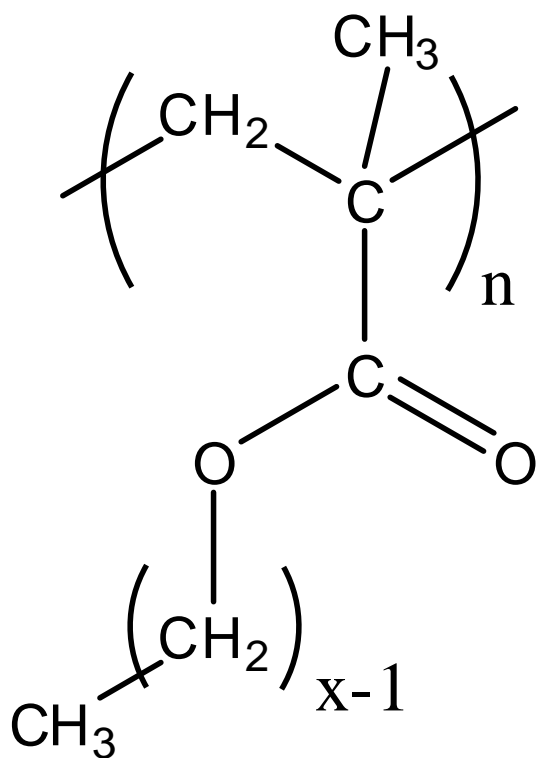


Figure 2. Pulse scheme of the NOE experiment with dipolar filter, adapted from ref. [9].

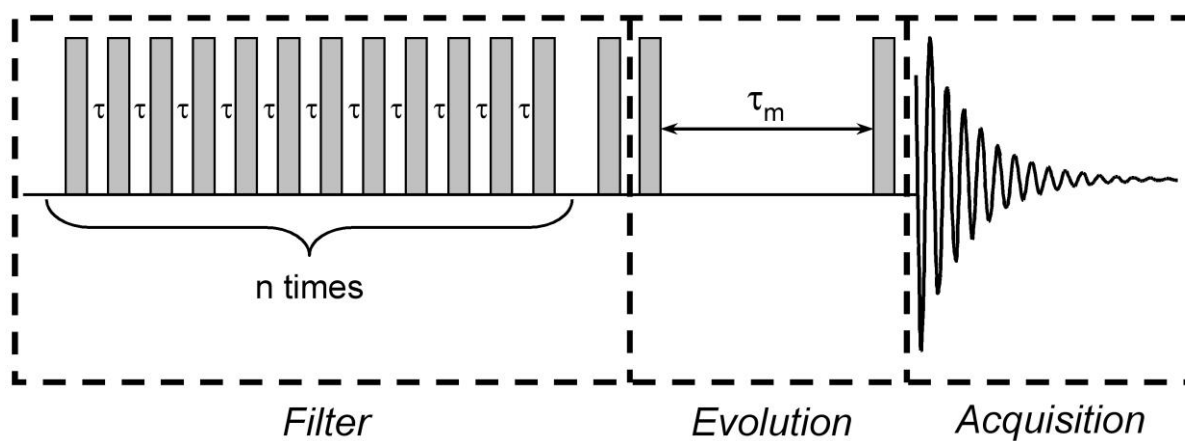


Figure 3. Influence of the temperature on the shape of the ^1H spectrum of sample PBMA (recorded under static conditions).

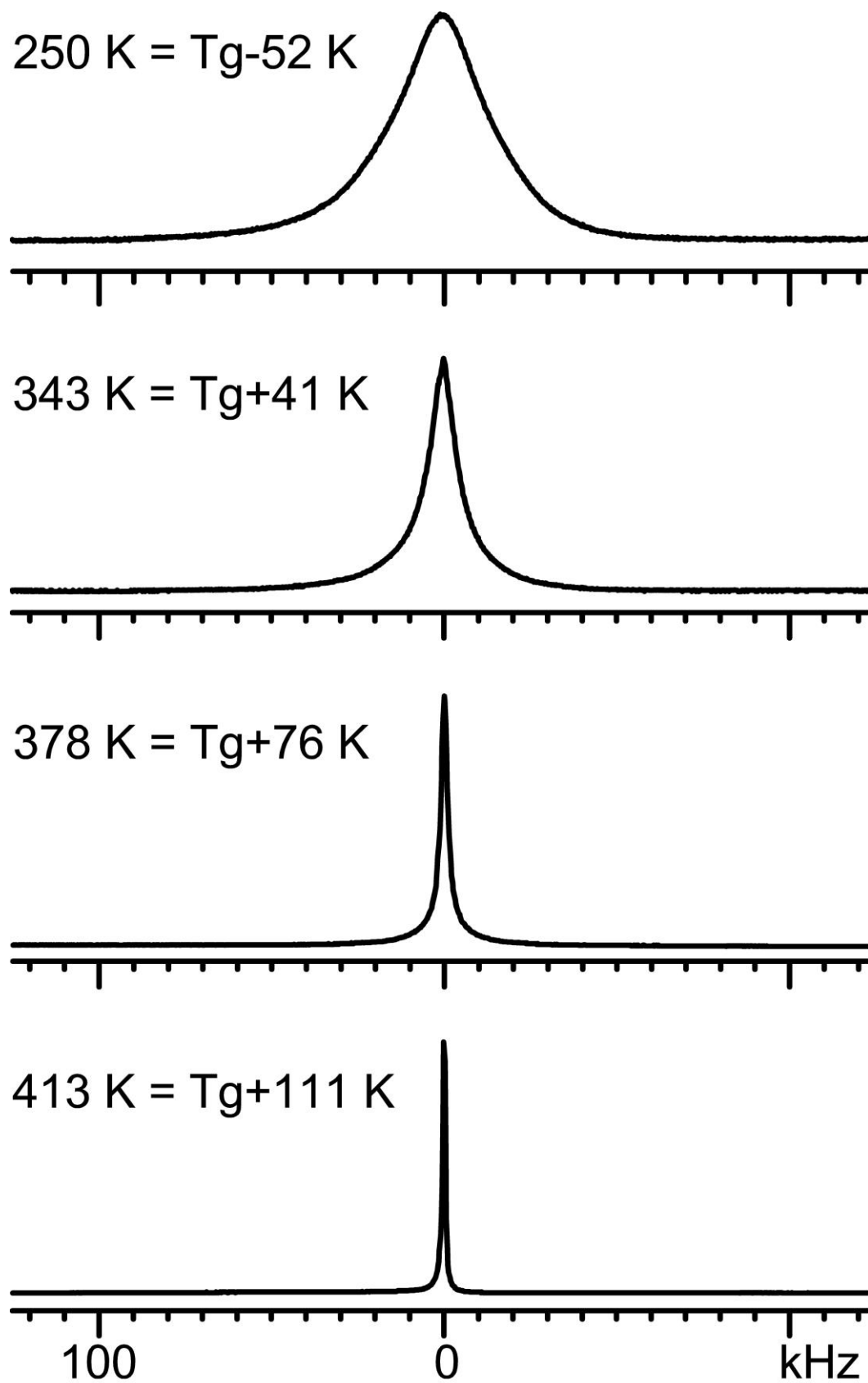


Figure 4. ^{13}C LG-CP spectra of sample PBMA at ca 370 K (ca T_g+70 K) at 75.47 MHz under 3 kHz MAS with 500 μs contact time; (a) LG-CP; (b) dipolar filter with 15 μs delay and 1 cycle, no mixing time and LG-CP; (c) dipolar filter with 15 μs delay and 1 cycle, 5 ms mixing time and LG-CP; (d) dipolar filter with 15 μs delay and 1 cycle, 50 ms mixing time and LG-CP; the abbreviations MC and SC designate main chain and side chain respectively.

