SOLID-STATE NMR STUDY OF SPIN DYNAMICS AND LOCAL DISORDER IN SMART POLYMERS: PDMAEMA

V. Klimavičius a, V. Klimkevičius b, L. Dagys c, K. Aidas a, R. Makuška b, and V. Balevičius a

a Institute of Chemical Physics, Vilnius University, Saulėtekio 9, 10222 Vilnius, Lithuania
b Institute of Chemistry, Vilnius University, Naugarduko 24, 03225 Vilnius, Lithuania
c NVision Imaging Technologies GmbH, D-89081 Ulm, Germany
Email: vytautas.balevicius@ff.vu.lt
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The solid-state 1H and 13C NMR spectra as well as the 1H–13C cross-polarization upon magic angle spinning (CP MAS) kinetics were studied for poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA), i.e. a smart pH- and thermo-responsive polymer. The stereochemical content of PDMAEMA was determined from the complex shaped 13C MAS signal of CH3 group. The kinetic data were processed using the Hirschinger and Raya spin dynamics model that includes the complete scheme of rotating frame spin-lattice relaxation pathways. The general solution was adapted for the spin cluster treatment. The earlier studied experimental CP MAS kinetics data of poly [2-(methacryloyloxy)ethyl trimethylammonium chloride] (PMETAC), i.e. one of its quaternized form, were revisited and newly processed applying this model. The spin-lattice relaxation of protons in the rotating frame in PDMAEMA and PMETAC occurs in the same scale from one to tens of milliseconds. Very high anisotropy of spin-diffusion was found for both polymers. However, the local disorder of various spin sites in PDMAEMA is significantly higher than in PMETAC. It is characterized by the order parameters 0.71–0.77 and 0.87–0.91, respectively. The main chain in PDMAEMA is also more disordered and more flexible than in PMETAC.

Keywords: solid-state NMR, cross-polarization, smart polymers, poly[2-(dimethylamino)ethyl methacrylate]

1. Introduction

Cross-polarization (CP), combined with magic-angle spinning (MAS), is one of the most widely used techniques in solid-state NMR spectroscopy [1–3]. The processing of CP kinetic data, i.e. the consideration of the time evolution (contact time) of communication between spins, provides the rates of spin-diffusion and spin-lattice relaxation, the profiles of distribution of dipolar coupling and some other parameters accounting for the effective sizes of spin clusters [4–6]. Hence, it is a powerful method studying fine structural details and dynamics in advanced complex materials and polymers among those [7–10].

In the present work, the CP MAS kinetics was applied studying a representative of a very important class of materials – smart polymers. Poly[(dimethylamino)ethyl methacrylate] (PDMAEMA) was chosen for this study for several reasons. It has a tertiary amine structure as a pendant group, which in an acidic medium or in the form of quaternary ammonium salt acquires a cationic character. PDMAEMA is known as a smart pH- and thermo-responsive polymer [11–13]. The physical properties of such polymers, like chain conformation and solubility, can be tailored by manipulating the pH, ionic strength or temperature. pH-sensitive polymers combined with nanoparticles are intended to be used in chemotherapy to overcome major problems related to tumor heterogeneity, non-specific distribution of the drugs in tissues and multidrug resistance against anticancer drugs [12, 13]. In combination with a suitable hydrophobic block,
PDMAEMA enables formation of micelles [14]. Micelles have gained significant attention since they can be used to encapsulate and subsequently release compounds, which is very important in drug delivery. However, PDMAEMA is susceptible to hydrolysis, therefore its quaternized form, containing a permanent charge, is preferred in water-based applications [14]. Interactions between water molecules and PDMAEMA are more complex than those occurring in the most nonionic thermoresponsive polymers [11]. Water solubility of atactic PDMAEMA is strongly pH-dependent. Quaternized PDMAEMA is a versatile polymer that can be applied in antimicrobial systems, such as films with porous surfaces of narrow size, cationic coatings for silica nanoparticles, recognition elements against bacteria, tandem systems with fungicide properties, and as a material for antibacterial fibres or nanocrystals [15]. PDMAEMA-based advanced materials with well-defined compositions, architectures and functionalities are promising for gene transfection [16].

