Nanostructure of Materials Determined by Relayed Paramagnetic Relaxation Enhancement.

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Supplementary Information

Experimental Details

The samples studied are coated pellet samples, consisting of a microcrystalline cellulose (MCC) core, spray coated with a film of Ethyl cellulose (EC) and Hydroxypropyl cellulose (HPC) in a ratio of 70/30. Dried 'Aquacoat ECD', which is a water based EC dispersion with known particle size was chosen as a test system.
AMUpol[1] in a 90/10 mixture of D_2O and H_2O in two different concentrations (15mM and 30mM) was chosen as a doping agent. Typically about 18 µl of radical solution were added to 30 mg of cellulose sample. For the reference experiment without doping a mixture of D_2O and H_2O was added. All NMR experiments were performed on a 700 MHz Bruker Avance III spectrometer equipped with a 3.2mm MAS probe. The MAS rate was 8000 Hz in all cases and the temperature was regulated to be constant at 295K. Standard saturation recovery experiments to determine ^{1}H T_1 relaxation rates followed by a cross polarization step and acquisition on ^{13}C were carried out for undoped and doped samples. For all CP experiments the amplitude of the ^{1}H r.f. field was ramped during the contact time[2]. SPINAL64 decoupling[3] was applied during acquisition.
Figure S01 shows a ^{13}C CP spectrum (as obtained from T_1 saturation recovery experiments) of EC/HPC coated MCC pellets with AMUpol solution.

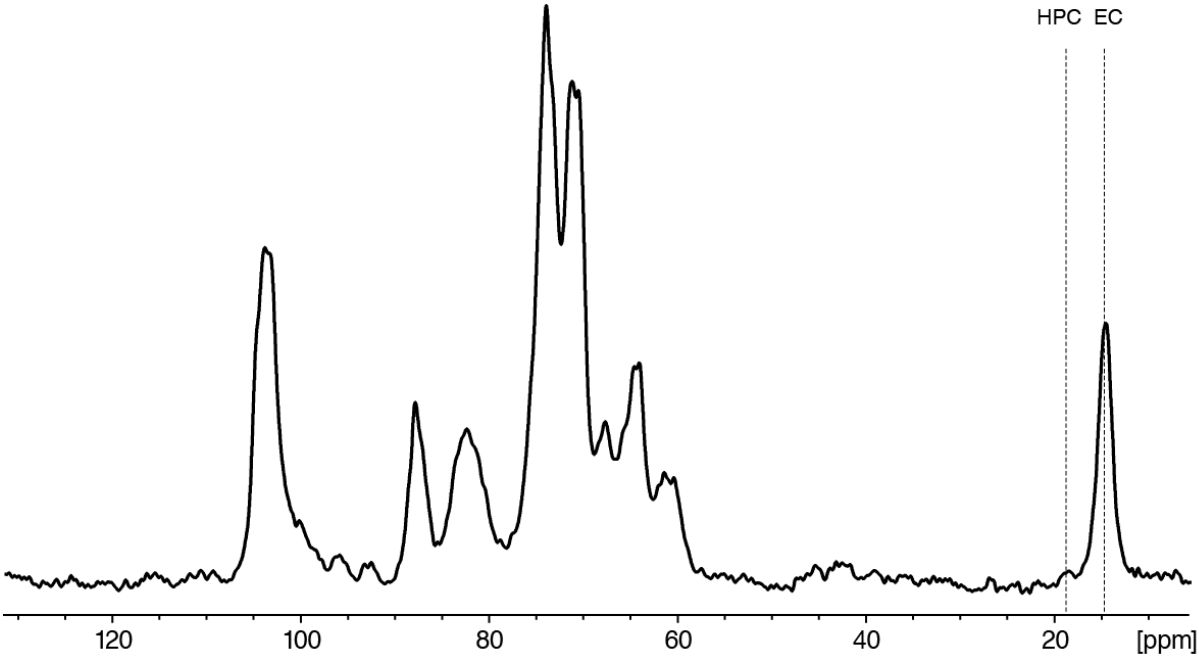

Figure S01 ^{13}C CP spectra from pellets samples with 30mM AMUpol solution obtained at 700 MHz at 295 K

High resolution in the ^{13}C dimension is especially interesting in the case of the pellet samples to distinguish the different cellulose components (MCC, EC and HPC). To measure the build up curves the signal originating from the CH_3 groups in EC at 15ppm was integrated, since the peaks between 60 and 110 ppm overlap with the MCC component of our sample. It has to be noted that hardly any HPC signals are visible in this spectrum due to the selective doping of the HPC domains leading to signal broadening and large chemical shifts due to the high radical concentration as well as inefficient CP transfer due to the solubility of HPC in water. All experiments were repeated three times for all radical concentrations (0mM, 15mM, 30mM AMUpol) to check reproducibility of the selective doping. The measurements were carried out directly after preparation of the samples. However, in a test of repeated measurements within six hours of sample packing no significant difference in the build-up curves was noticed. R-PRE enhancement curves were obtained by calculating the integral ratio of the signals obtained with and without radicals. Figure S02 shows R-PRE enhancement curves obtained for the EC aquacoat sample with the two different radical solutions described above.