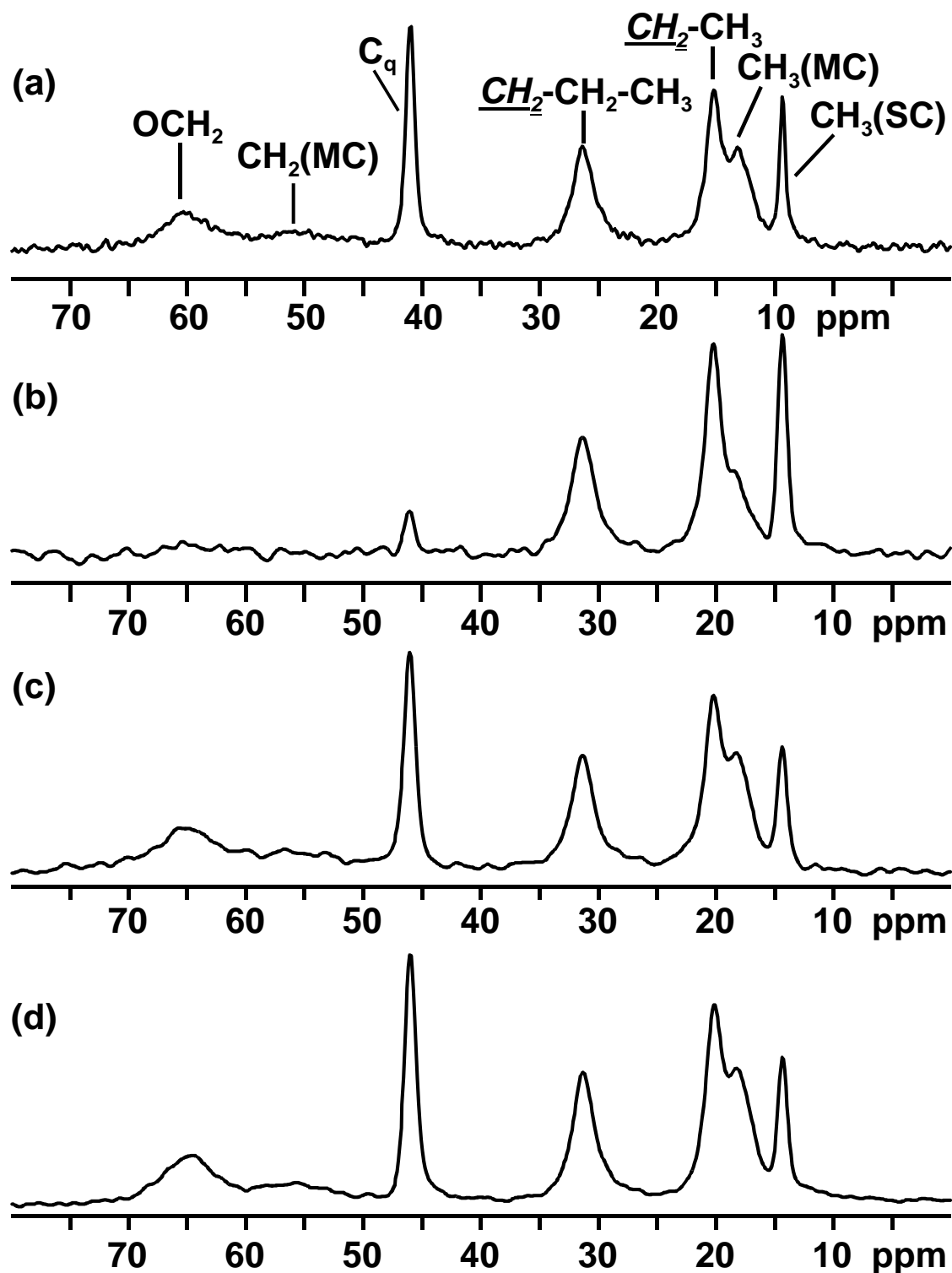


Figure 5. Evolution of the ^1H magnetization of mobile species for the sample PBMA at 402 K ($T_g + 100$ K): with the square of the mixing time on a linear scale (top), with the mixing time on a logarithmic scale (bottom). Each curve corresponds to a different set of parameters for the filter (delay between pulses, number of cycles).

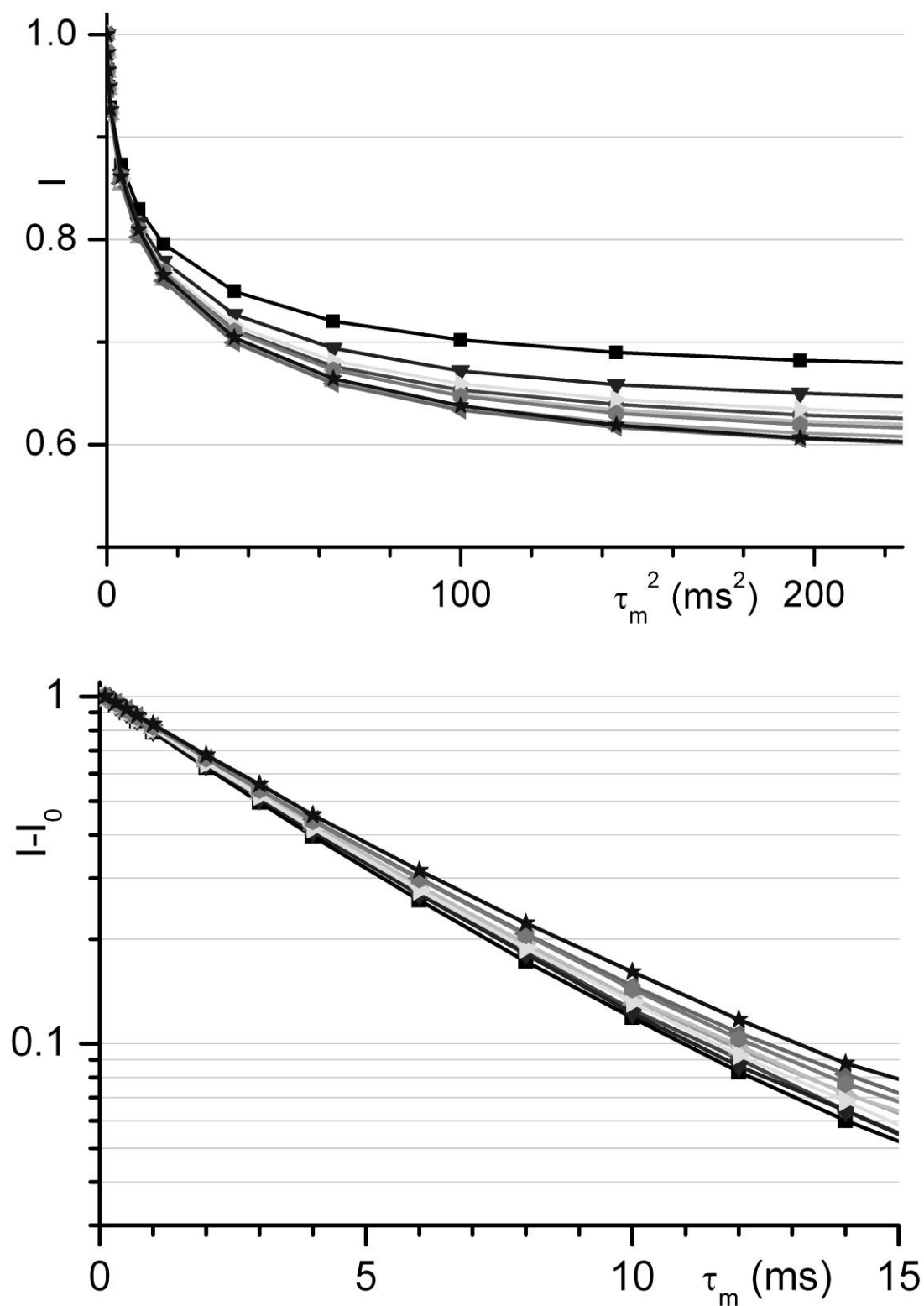


Figure 6. Arrhenius plot of the correlation times extracted for samples PBMA (a) and PHMA (b) using the solid-state NMR experiment with dipolar filter: single process (or slow process) for non-labeled sample (\blacktriangle), fast process for non-labeled sample (\blacktriangledown , estimate), slow process for ^{13}C labeled sample (\times). Literature data obtained by ^{13}C solid-state NMR, photocorrelation spectroscopy, rheology and dielectric spectroscopy are indicated as hollow symbols and small crosses^[7] for comparison.