The purpose of the present work was to study $^{1}\text{H}--^{13}\text{C}$ CP MAS kinetics in PDMAEMA determining the rates of spin-diffusion processes and spin-lattice relaxation in the rotating frame, and also the dipole–dipole coupling constants and the local dynamic order parameters for various molecular segments. An especial interest was to compare the solid-state NMR data for PDMAEMA and its quaternized derivative PMETAC evaluating the local disorder and chain flexibility in both polymers.

2. Experiment

Poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) was synthesized via radical addition-fragmentation chain transfer (RAFT) polymerization according to previously published data with minor adjustments [17, 18]. Polymerization of DMAEMA was carried out in 1,4-dioxane (DO) in the presence of 4,4-azobis(4-cyanovaleric acid) (ACVA, 98%, Fluka) as an initiator and 4-(((butylthio)carbonothioyl)thio)-4-cyanopentanoic acid as a highly efficient RAFT chain transfer agent (CTA) [19]. Shortly, DMAEMA (1.57 g, 10 mmol), RAFT CTA (0.014 g, 0.05 mmol) and ACVA (0.0046 g, 0.016 mmol) were placed into a round-bottomed 25 mL flask equipped with a magnetic stirrer and dissolved in 15.4 mL of DO. The stirred solution was bubbled for 30 min under argon gas, sealed and heated at 70°C. The copolymerization reaction was carried out for 24 h and then quenched by cooling the flask down to −80°C and opening to the air. The copolymers were separated and purified by precipitation into cold diethyl ether. The reaction products are yellowish to white powder, yield 89%. The chemical structure of PDMAEMA is shown in Fig. 1.

The solid-state NMR experiments were carried out on a Bruker AVANCE III HD spectrometer using a 4 mm double resonance CP MAS probe. The experiments were performed at 298 K in 9.4 T magnetic field using an Ascend wide bore superconducting magnet. The resonance frequencies of the $^{1}\text{H}$ and $^{13}\text{C}$ nuclei are 400.2 and 100.6 MHz, respectively. The samples were spun at magic-angle at the rate of 10 kHz using a 4 mm zirconia rotor. To fulfill one of the Hartmann–Hahn matching conditions in CP MAS experiments, rectangular (63 kHz RF field for $^{13}\text{C}$) variable contact time pulses were used. In the present work, all experiments were adjusted to fulfill the $n = +1$ condition. The experimental and computed $^{13}\text{C}$ CP MAS spectra of PDMAEMA are shown in Fig. 1. The CP MAS kinetics were recorded by varying the contact times from 50 $\mu$s to 10 ms in increments of 25 $\mu$s. The $^{1}\text{H}--^{13}\text{C}$ CP MAS FSLG HETCOR spectra (Fig. 2) were measured using 128 scans per 128 increments using a short (70–100 $\mu$s) ramped (50–100%) CP contact. All spectra were referenced to TMS using adamantane as an external reference ($\delta^{(1}\text{H}) = 1.85$ ppm, $\delta^{(13}\text{C}) = 38.52; 29.47$ ppm). NMR spectra were processed using the Topspin 3.2 software. Some additional processing was carried out using the Microcal Origin and MathCad packages.

3. DFT calculations

Calculations of NMR isotropic magnetic shielding constants for $^{1}\text{H}$ and $^{13}\text{C}$ nuclei in PDMAEMA have been performed using the density functional theory (DFT). The B3LYP exchange-correlation functional in combination with the 6-311G** basis set was used for geometry optimization of isolated fragments of PDMAEMA. The magnetic shielding tensors have been calculated in vacuo by using the modified hybrid functional of Perdew, Burke and Ernzerhof (PBE0) along with the 6-311+G(2d,2p) basis set. The gauge-including atomic orbital (GIAO)
Fig. 1. The experimental and computed (vertical bars) $^{13}$C CP MAS spectra of neat PDMAEMA. Note the strong overlaps of the CH$_2$ main chain signal with that of N-CH$_2$ and the quaternary carbon (q) with N-(CH$_3$)$_2$, respectively. The overlapped experimental contours were separated using Voigt functions. More comments in the text.