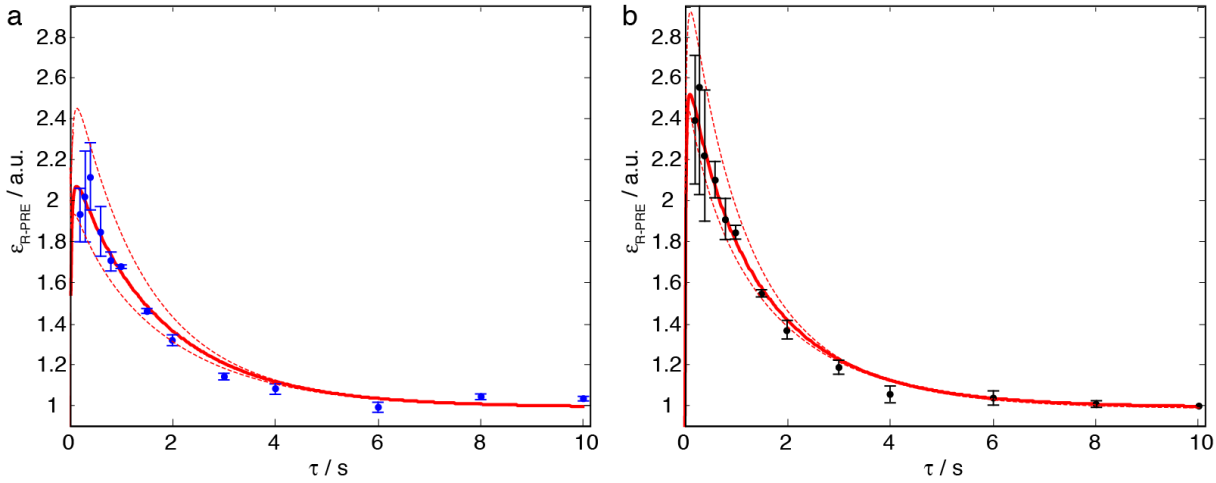

Figure S02 R-PRE enhancement curves of the EC aquacoat sample from ^{1}H-^{13}C saturation recovery experiments as function of recovery delay τ. The curves correspond to the ^{13}C methyl resonance of EC at 15 ppm. (a)Blue

dots are values obtained from experiments after impregnation with 15mM AMUpol, (b) black dots are R-PRE enhancement values obtained from experiments using 30mM AMUpol solution. Experimental data are means of three experiments. Error bars on experimental data represent the standard deviation. The lines are results from the fit using the model described below. Dashed red lines indicate error margins (obtained domain size from fit ±30nm).

0.8 nm^2/ms was chosen as a typical value for spin diffusion coefficients in polymers[4]. Its influence on the model was tested by refitting the data using spin diffusion coefficients of 0.6 nm^2/ms and 1 nm^2/ms instead. In the case of D=0.6 nm^2/ms the domain sizes / particle sizes we obtained are 4-6 nm smaller, in the case of D=1.0 nm^2/ms the domain sizes / particle sizes are 4-6 nm bigger than what we obtained for the originally used value of D=0.8 nm^2/ms. The introduced change in the obtained domain / particle size is small compared to the overall error of the experiment.

Matlab program:

The Matlab program to numerically find solutions to the spin diffusion equation, to model the build-up curves with and without radicals and R-PRE enhancement curves is shown below.

```
function [epsilon,normSignalPol,normSignalRef]=twoT1_PRE(rmax,rstep, tmax, tstep, T1short,
T1long, epsilon0,D)

m = 2;

r=linspace(0,rmax,rstep);
t = linspace(0,tmax,tstep);
rmax1=rmax;


%Set symmetry, time and space domain.

global rmax2 T1inf T1surf e0 c0;
rmax2=rmax;
T1inf=T1long;
T1surf=T1short;
e0=epsilon0;
c0=1/D;

%declare the global variables to be used in the handle functions.

sol = pdepe(m,@pdex1pde,@pdex1ic,@pdex1bc,r,t);
p = sol(:,:,1);
sol2= pdepe(m,@pdex1pdenoDNP,@pdex1icnoDNP,@pdex1bcnoDNP,r,t);
pref=sol2(:,:,1);

figure;
surf(r,t,p);
xlabel('Distance r [nm]');
ylabel('Time t [ms]');
zlabel('magnetization');

%figure;
%surf(r,t,pref);
%xlabel('Distance r [nm]');
%ylabel('Time t [ms]');
%zlabel('magnetization');

% Extract the first solution component as p.
T1=zeros(size(1,rstep));
for i=1:rstep
T1(i)=1/(1/T1inf+(2e-3)^6/(T1surf*(2e-3+rmax2-r(i))^6));
end

figure;
plot(r,T1);

[epsilon,SignalPol,SignalRef,normSignalPol,normSignalRef]=CalcEpsilon(p,pref,r,t);
```

```
% Define the T1 profile for PREs.


% calculate epsilon as a function of t.
function [epsilon,SignalPol,SignalRef,normSignalPol,normSignalRef]=CalcEpsilon(p,pref,r,t)
global rmax2;
% Calculate Polarized and Reference signal as a function of time.
Presign=zeros([size(t,2),size(r,2)]);
Presignref=zeros([size(t,2),size(r,2)]);
%Calculate the functions to be integrated over the crystal.



    for j=1:size(t,2)
        for i=1:size(r,2)
            if r(i)>(rmax2-0.00015)
            %r_cut(i) = [];
            Presign(:,i) = zeros(size(t,2),1);
            Presignref(:,i) = pref(j,i)*4*pi*(r(i))^2;
            else
            Presign(j,i)=p(j,i)*4*pi*(r(i))^2;
            Presignref(j,i)=pref(j,i)*4*pi*(r(i))^2;
            end
        end

    end


    SignalPol=zeros([1,size(t,2)]);
    normSignalPol=zeros([1,size(t,2)]);
    SignalRef=zeros([1,size(t,2)]);
    normSignalRef=zeros([1,size(t,2)]);
    epsilon=zeros([1,size(t,2)]);

    for i=1:size(t,2)
     SignalPol(i)=trapz(Presign(i,:));
     SignalRef(i)=trapz(Presignref(i,:));
    end


    for i=1:size(t,2)
        normSignalPol(i)=SignalPol(i)./SignalPol(size(t,2));
        normSignalRef(i)=SignalRef(i)./SignalRef(size(t,2));
    epsilon(i)=SignalPol(i)./SignalRef(i);
    %epsilon(i)=epsilon(i)./2;
    end

    figure;
    hold on;

    plot(t,normSignalPol);
    plot(t,normSignalRef,'r');

    figure;
    plot(t,epsilon,'r'); hold on;



% Definition of the functions called by pdepe.
%c is
function [c,f,s] = pdex1pde(x,t,u,DuDx)
global rmax2 T1inf T1surf c0 e0;
c = c0;
f = DuDx;
if rmax2-x<2e-4
    s=-c0*(u-e0)*(1/T1inf+(2e-3)^6/(T1surf*(2e-3+rmax2-x)^6));
else
    s=-c0*(u-1)*(1/T1inf+(2e-3)^6/(T1surf*(2e-3+rmax2-x)^6));
end




% --------------------------------------------------------------------


function u0 = pdex1ic(x)
```

```
global rmax2  e0
    u0=0;



% --------------------------------------------------------------------
function [pl,ql,pr,qr] = pdex1bc(xl,ul,xr,ur,t)
global e0 rmax2 c0 T1inf T1surf;
pl = 0;
ql = 1;
pr = 0; %c0*rmax2*(ur-e0)*1/T1surf;
qr = 1;


function u0 = pdex1icnoDNP(x)
    u0=0;

function [c,f,s] = pdex1pdenoDNP(x,t,u,DuDx)
global rmax2 T1inf T1surf c0;
c = c0;
f = DuDx;

s=-c0*(u-1)*(1/T1inf);


% --------------------------------------------------------------------
function [pl,ql,pr,qr] = pdex1bcnoDNP(xl,ul,xr,ur,t)
global c0 rmax2 T1inf T1surf;
pl = 0;
ql = 1;
pr = 0;
qr= 1;
```


(1) Sauvée, C.; Rosay, M.; Casano, G.; Aussenac, F.; Weber, R. T.; Ouari, O.; Tordo, P. *Angew. Chem. Int. Ed.* **2013**, *125*, 11058.

(2) Peersen, O. B.; Wu, X. L.; Kustanovich, I.; Smith, S. O. *J. Magn. Res., Ser. A* **1993**, *104*, 334.

(3) Fung, B. M.; Khitrin, A. K.; Ermolaev, K. *J. Magn. Res.* **2000**, *142*, 97.

(4) K.Schmidt-Rohr; H.W.Spiess *Multidimensional Solid-State NMR and Polymers*; Academic Press: London, 1994.