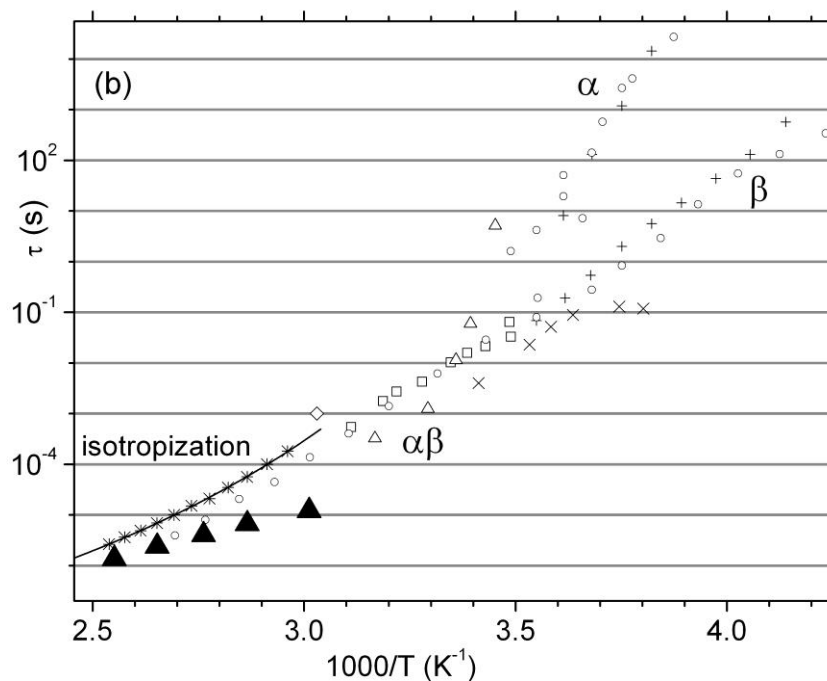
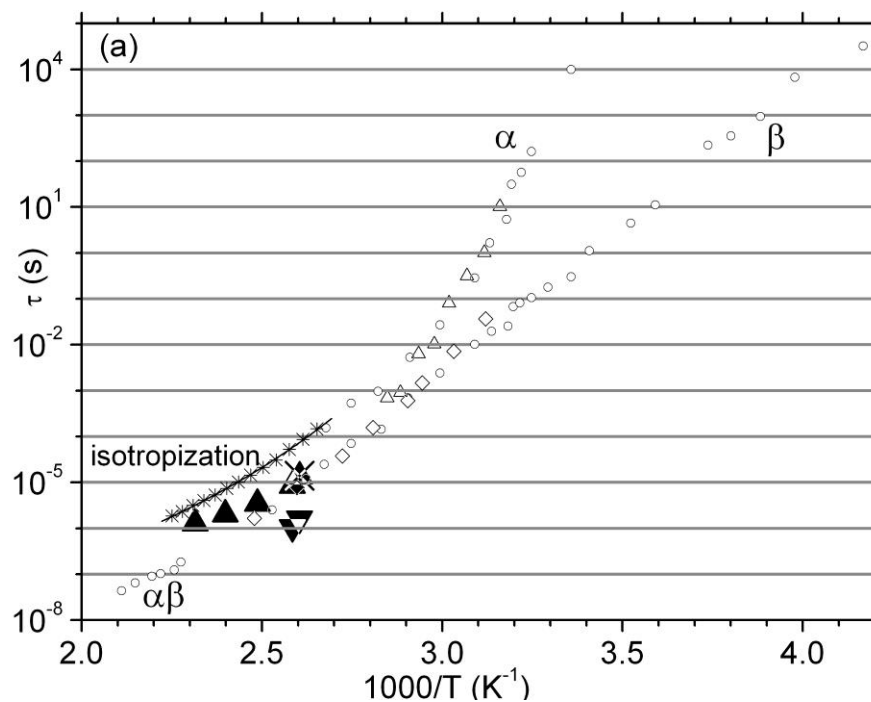


Figure 7. Evolution of the static C=O tensor line shape with temperature for poly(ethyl acrylate) measured by ^{13}C NMR.

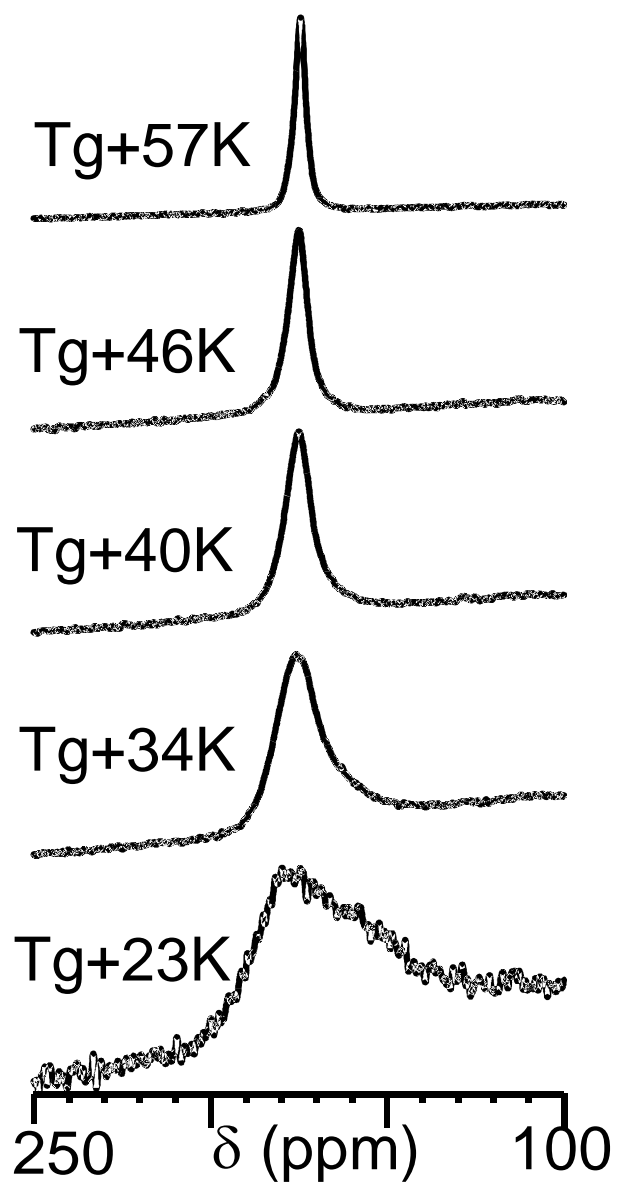


Figure 8. Idealized local structure proposed for PnAAs and PnAMAs; the shown slices must be repeated to obtain alternating layers of side chains and main chains^[8, 20] or nanodomains of side chains separated by main chains.^[37] Note that this structure is valid only for a few monomeric units long along the backbone.^[7]

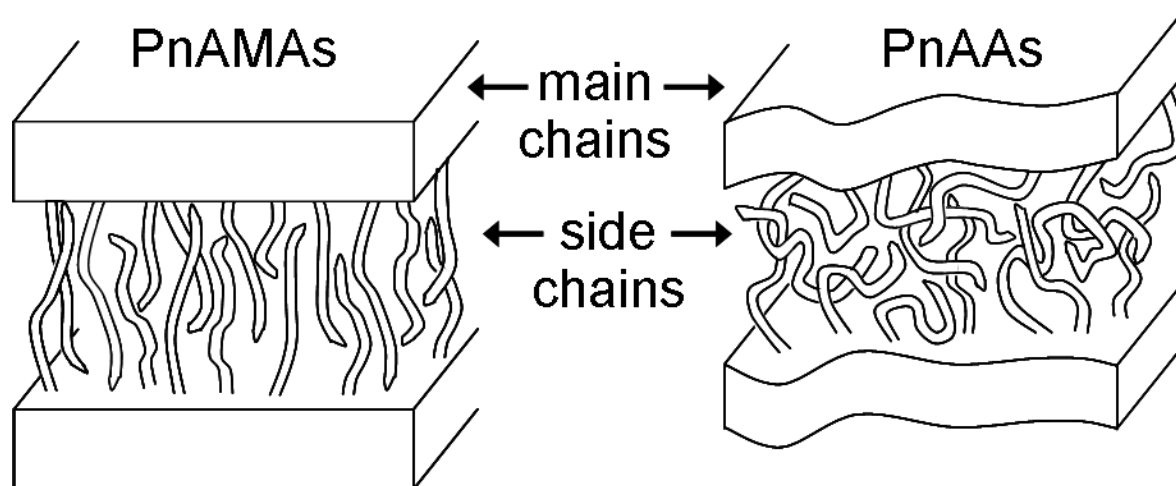


Figure 9. Correlation times extracted for samples PEMA (□), PEMADMC (○), PBMA (Δ), PBMA13C (×) and PHMA (▽) using solid-state NMR experiment with dipolar filter, plotted versus (a) the temperature difference to the crossover transition temperature, (b) the temperature difference to the glass transition temperature. The lines are merely a guide for the eyes.