4. Theoretical model of CP kinetics

The most widely used kinetic models that exhibit the coherent oscillatory behaviour of CP intensity originate from the pioneer work of Müller et al. [23]. The spin system is treated as a strongly coupled 1–S spin pair immersed in a spin-bath consisting of the remaining I spins (I = $^1$H and S = $^{13}$C in the present work). There it is assumed that only one spin I* interacts with the I-spin bath (or infinite energy reservoir of I spins), which is described in a phenomenological way. It was called as the I–I*–S model. Later the model was developed by Naito and McDowell [24] revealing the anisotropy of spin-diffusion processes and adding the spin-lattice relaxation of I and S spins in the rotating frame ($T_{1I}$ and $T_{1S}$). The topic of CP kinetics, i.e. the dependence of CP signal intensity $I(t)$ on the contact time ($t$), was reviewed and discussed in Refs. [1, 6, 25]. However, as it was noted in Ref. [6], the kinetic equation originally derived by Naito and McDowell [24] is incorrect in the presence of $T_{1p}$ relaxation. In the present work, the correct solution derived by Hirschinger and Raya [26] was used. In its general form this solution contains a complete scheme of the spin-lattice relaxation in the rotating frame with the rates $R_{1p}^I = 1/T_{1p}^I$, $R_{1p}^{I*} = 1/T_{1p}^{I*}$, $R_{1p}^S = 1/T_{1p}^S$ for the spins I, I*, and S, respectively, and is rather cumbersome to apply. However, it can be simplified under certain dynamic constrains. For instance, if the relaxation rates of the remote and strongly coupled protons are almost equal, i.e. $R_{1p}^I = R_{1p}^{I*}$, the kinetic equation is written as
Fig. 2. Comparison of $^1$H–$^{13}$C CP MAS frequency switched Lee–Goldberg (FSLG)-heteronuclear correlation (HETCOR) spectra of PDMAEMA (upper panel) and PMETAC (lower panel). The DFT calculated $^1$H and $^{13}$C chemical shifts are shown by the horizontal and vertical bars, respectively. The experimental and calculated carbonyl signals are out of the present scale and not shown. More comments in the text.

\[
I(t) = I_0 \left[ \frac{1}{2} - \frac{R_s^e}{R_{dp}^e + R_{dp}^i / 2 - R_{dp}^i / 2} \right] e^{-\left(\frac{\delta^e_{dp} + \delta^e_{dp}}{2}\right)t} \\
+ \left\{ \frac{R_s^e}{R_{dp}^e + R_{dp}^i / 2 - R_{dp}^i / 2} \right\} e^{-\delta_s^e t} \\
- \frac{1}{2} e^{-\left(\delta_s^e + \delta^e_{dp} + \delta^e_{dp} / 2\right)t} \langle \cos (b t) \rangle_{AA},
\]

where $R_{dp}^i$ and $R_{dp}^e$ are the (homonuclear) spin-diffusion rate constants of the I spin, $R_{dp}^s$ is that of the S spin (heteronuclear), $R_s^e = R_{dp}^e + R_{dp}^i$ (the physical meaning of the rate constants $R_{dp}^e$, $R_{dp}^i$, and $R_{dp}^s$ was thoroughly discussed in [1, 27, 28]), $R_{dp}^e = R_{dp}^i + R_{dp}^i$, and the brackets $\langle \ldots \rangle_{AA}$ mean the angular averaging [3, 29]. The cosine-oscillation frequency $b$ (Eq. (1)) depends on the gyromagnetic ratios ($\gamma_I$, $\gamma_S$) of the two interacting nuclei (I and S), the distance $r$ between them and the angle $\theta$ between the $r$ vector and the magnetic field

\[
b = \frac{\mu_0 \gamma_I \gamma_S h}{4 \pi} \left( \frac{3 \cos^2 \theta - 1}{2} \right) = D_{IS} P_2(\cos \theta),
\]

where $D_{IS}$ is the heteronuclear I–S dipolar coupling constant $D_{IS} = (1/2\pi) (\mu_0/4 \pi) \gamma_I \gamma_S (h/2\pi)/r^3$ (in Hz).

As the dipolar splitting $b$ is an ‘angular’ function, the proper angular averaging has to be performed in order to adapt this equation to powder samples [3, 29]. The angular averaging (AA) for CP experiments applying MAS is carried out as
where $\beta$ is the polar angle between the $r$ vector and the MAS rotor axis [29]. Depending on the HH matching condition $\omega_{1I} - \omega_{1S} = n\omega_{\text{MAS}}$ is fulfilled ($n = \pm 1$, the present work), the AA procedure has to be carried out on the $\cos(b(t))$ oscillation that contains the spherical components of the $b$-tensor

$$b_{z1} = \frac{D_{zz}}{2\sqrt{2}} \sin(2\beta).$$

In the present work, the angular averaging (Eq. (3)) was carried out analytically using the series of Bessel $J$ functions [29, 30].

Equation [11] was successfully applied for $^1$H--$^{31}$P CP MAS build-up curves in amorphous phosphates [6]. However, the I–I–S model considers an I–S pair. It is known that the relative amplitudes of the coherent and incoherent stages of the polarization transfer are strongly dependent on the considered spin subsystem or cluster. Therefore, in order to handle CH$_2$ and CH$_3$ groups in PDMAEMA, the treatment should be modified.

The Naito and McDowell analytical solution [24] was modified for the I–S spin clusters introducing the additional parameter $\lambda$ that is related to the cluster size $n$ [25]. If the I–S coupling constant is much larger than the spin diffusion rate constants ($|b| \gg R_1^{IS} R_1^{IP}$ and $R_2^{IS} \gg R_1^{IP}$ is valid, the modified solution is written as

$$I(t) = I_0 e^{-R_1^{IP}t} \left\{ 1 - \lambda e^{-R_2^{IS}t} - (1-\lambda) e^{-\frac{t}{2} \left[R_0^{IS} + R_0^{IP}\right]} \right\} \langle \cos(b(t)) \rangle_{\lambda \lambda} \right\} \langle \cos(b(t)) \rangle_{\lambda \lambda},$$

where the kinetic parameters $A$ and $B$ depend on the relaxation regime (Table 1). The ‘size’ parameter $\lambda$ was introduced in the same manner as in Ref. [25], i.e. by replacing the relative magnitudes of the exponents of incoherent and coherent CP stages by $\lambda$ and $1 - \lambda$, respectively. As $\lambda$ depends on the cluster size and group mobility, it must be adjusted for each kinetics by the fitting of experimental and calculated CP build-up curves.

In the present work, the nonlinear curve fitting to experimental data was carried out using Eq. (6) and applying the Levenberg–Marquardt algorithm implemented in the Microcal Origin and MathCad packages.

5. Results and discussion

It is known that PDMAEMA can exist in three steric configurations – isotactic, atactic and syndiotactic [11]. These stereochemically different forms can be distinguished in the high resolution $^1$H and $^{13}$C NMR spectra of PDMAEMA in DMSO and CDCl$_3$ solutions [11, 14]. Unfortunately, these configurations cannot be well resolved by the solid-state NMR because of motional slow-down and the line broadening. However, the decomposition of the CH$_3$ signal was successful in the $^{13}$C MAS spectrum into three components (Fig. 1). According to the assignment given in [11] these three peaks correspond to isotactic (25.7 ppm), syndiotactic (20.3 ppm) and atactic (17.2 ppm) conformers, respectively. The relative intensities of the peaks allow one to state that