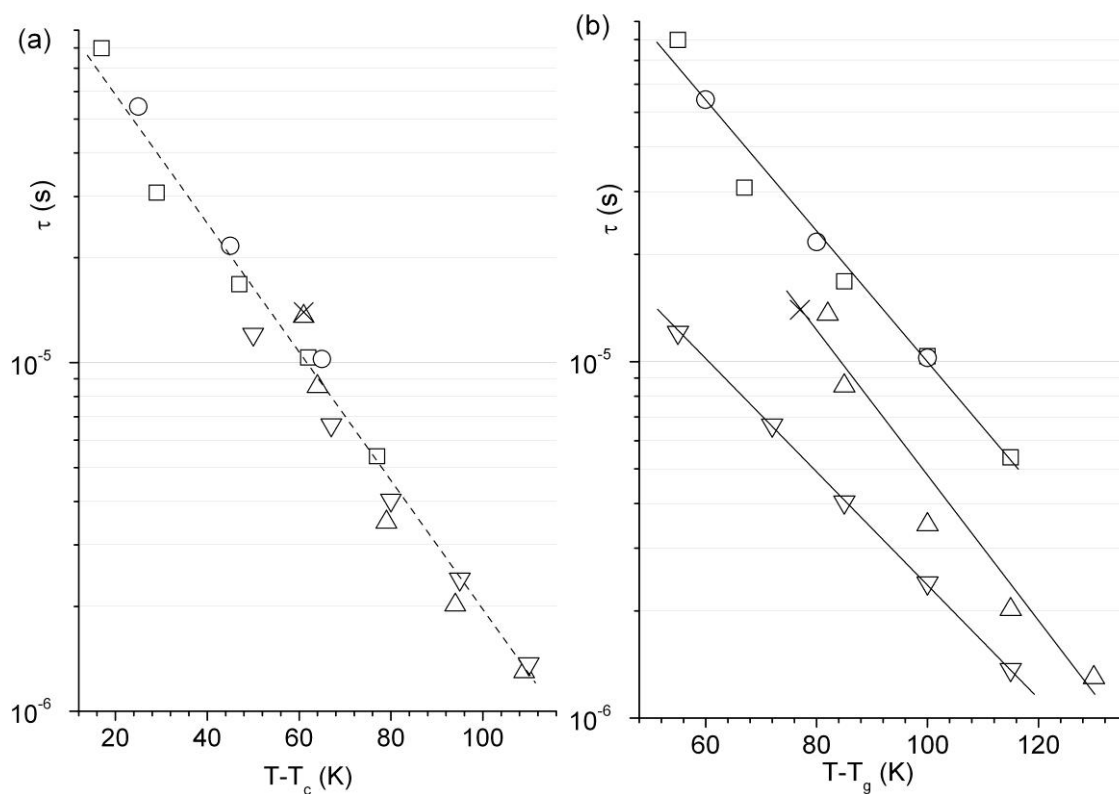
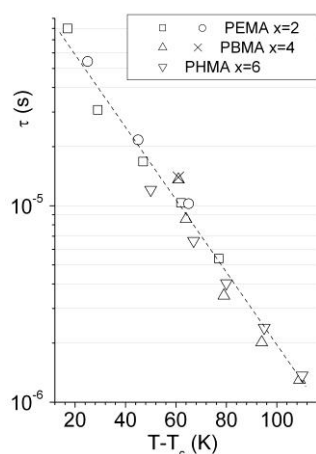
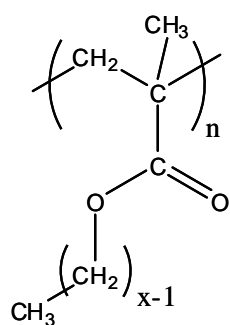


Table of contents



Poly(*n*-alkyl methacrylates) are investigated in the melt with a recently developed solid-state NMR method: NOE with dipolar filter. The correlation times of the detected processes are interpreted in the context of local nanophase separation as coupled motions of the main chain and of hindered local modes in the side chain. They exhibit a higher anisotropy of the main chain motions and a better organized local nanophase separation than the poly(*n*-alkyl acrylates).

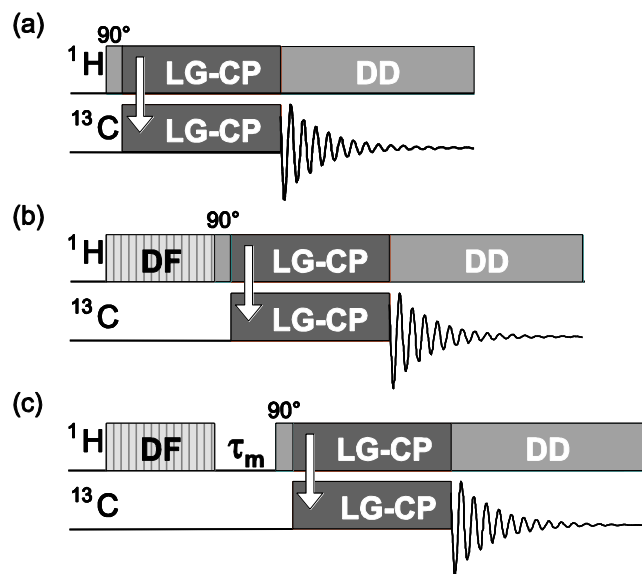
**Supporting Information for “Investigation of Chain Dynamics in Poly(*n*-alkyl methacrylates) by Solid-state NMR - Comparison with poly(*n*-alkyl acrylates)”,
by Marianne Gaborieau, Robert Graf and Hans Wolfgang Spiess,
in Macromolecular Chemistry and Physics**

Presentation and glass transition temperature of the studied poly(*n*-alkyl methacrylates)^[1]

More details can be found in the Ph.D. theses of Wind^[2] and Kuebler^[3], as well as in published articles^[4, 5].

<i>Sample</i>	<i>Polymer, label</i>	<i>T_g (K)</i>
PMMADMC	poly(methyl methacrylate), ² H on main chain (100 %)	398 (125 °C)
PEMA	poly(ethyl methacrylate), no label	342 (69 °C)
PEMA13C	poly(ethyl methacrylate), ¹³ C at C=O (20 %)	338 (65 °C)
PEMADSG	poly(ethyl methacrylate), ² H on side chain (100 %)	353 (80 °C)
PEMADMC	poly(ethyl methacrylate), ² H on main chain (100 %)	345 (72 °C)
PBMA	poly(<i>n</i> -butyl methacrylate), no label	302 (29 °C)
PBMA13C	poly(<i>n</i> -butyl methacrylate), ¹³ C at C=O (20 %)	307 (34 °C)
PHMA13C	poly(<i>n</i> -hexyl methacrylate), ¹³ C at C=O (20 %)	277 (4 °C)

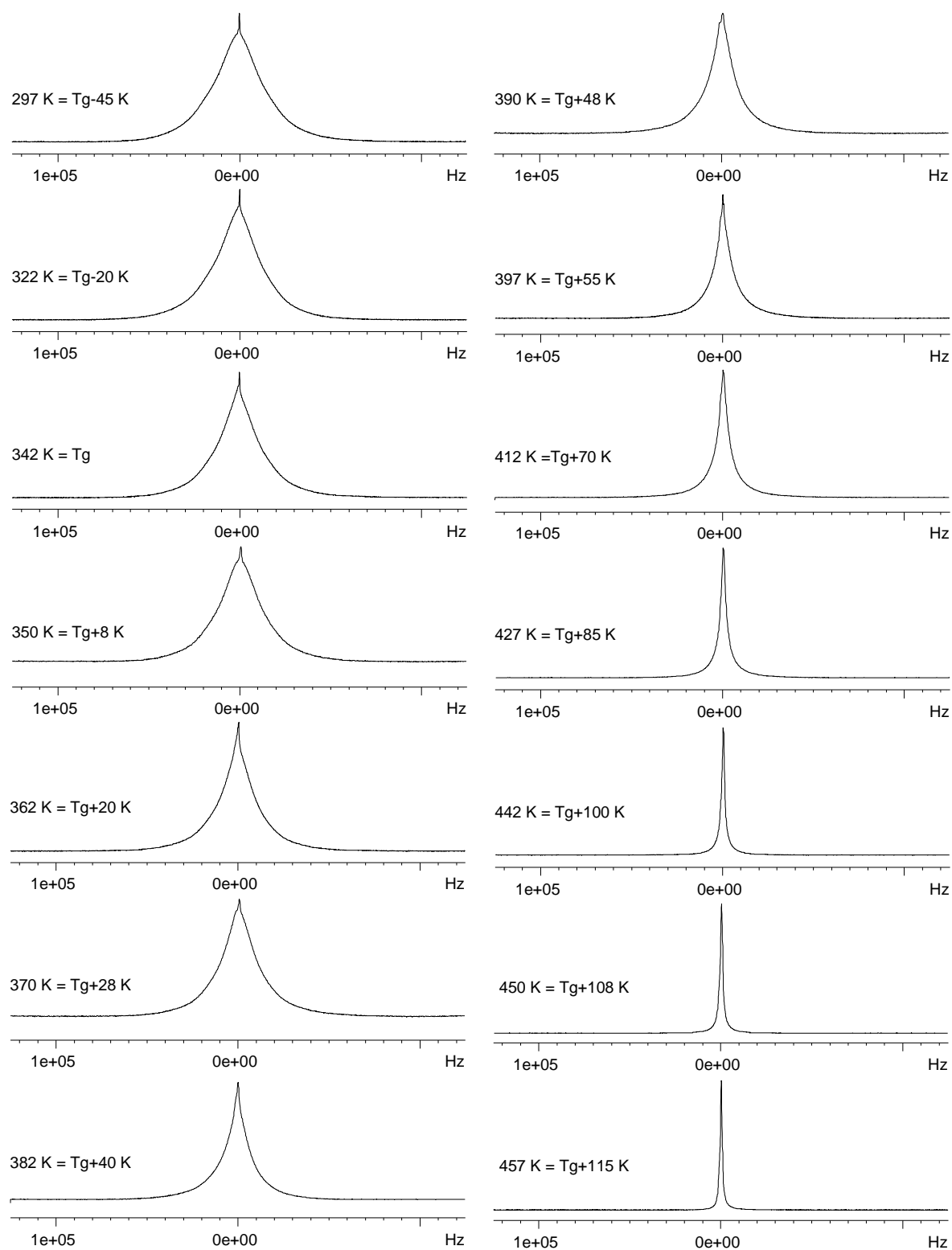
Pulse schemes for LG-CP experiments^[6]