<table>
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<tr>
<th>Regime</th>
<th>$A$</th>
<th>$B$</th>
<th>Comment</th>
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<tbody>
<tr>
<td>$R_{1}^{IS} R_{1}^{IP} \rightarrow 0$</td>
<td>$R_{1}^{IP}/2 - R_{1}^{IP}/4$</td>
<td>$R_{1}^{IP}/2$</td>
<td>For diluted spins S and single I-bath; it is often set for $^{13}$C--$^1$H pairs [25].</td>
</tr>
<tr>
<td>$R_{1}^{IS} = R_{1}^{IP}$</td>
<td>$R_{2}^{IP}$</td>
<td>$R_{2}^{IP}$</td>
<td>The case of the global ‘isotropic’ rotating frame relaxation.</td>
</tr>
<tr>
<td>$R_{1}^{IS} \neq R_{1}^{IP}$</td>
<td>$R_{2}^{IP}$</td>
<td>$R_{2}^{IP} + R_{2}^{IP} - R_{1}^{IP}$</td>
<td>In the case of very strong I–S coupling both spins relax with the near rates.</td>
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the PDMAEMA synthesized via RAFT polymerization is predominantly atactic (56%) with a comparable amount of the syndiotactic form (36%). The isotactic form is present in a much lower concentration (ca 8%).

Because of the line broadening and strong overlap (Fig. 1) the \(^1\)H–\(^{13}\)C CP MAS kinetics in PDMAEMA were studied only for three different spin sites, viz. O–CH\(_2\) (64 ppm), N–CH\(_2\) (59 ppm) and N–(CH\(_3\))\(_2\) (47 ppm). The build-up kinetic curves for them are presented in Fig. 3. The high-density experimental data set allows one to reduce the excessive freedom in the non-linear curve fitting that increases the stability of the flow towards the ‘true’ minimum on the multi-parameter surface \(\chi^2\), i.e. to the minimal sum of weighted squares of deviations of the chosen theoretical model curve from the experimental one.

The nonlinear curve fitting was carried out using Eq. (6) on the six parameters surface \(\chi^2(A, B, b, R^{I}_1, \lambda, I_0) \rightarrow\) minimum. The fitted parameters are presented in Table 2.

\[ B \gg A \] was found for all studied spin sites (Table 2). This means that \(R^{I}_1, \gg R^{E}_1\) at any relaxation regime (Table 1) and the spin diffusion in PDMAEMA is highly anisotropic. It looks that the Ising-type interaction \(R^{I}_1 = R^{E}_1 = 0\) should be dominant. An exceptional situation may arise in the case of a very fast relaxation of I* spins, i.e. \(R^{I*}_I \gg R^{I}_I\). Unfortunately, the precision of the separate determination of \(R^{I*}_I\) and \(R^{I}_I\) is rather low as the sum of \(R^{E}_I R^{I*}_I\) and \(R^{I}_I R^{I*}_I\) appears in the general kinetic equation [26].

This is not the case for the relaxation rate of I-protons \(R^{I}_I\) because it solely drives the exponential decay of the magnetization through the second term (Eq. (1)).

For polycrystalline as well as for powder materials, the destructive interference of the orientation-dependent coherences significantly contributes to the decay of transient oscillations. Thus, the calculations implementing the angular averaging (Eq. (6)) should provide a more accurate evaluation of the spin-diffusion rates and the dipole–dipole coupling constants. Analysis of the dipole–dipole coupling strength allows the identification of dynamic disordering in the sample [31]. The local dynamic order parameter \(S\) is defined as the ratio of the experimental dipolar coupling constant and the calculated static dipolar coupling constant \([32–35]\)

\[ S = \frac{D_{\text{CH}}}{D_{\text{stat}}} = \langle P_2(\cos \alpha) \rangle, \]

Fig. 3. The experimental \(^1\)H–\(^{13}\)C CP MAS kinetics (circles) for various spin sites in PDMAEMA at 10 kHz MAS rate, processed using Eq. (6) (lines). The optimized parameters are presented in Table 2.

where \(\alpha\) is the angle of the instantaneous orientation of the dipole–dipole coupling tensor to the ‘symmetry axis of fast motion’ [32] or the polar angle between the internuclear vector \(r_{IS}\) and the end-to-end
The static coupling constant $D_{\text{stat}}$ for the $^{13}$C–$^1$H dipolar coupling is usually taken as $23.0 \pm 0.3$ kHz that corresponds to the bond length $r_{\text{C–H}} \approx 1.09–1.10$ Å (Eq. (2)).

However, the above definitions of the angle $\alpha$ in Eq. (7) is unwelcoming for the visualization of the local disorder. The simplified visualization can be done if the internal motion of vector $\mathbf{r}_{\text{int}}(t)$ is modelled as a restricted movement in a cone with the semi-angle $\theta_0$. The order parameter is then given by $S = \cos \theta_0 (1 + \cos \theta_0)/2$ [31, 33]. The amplitude of this movement is qualitatively visualized by the cone semi-angle $\theta_0$. The $S$ and $\theta_0$ values for the studied carbon sites in PDMAEMA are given in Fig. 4. These values significantly differ from those obtained for proteins, biological macromolecules and some more rigid systems [31, 33, 34].

Despite the wide use of quaternized PDMAEMA, and cationic polymers in general, there are few contributions related to investigations of quaternization reactions of tertiary amino groups and the properties of both forms. Therefore, the results

Table 2. The nonlinear curve fitting parameter values of $^1$H–$^{13}$C CP MAS kinetics in PDMAEMA (Fig. 3) and PMETAC (the experimental data from Ref. [8] were newly processed using Eq. (6)).

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<tr>
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<th>PDMAEMA</th>
<th>PMETAC</th>
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<tr>
<td>$A$, s$^{-1}$</td>
<td>470</td>
<td>790</td>
</tr>
<tr>
<td>$B$, s$^{-1}$</td>
<td>4500</td>
<td>17800</td>
</tr>
<tr>
<td>$D_{\text{CH}}$, Hz$^*$</td>
<td>2900</td>
<td>16500</td>
</tr>
<tr>
<td>$R'$, s$^{-1}$</td>
<td>52</td>
<td>130</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.43</td>
<td>0.33</td>
</tr>
<tr>
<td>$R^2/\chi^2(%)$</td>
<td>0.978/2.2</td>
<td>0.994/2.2</td>
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</table>

* The coupling constants $D_{\text{CH}}$ were determined from $b$ values, rescaling them by the factor of $\sqrt{2}$ because the HH matching for $n = +1$ was fulfilled (Eq. (4).

** The value $\lambda \approx 0.33$ was optimized for a $\mathbf{I}_2$–$S$ spin system and fixed in order to ensure the stable convergence of the nonlinear fitting flow.

![Fig. 4. The local dynamic disorder in PDMAEMA and PMETAC modelled as restricted movement of the internuclear vector $\mathbf{r}_{\text{C-H}}(t)$ in a cone: the order parameters $S$ and the visualization of the local disorder for the studied carbon sites. The full widths at the half-height (FWHH) of the carbon signals in the main chain were determined separating the overlapped contours and approaching them by Voigt functions (Fig. 1).](image-url)
obtained for PDMAEMA were compared with those for PMETAC, which is the quaternized derivative of PDMAEMA [8].