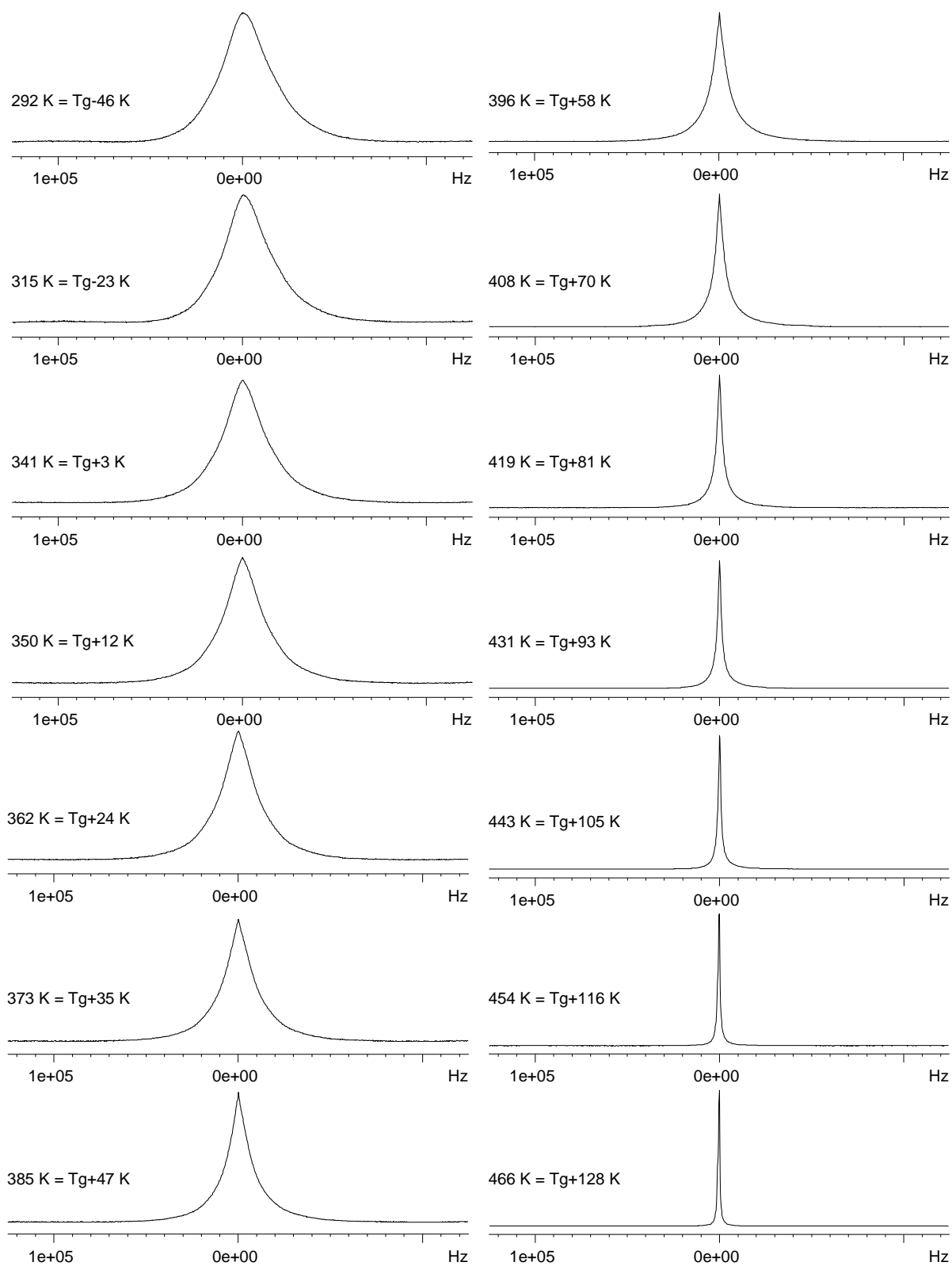
Influence of the temperature on the shape of the ^1H spectrum of poly(*n*-alkyl methacrylates) recorded under static conditions.

Selected spectra were shown for PEMA in [6] and for PBMA in the main text.

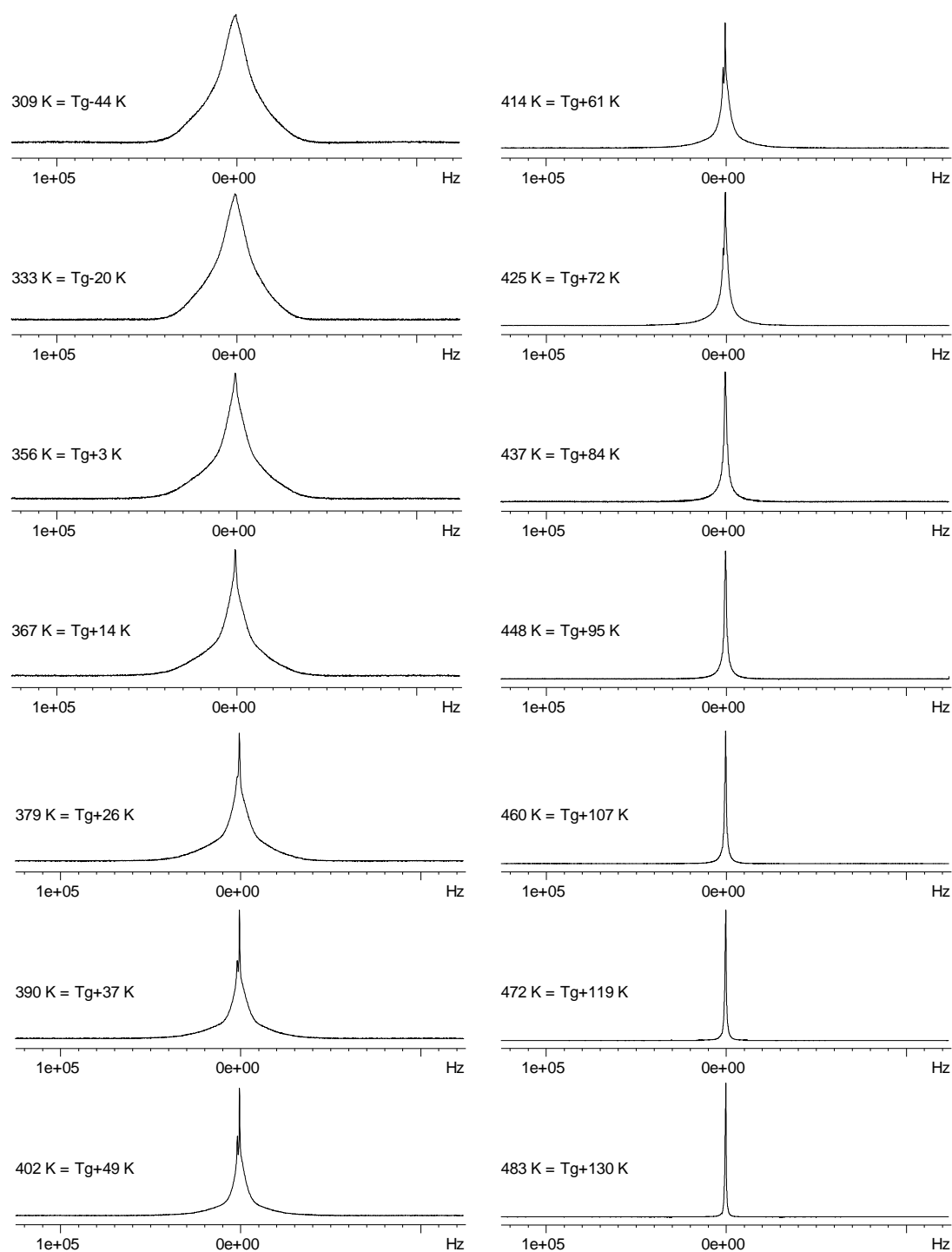
sample PEMA:



sample PEMA13C:

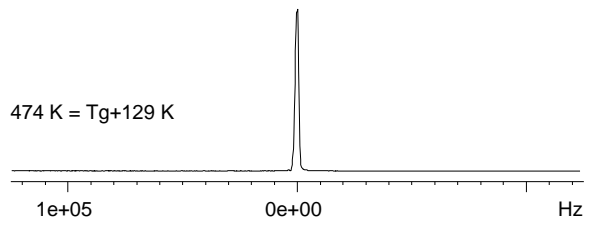
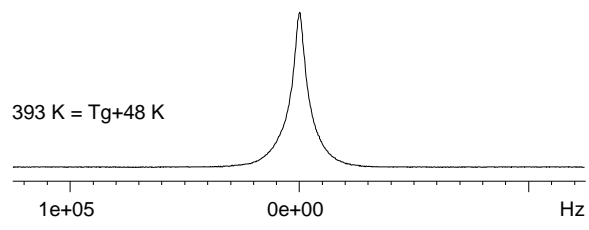
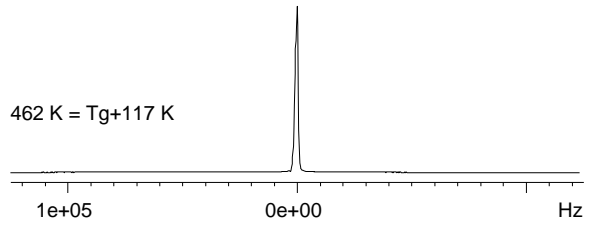
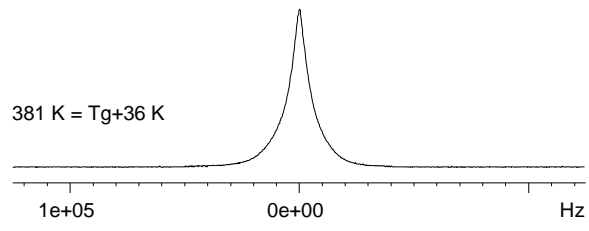
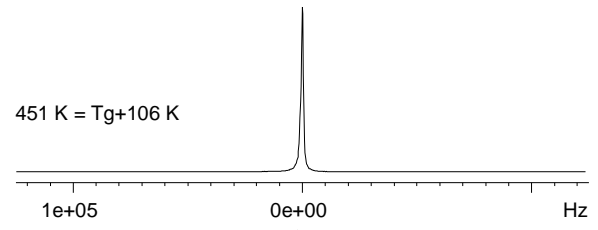
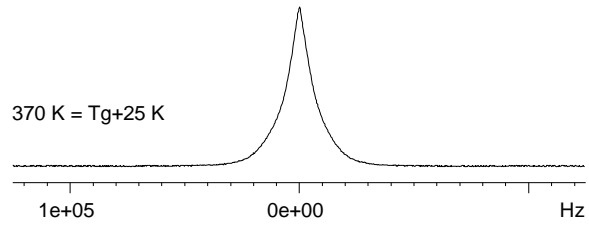
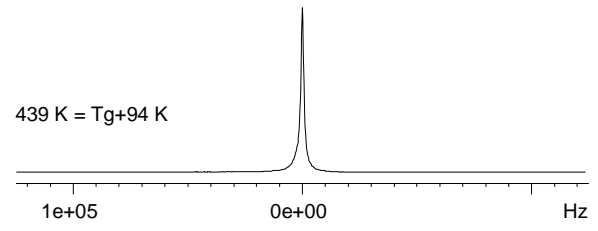
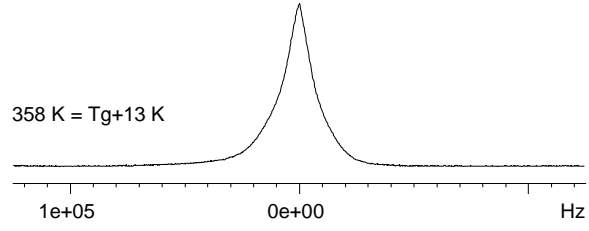
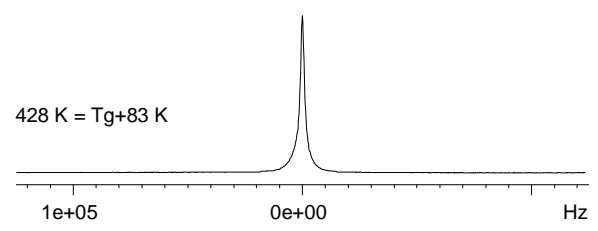
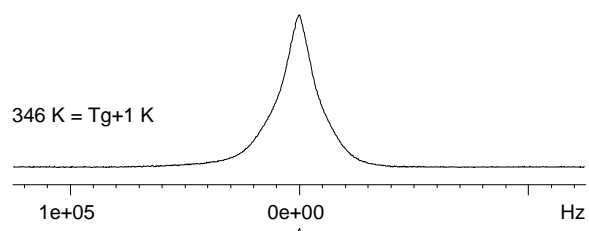
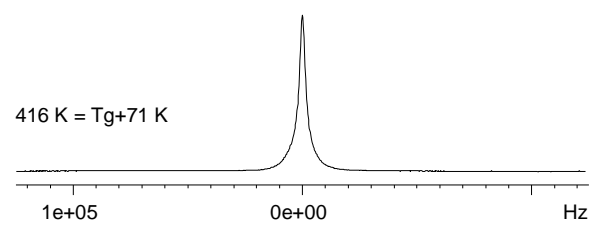
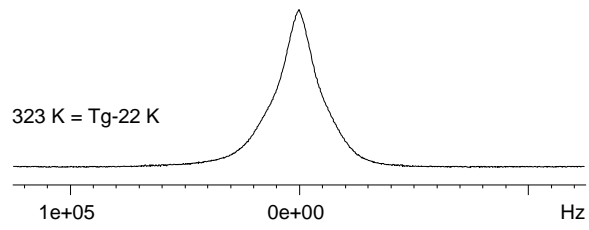
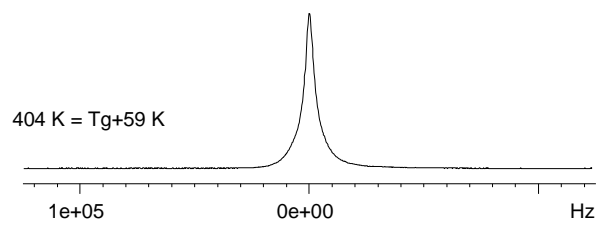
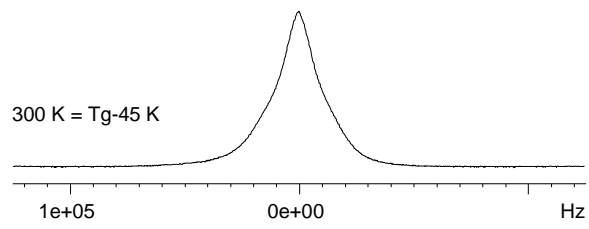


sample PEMADSG:

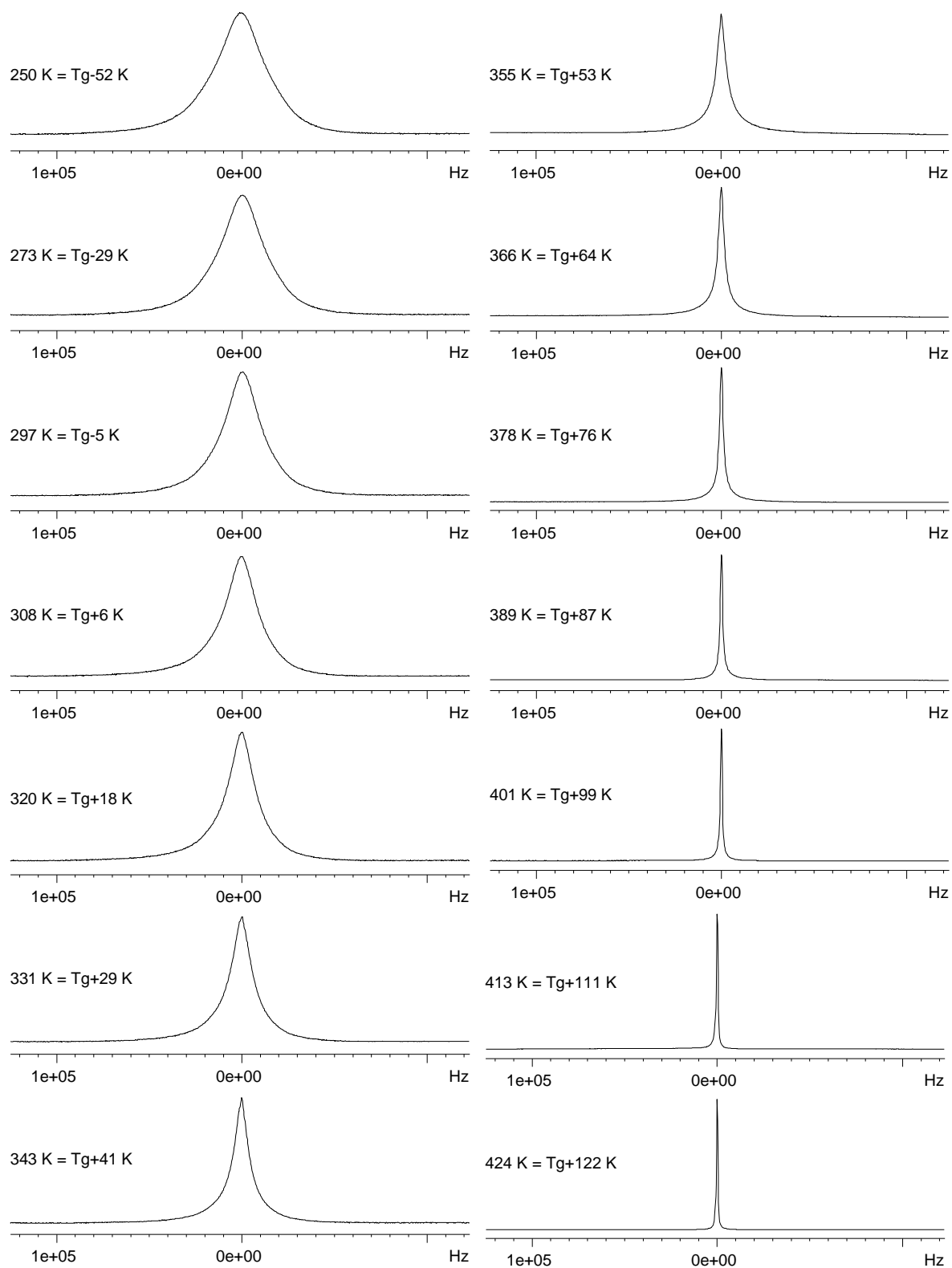


Note that for sample PEMADSG, the spectra were recorded using single pulse excitation followed by a solid echo^[7] in order to avoid artifacts coming from the absence of the first points of the FID; no line width was extracted for this sample.

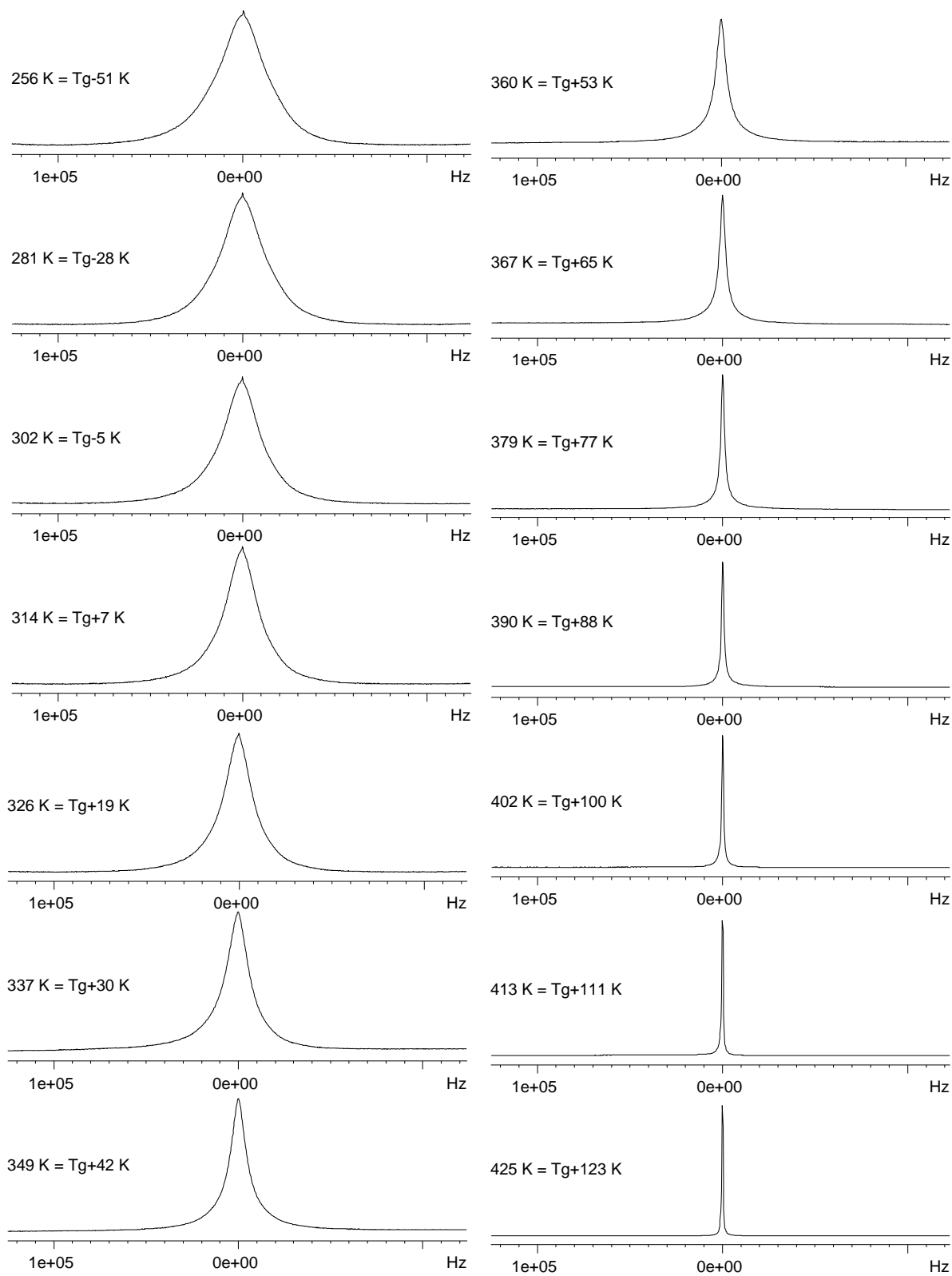
sample PEMADMC:



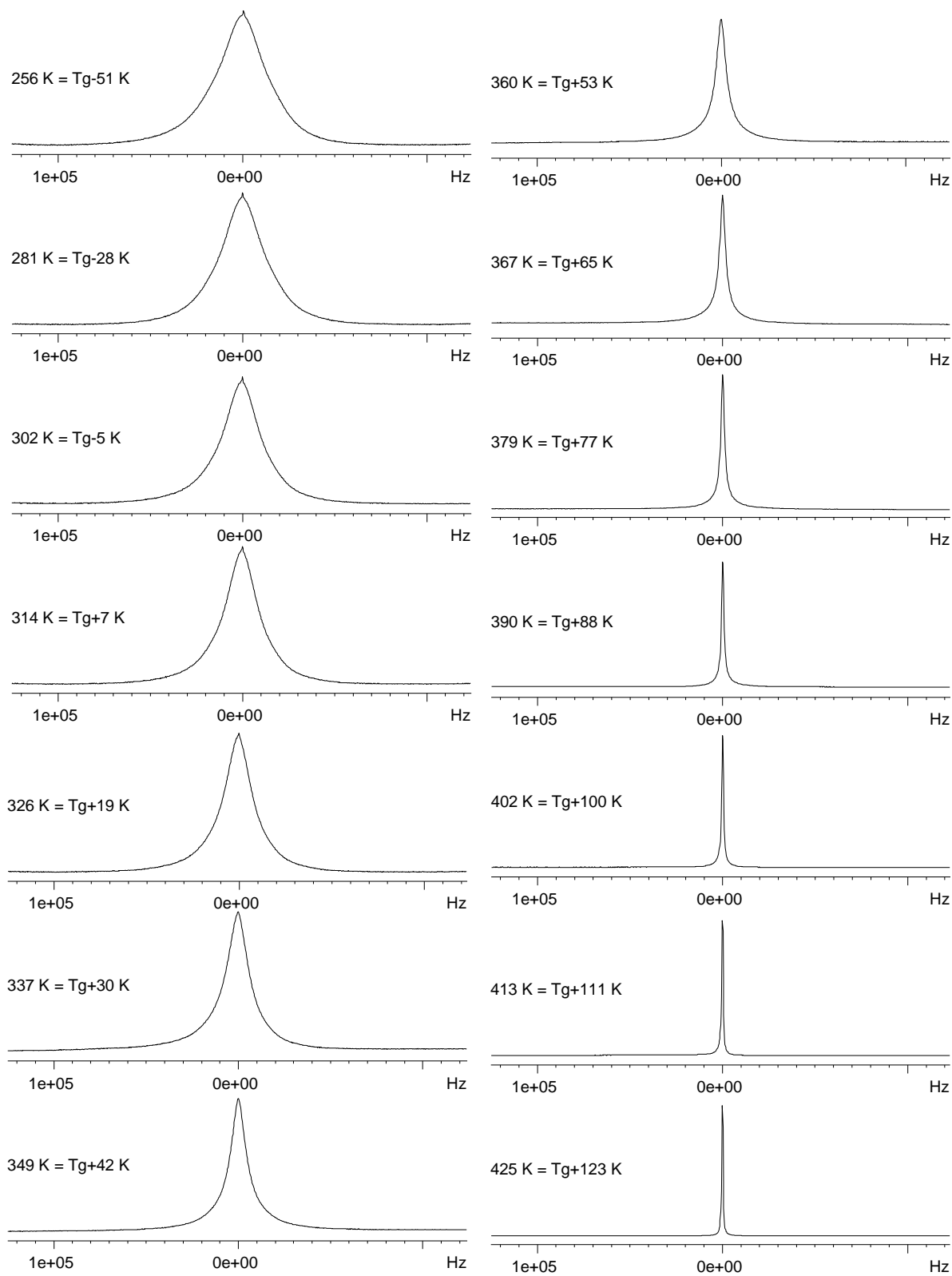
sample PBMA:



sample PBMA13C:



sample PHMA13C:



Correlation times τ_C determined with the NOE experiment with dipolar filter for all PnAMAs

<i>Sample</i>	<i>T (K)</i>	<i>T- T_g (K)</i>	<i>τ_C (s)</i>	<i>Nb. of exp.</i>
PEMA	397	55	$8.0 \cdot 10^{-5} \pm 1.6 \cdot 10^{-5}$ and $8.6 \cdot 10^{-6} \pm 7.1 \cdot 10^{-6}$	9
	409	67	$3.08 \cdot 10^{-5} \pm 9 \cdot 10^{-7}$	8
	427	85	$1.7 \cdot 10^{-5} \pm 1 \cdot 10^{-6}$	8
	442	100	$1.0 \cdot 10^{-5} \pm 1 \cdot 10^{-6}$	17
	457	115	$5.4 \cdot 10^{-6} \pm 5 \cdot 10^{-7}$	12
PEMADMC	405	60	$5.4 \cdot 10^{-5} \pm 1.3 \cdot 10^{-5}$ and $3.7 \cdot 10^{-6} \pm 5.6 \cdot 10^{-6}$	6
	425	80	$2.2 \cdot 10^{-5}$ and $5.4 \cdot 10^{-7}$	1
	445	100	$1.0 \cdot 10^{-5} \pm 1 \cdot 10^{-6}$	5
PBMA	384	82	$1.4 \cdot 10^{-5} \pm 4 \cdot 10^{-6}$ and $1.6 \cdot 10^{-6} \pm 2.3 \cdot 10^{-6}$	15
	38	85	$8.5 \cdot 10^{-6} \pm 2.6 \cdot 10^{-6}$ and $1.1 \cdot 10^{-6} \pm 1.1 \cdot 10^{-6}$	10
	402	100	$3.5 \cdot 10^{-6} \pm 3 \cdot 10^{-7}$	9
	417	115	$2.02 \cdot 10^{-6} \pm 6 \cdot 10^{-8}$	8
	432	130	$1.30 \cdot 10^{-6} \pm 8 \cdot 10^{-8}$	12
PBMA13C	384	77	$1.4 \cdot 10^{-5} \pm 1 \cdot 10^{-6}$	6
PHMA13C	332	55	$1.2 \cdot 10^{-5} \pm 1 \cdot 10^{-6}$	8
	349	72	$6.6 \cdot 10^{-6} \pm 5 \cdot 10^{-7}$	8
	362	85	$4.0 \cdot 10^{-6} \pm 4 \cdot 10^{-7}$	9
	377	100	$2.4 \cdot 10^{-6} \pm 1 \cdot 10^{-7}$	8
	392	115	$1.37 \cdot 10^{-6} \pm 8 \cdot 10^{-8}$	9

Arrhenius fits for NOE and β -relaxation processes for all PnAMAs

The fits were done according to the Arrhenius equation $\tau_c = A \cdot \exp\left(\frac{E_a}{RT}\right)$. R^2

designates the coefficient of determination.

Sample	Process	logA	A (s)	E_a/R	E_a (kJ.mol ⁻¹)	R^2	data from ref.
PEMA and PEMADMC	β -relaxation	-12.2	$6 \cdot 10^{-13}$	3.21	26.7	0.998	[8], \ominus O
		-13.7	$2 \cdot 10^{-14}$	3.77	31.3	0.9998	[8], \oplus
	NOE	-12.5	$3 \cdot 10^{-13}$	3.30	27.5	0.976	[6]
PBMA and PBMA13C	β -relaxation	-21.4	$3.7 \cdot 10^{-22}$	6.29	52.3	0.995	[5]
	γ -relaxation	-12.4	$4 \cdot 10^{-13}$	2.72	22.6		[9]
	NOE	-14.2	$6 \cdot 10^{-15}$	3.56	29.6	0.970	this work
PHMA13C	β -relaxation	-21.2	$6 \cdot 10^{-22}$	5.65	47.0	0.990	[5]
		-24.4	$5 \cdot 10^{-24}$	6.54	54.4	0.998	[5]
	NOE	-11.1	$9 \cdot 10^{-12}$	2.05	17.0	0.997	this work

Crossover temperatures for PnAMAs.^[10]

Sample	T_c (K)
poly(ethyl methacrylate)	380
poly(<i>n</i> -butyl methacrylate)	323
poly(<i>n</i> -hexyl methacrylate)	282

References:

- [1] M. Gaborieau, "Solid-state NMR investigation of spatial and dynamic heterogeneity in acrylic pressure sensitive adhesives (PSAs) compared to model poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates)", PhD thesis, University Louis Pasteur, Strasbourg, France, 2005, <http://eprints-scd-ulp.u-strasbg.fr:8080/301/>.
- [2] M. Wind, "Festkörper NMR Spektroskopie: Anisotrope Dynamik polymerer Schmelzen und dendritischer Systeme", Ph.D. thesis, Johannes Gutenberg University, Mainz, Germany, 2001,
- [3] S. C. Kuebler, "Molekulare Dynamik und Anisotropie polymerer und flüssigkristalliner Materialien", Ph.D. thesis, Johannes Gutenberg University, Mainz, Germany, 1996,
- [4] A. S. Kulik, H. W. Beckham, K. Schmidt-Rohr, D. Radloff, U. Pawelzik, C. Boeffel, H. W. Spiess, *Macromolecules* **1994**, 27, 4746.
- [5] M. Wind, R. Graf, S. Renker, H. W. Spiess, *Macromol. Chem. Phys.* **2005**, 206, 142.
- [6] M. Gaborieau, R. Graf, H. W. Spiess, *Solid State Nucl. Magn. Reson.* **2005**, 28, 160.
- [7] J. G. Powles, J. H. Strange, *Proc. Phys. Soc. London* **1963**, 82, 6.
- [8] M. Wind, R. Graf, A. Heuer, H. W. Spiess, *Phys. Rev. Lett.* **2003**, 91, 1557021.
- [9] K. Schroeter, S. Reissig, E. Hempel, M. Beiner, *J. Non-Cryst. Solids* **2007**, 353, 3976.
- [10] M. Beiner, H. Huth, K. Schroeter, *J. Non-Cryst. Solids* **2001**, 279, 126.