5.1. The $^1$H and $^{13}$C chemical shifts

The positional sequence of the signals in the $^1$H NMR spectra is the same in both polymers (Fig. 2). This is in agreement with the solution (in CDCl$_3$) data [14, 15]. Also, the computed $^1$H chemical shifts fairly well agree with the experiment. The assignments of $^1$H peaks for PDMAEMA are taken from Ref. [14] and for one of its quaternized analogue (BuI-Q60) from Ref. [15]. The solid-state $^{13}$C NMR spectra of the neat PDMAEMA and PMETAC were not found in the literature. Only the high resolution $^{13}$C NMR spectrum of PDMAEMA in the DMSO-$d_6$ solution is presented in Ref. [11] and analyzed with the purpose to identify its stereochemical configurations. Therefore, it is interesting to note that the mutual interchange in the positions of N-CH$_2$ and O-CH$_2$ signals in the $^{13}$C MAS NMR spectra of PDMAEMA and PMETAC is observed (Fig. 2). This means that the charge of the N$^+$ ion causes a very strong deshielding effect of the neighbouring carbon. The calculated $^{13}$C chemical shifts also confirm this fact. However, the quantitative coincidence with the experimental spectra is not so perfect as in the case of protons.

5.2. The local disorder

The analysis of the dipolar coupling constants has revealed that the local disorder around various spin sites in PDMAEMA is significantly higher than in PMETAC (Fig. 4). Note that the local order around the N$^+$-CH$_3$ site in PMETAC is characterized by $S = 0.91$ that is intrinsic for quite rigid molecular systems [3, 33–35]. Hereby it is intriguing to compare the dynamic behaviour and disorder of the main chains. Unfortunately, there are strong overlaps of the CH$_3$ main chain signal with the neighbouring N-CH$_2$ peak in PDMAEMA (57 and 59 ppm, respectively (Fig. 1)) and that with the quaternary carbon (q) peak in PMETAC (46.5 and 45 ppm, see [8]). The signals can be separated applying the standard computing routines. Nevertheless, doing this, it has to be realized that the multi-parametrical curve fitting reduces the fidelity of deduced parameters. The overlapped experimental contours were separated using Voigt functions. The Voigt function is the convolution of Gauss ($G$) and Lorentz ($L$) profiles, i.e. $V = G * L$. It can be assumed that the presence of disorder enhances the Gauss contribution to the Voigt-shaped signals, whereas the Lorentz contribution is originated from the uniform spin interactions and dynamics. Gauss and Lorentz contributions ($w_G$ and $w_L$) to the full width at the half-height (FWHH) of the main chain signal were found (Fig. 3). These are $w_G = 450$ Hz and $w_L = 120$ Hz for PDMAEMA and $w_G = 0$ and $w_L = 320$ Hz for PMETAC. This means that the main chain in PDMAEMA is highly disordered and more flexible than in PMETAC.

The local dynamic disorder of methyl groups attached to the nitrogen (N$^+$-(CH$_3$)$_3$ and N-(CH$_3$)$_2$) is extremely high in both polymers ($S = 0.1$). However, this result has to be treated with a certain reservation. The secularity condition $|b| \gg R_{1p} / R_{1p}$ is not fulfilled for these spin systems, and thus the use of the above models (Eq. (5) or (6)) is not rigorously legitimated. The ordering of CH$_3$ groups attached to the main chain was not studied as their signal consists of three peaks from stereochemically different forms (Fig. 1).

5.3. The spin dynamics

The rates of spin-lattice relaxation in the rotating frame and the anisotropy of spin-diffusion in PDMAEMA and PMETAC are found to be similar ($B/A \sim R_{1p} / R_{1p} \sim 10 – 100$, $R_{1p} \sim 100$ s$^{-1}$, Table 2). The highest anisotropy in both polymers was found for CH$_2$ spins adjacent to the nitrogen.

6. Concluding remarks

The solid-state $^1$H and $^{13}$C spectra of the neat PDMAEMA were registered for the first time. The stereochemical content of PDMAEMA was determined from the complex shaped $^{13}$C NMR signal of CH$_3$ group. The $^1$H–$^{13}$C CP MAS HETCOR spectra have revealed the mutual interchange in the positions of N-CH$_2$ and O-CH$_2$ peaks in PDMAEMA and one of its quaternized analogue – PMETAC, whereas the sequences of proton signals are identical in both polymers. This experimental finding was confirmed by the DFT calculation.
The general Hirschinger and Raya spin dynamics solution was simplified and adapted for the spin cluster treatment. It was applied for the processing of the experimentally measured $^1$H–$^{13}$C CP MAS kinetics in PDMAEMA and PMETAC. A priori constrains concerning the regime of the relaxation in the rotating frame are necessary for the precise determination of spin-diffusion rates. It was found that the rates of spin-lattice relaxation of protons and the anisotropy of spin-diffusion were very similar in both polymers.

The analysis of the dipolar coupling constants for various spin sites shows that the local disorder in PDMAEMA is significantly higher than in PMETAC. Moreover, the disorder in PDMAEMA increases going from the main chain along the pendant fragments. An opposite trend in PMETAC can be due to strong electrostatic interactions in the network of $\text{N}^+$ and $\text{Cl}^-$ ions that restrict the mobility of the pendant branches. It was also determined that the main chain in PDMAEMA is highly disordered and more flexible than in PMETAC.

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References


SUKINIŲ DINAMIKOS IR LOKALIOSIOS NETVARKOS IŠMANIUOSIUOSE POLIMERUOSE TYRIMAS KIETOJO KŪNO BMR METODO: PDMAEMA

V. Klimavičius *, V. Klimekevičius †, L. Dagys ‡, K. Aidas *, R. Makuška †, V. Balevičius *

* Vilniaus universiteto Cheminės fizikos institutas, Vilnius, Lietuva
† Vilniaus universiteto Chemijos institutas, Vilnius, Lietuva
‡ NVision Imaging Technologies GmbH, Ulmas, Vokietija

Santrauka
Ištirti kietojo kūno $^1$H ir $^{13}$C BMR spektra bei $^1$H–$^{13}$C CP („kryžminės poliarizacijos”) MAS („magiško kam-po sukim” ) kinetika poli[2-(dimetilamino)-etilmeta-krilate] (PDMAEMA), t. y. išmanijame polimere, kuris pasižymi jautrumo pH ar temperatūros pokyčiams. Stereocheminė PDMAEMA sudėtis buvo nustatyta iš $^{13}$C grupių $^{13}$C MAS signalo kontūro formos, atliekant persiklojusių smailių atskyrimą ir aproksimuojant jas Voigt funkcijomis. Eksperimentiniai CP MAS kinetikos duomenys buvo apdoroti taikant Hirschinger ir Raya sukinių dinamikos modelį, kuriame įtraukia pilnoji sukinių ir gardelės relaksacijų schema. Bendroji kinetinė lygtis buvo adaptuota sukinių spiečių nagrinėjimui. Siekiant palyginti, buvo peržiūrėti eksperimentiniai anksciausiai tirtos CP MAS kinetikos poli[2-(metakriloiloksi)etiltrimetilamonio chloride] (PMETAC), t. y. vienoje iš kvaternizuotų PDMAEMA formų, duomenys ir apdoroti pritaikius jį modelį. Nustatytos ir palygintos sukinių difuzijos bei sukinių ir gardelės relaksacijų spartos, taip pat $^1$H ir $^{13}$C sukinių šaunimų konstantos. Pastarąjį duomenis buvo naujai išmaniusios lokaliosios tvarkos parametrus įvertinti. Aptiktas anomaliai didelė sukinių difuzijos anizotropija; jį didžiausia $^{13}$C grupėms, esančioms šalia azoto atomų. Tai būdinga sukinių sistemoms, kuriose dominuoja Ising tipo sąveika. Nustatyta, kad protonų sukinių ir gardelės relaksacijų spartos abiejose polimereose yra panašios, ir šie vyksmai yra milisekundžių eilės. Lokalioji netvarka PDMAEMA yra žymiai didesnė. Ji apibūdinama lokaliosios tvarkos parametrais 0,71–0,77 PDMAEMA fragmentams ir atitinkamai 0,87–0,91 PMETAC fragmentams. Nustatyta, kad pagrindinė PDMAEMA grandinė taip pat labiau netvarka ir lankstesnė nei PMETAC.